SUBSTITUTION IN THE
NAPHTHALENE SERIES.

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Philosophy

by

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Abstract.

The introductory section deals with modern views on the nature of substitution in the benzene nucleus and on the mechanisms whereby substituents exert their influences upon the nucleus. These ideas, mainly due to Ingold & Robinson, are applied to the naphthalene molecule.

Arguments put forward for the symmetrical structure of naphthalene are discussed and the differences in chemical and physical properties of 1-bromo- and 3-bromo-β-naphthylamines provide evidence for a symmetrical structure. Substitution of naphthalene is compared with and shown to be closely analogous to substitution of diphenyl.

The directive powers of the hydroxyl and derived substituents are shown to fall off in the order OH > OR > OSO₂R. 4-Nitro-α-naphthylamine, like α-naphthylamine, is shown to be capable of direct bromination, but can also give 2:4-dibromo-1-naphthalenediazoperbromide and the mechanism for this reaction is discussed.

The directing power of the acetamido substituent is discussed and the o/p ratio derived from the nitration of α-acetanaphthalide. Nitration experiments show the arylsulphonamido group to be far more powerfully orienting than the acetamido group and comparable in reactivity to the phenolic substituent. A marked difference between bromination and nitration of α-sulphon-naphthalides is observed but there is no such difference in the case of β-naphthalides. In these respects α-sulphon-naphthalides are closely analogous to 2-sulphonamido-diphenyls and β-naphthalides analogous to 4-sulphonamido diphenyls.
The difficulty with which \( \beta \)-naphthalides undergo bromination in the 2- position is shown by comparison with the substitution of disulphonamido derivatives of \( \beta \)-phenylenediamine not to be due to steric factors. The disulphonamido substituent is shown to have a far smaller orienting influence than either the acetamido or sulphonamido groups both in the benzene and the naphthalene series.

Substitution in 1:5-amino naphthol proceeds normally; a feebly orienting group in one ring does not modify positions of substitution due to a powerfully orienting group in the other ring.

Electronic principles applied to the symmetrical structure of the naphthalene molecule supply a fairly consistent basis for the interpretation of substitution processes in the naphthalene molecule.
The work described in this thesis was carried out at Battersea Polytechnic, under the general supervision of Dr. J. Kenyon, to whom I wish to express my thanks for his interest and advice. To Dr. F. Bell, formerly lecturer in Chemistry at the Battersea Polytechnic and now Head of the Chemistry Department, Blackburn Technical College, I am sincerely grateful for his great help and guidance during the course of my research. Thanks are due also to the Salters' Institute of Industrial Chemistry for financial assistance.

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MODERN IDEAS ON SUBSTITUTION IN THE BENZENE RING.

Since the naphthalene molecule in many ways resembles the simpler benzene, it will be of advantage to consider modern theories which have been put forward to account for substitution in the benzene molecule itself and then apply these ideas to the case of naphthalene.

The discovery of the electron some forty years ago was an important one and destined to revolutionise our conception of the nature of chemical reactions. It was ultimately realised that the outer shell of electrons surrounding the atomic nucleus played a fundamental part in the chemical reactions of an element. A marked advance was made in 1916 by G.N. Lewis & Kossel who, on the basis of the Bohr-Rutherford atom showed that chemical combination arose out of a tendency to gain or lose electrons in order to acquire an inert gas configuration. Alternatively expressed, each atom tends to have an outermost grouping of eight electrons (a complete octet). Consequently, sodium with one electron in its outer shell readily combines with chlorine, which has seven, by transferring its electron. After combination, therefore, the two atoms are held together by an electrostatic force, the sodium atom having acquired a unit positive charge and the chlorine a unit negative charge. Similarly, calcium with two electrons in its outer shell gives the electrovalent ionised compound Ca\textsuperscript{++} Br\textsubscript{2}⁻⁻.

1. INTRODUCTION.
This type of linkage, however, cannot serve to account for the large number of compounds in which electrostatic forces are absent, and so in the same year, Lewis put forward the conception of electrons being shared between atomic nuclei. Thus chlorine, which is one electron short of the stable octet, combines with another atom of chlorine so that the resulting molecule consists of two chlorine atoms sharing two electrons, and the octet around each is maintained: 

\[ \text{Cl} - \text{Cl} - \rightarrow \text{Cl}: \text{Cl} : \]

In this case both octets are complete and there is no transference of electron or charge. This type of valency bond, which was named covalency by Langmuir, can be applied to a large number of organic compounds. Thus, carbon with four electrons short of its octet will combine with four hydrogen or chlorine atoms and the resulting molecules will be uncharged and will be held together by covalencies. This is the normal type

\[ \text{Cl} : \text{H} - \text{H} - \text{H} \]

A further type of linkage was envisaged by Lewis, which was termed a semi-polar double bond by Lowry, and later a coordinate by Sidgwick. This type of link consists of the donation of unshared electrons towards a group, or atom, which
is short of its stable octet:
\[
\begin{array}{ccc}
\text{R} & \text{R}:\text{A} & \text{B}: \\
\text{R} & \text{R} & \text{R}:\text{A}:\text{B} \\
\end{array}
\]

For example, the two uncharged electrons, or lone pair, of the nitrogen atom in ammonia is utilized to make up the octet of boron in the compound, boron trifluoride
\[
\begin{array}{ccc}
\text{H} & \text{F}^6 & \text{H} & \text{F}^6 \\
\text{H}:\text{N}: & \text{B}:\text{F}^6 & \rightarrow & \text{H}:\text{N}:\text{B}:\text{F}^6 \text{ or } \text{H}_3\text{N}^+ \rightarrow \text{BF}_3 \\
\text{N} & \text{F}^6 & \text{H} & \text{F}^6 \\
\end{array}
\]

Such a linkage involves the generation of intramolecular charges and is conveniently represented by an arrow pointing from the "donor" atom to the "acceptor" atom. The two charged neighbouring atoms are said to constitute a dipole. Sugden showed that compounds containing this linkage e.g. nitro bodies (\(\text{R} - \text{N}^+\text{O}\)) had abnormal parachors, and Phillips in 1925 succeeded in preparing ethyl-\(\alpha\)-toluenesulphinate in an optically active state, showing quite definitely that the old accepted structure \(\text{R}^1\text{S} = 0\) was inaccurate. In a sulphinate, however, there is a lone pair of electrons, and further co-ordination with oxygen is possible to give a sulphonate which is no longer asymmetric:
\[
\begin{array}{ccc}
\text{R}^1 & \text{S} \rightarrow \text{O} \\
\text{R} & \text{R}^1 \text{S} \rightarrow \text{O} \\
\end{array}
\]

One of the most important applications of the Electronic Theory is to the course of chemical reactions in organic chemistry. Most molecules can assume activated forms distinct from their resting states and in the case of the benzene molecule,
we have to distinguish between two effects of substituents, first, the influence of a substituent on the resting state of the molecule, and second, the influence of a substituent on the ease of assumption of a specially activated form. In other words, the benzene ring may be polarised owing to the pressure of a substituent, and this polarisation may be a permanent one, or a temporary one, arising at the call of the re-agent.

Our knowledge of the permanent resting state of a molecule is furnished by dipole moment measurements. If the mean electrical centre of all the electrons in a molecule does not coincide with the corresponding centre of the atomic nuclei, which they surround, the molecule, as a whole, will possess a definite electrical moment. In the presence of an electrical field, such molecules will tend to orient themselves in the direction of the field until the total dipole moment, original and induced will be balanced by restoring forces. Measurement of the dielectric constant in the liquid state will give the total dipole field, and from this, by subtracting the "distortion effect" (obtained by measurement of the dielectric constant in the solid state) there will be obtained a measure of the effect of the molecular dipole. Values of dipole moments (u) for various substituents X in the benzene ring are given in the following table.

\[
\begin{array}{cccccc}
C_6H_5X & X = & H & CH_3 & Br & Cl & NO_2 & NH_2 \\
\mathbf{u} & = & 0 & 0.43 & 1.56 & 1.58 & 3.75 & 1.39 \times 10^{-18} \text{ e.s.u.}
\end{array}
\]
These data do not give the direction of the charge between the group and the nucleus, but measurements of $\mu$ for $p$-disubstituted benzenes, will enable this to be known, since the value for $\mu$ is as a first approximation the algebraical sum of the individual dipole moments.

$p$-substituted nitro benzenes.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\mu$</th>
<th>Deduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>0.8</td>
<td>approx. zero</td>
</tr>
<tr>
<td>Cl</td>
<td>2.52</td>
<td>NO$_2$ $\rightarrow$ Cl</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>4.30</td>
<td>CH$_3$ $\rightarrow$ NO$_2$</td>
</tr>
<tr>
<td>Br</td>
<td>2.69</td>
<td>NO$_2$ $\rightarrow$ Br</td>
</tr>
</tbody>
</table>

It must be assumed that the nitro group, by virtue of its semi-polar double bond $\text{N}^+\text{O}^-$ has a dipole in the direction indicated, and the above table shows that there is a permanent electron shift as shown in the following compounds:

\[
\text{C}_6\text{H}_5\leftrightarrow \text{CH}_3 \quad \text{C}_6\text{H}_5\rightarrow \text{NO}_2 \quad \text{C}_6\text{H}_5\rightarrow \text{Hal}
\]

As an illustration of these effects it will be sufficient to take the cases of chloroacetic acid and $p$-toluidine and compare their properties with those of the corresponding unsubstituted compounds.

Chloroacetic acid is a stronger acid than acetic, due to the attraction of electrons towards the chlorine atom and the consequent greater facility for the ionisation of the carboxylic hydrogen atom.

\[
\text{H} - \text{CH}_2 - \text{CO}_2 - \text{H} \leftrightarrow \text{OH}_2 \quad \text{Cl} \leftrightarrow \text{CH}_2\text{CO}_2 - \text{H} \leftrightarrow \text{OH}_2
\]

$\text{p}$-Toluidine is a stronger base than aniline owing to a readier acquisition of electrons by the nitrogen atom, due to
the repulsion of electrons by the methyl group:

\[
\begin{align*}
\text{H} & \quad \text{NH}_2 \leftrightarrow \text{H} \\
\text{CH}_3 & \quad \text{NH}_2 \leftrightarrow \text{H}
\end{align*}
\]

It is also seen that the effect of the methyl group can pass with facility from one side of the ring to the other, i.e. its effect can be induced through the ring. Groups like methyl, which have less attraction for electrons than a hydrogen atom induce a negative field into the benzene ring (-I effect) and groups which have a greater attraction for electrons than hydrogen, as shown by dipole measurements, induce a positive field (+1 effect).\footnote{The signs + and - for the I effect are arbitrary, but since we are considering these effects from the point of view of the benzene ring, the signs are chosen to represent the type of field induced by the substituent into the nucleus, and in this, the author is in agreement with Robinson ("Outline of an Electrochemical Theory of the Course of Organic Reactions" - Inst of Chem. p.34) on the necessity of reversing the signs which have been in general use in recent years.} It is well known that groups belonging to the -1 type direct substitution in ortho and para positions of the benzene ring, while groups such as -NO\textsubscript{2}, -NMe\textsubscript{3}, -COOH, which belong to the +1 type substitute largely in the meta position. Ingold, (Rec. trav. chim., 1929, 48, 308) has put forward a theory to account for the directive influence of these two types. Ortho and Para carbon atoms in toluene are directly
activated by the forcing of electrons into the nucleus by the methyl group, the effect of which can be transmitted directly across the nucleus. The $m$-carbon atom is activated also, but this is a second order effect, (fig.1). The $+1$ effect is illustrated by fig.2.

In the latter case $o$- and $m$- positions are directly deactivated whilst the $m$- position is deactivated by a second order effect, and hence substituents will enter mainly in this position.

Another effect which has been postulated is the direct effect produced by the field due to the displacement of electrons towards the benzene nucleus by a group such as methyl. In this case the degree of activation should fall off with distance and activation should be as $o > m > p$. The converse should be the case when a positive pole is attached to the nucleus and activation should then be $p > m > o$. The fact that substitution in toluene for example proceeds $o, p, m$, shows that this effect has small influence on the positions of substitution and this difficulty has been overcome by Ingold (described above).

Abundant evidence for the existence of a field effect, however, has been supplied by Lapworth and Robinson in a discussion upon different types of substituents (Mem. Manchester Phil.Soc. 1927, 72, 43). The main thesis in this paper is that the electrical fields in the molecule, due to the presence of substituents, control to a certain extent the availability of electrons in
different parts of the nucleus. In general substituents may be divided into two types A and B. A is a group which exerts a smaller attraction on electrons than a hydrogen atom. Hence as a result of the potential gradient in the molecular field, electron availability should be greater in the ortho than para positions. B is a group which attracts electrons more strongly than a hydrogen atom and thus electron availability is greater in p⁺ than q⁻ (figs. 3 and 4).

Thus groups of type A (e.g. CH₃) which are q→p⁻ directive by virtue of their +1 effect should yield a greater amount of o-substituted derivative, as in fact they do. Groups of type B (e.g. NO₂, NMe₃) are generally meta directive on account of their +1 effect.

The field effect is illustrated by the alteration in the o/p ratio by superimposing one type upon another. For example the B effect upon the A in benzyl chloride causes an increase in p/o ratio as compared with toluene as the following figures for nitration show:

- CH₃: 38%
- CH₂Cl: 55%

B effect added.

Other examples given by Lapworth and Robinson are:
Although the halogens are normally $o$- or $p$- directive, their $+I$ effect will result in high p/o ratios as follows:

These figures also show that the $+I$ effect decreases in the order $F > Cl > Br > I$.

Removal of a $B$ type of substituent to a position more remote from the nucleus will decrease the proportion of $m$-isomeride as the following examples show:

The $A$ effect superimposed on $B$ is illustrated by the following series. (The $-SO_2R$ group is regarded as a $B$ type in virtue of the large positive charge on the sulphur atom.)
Many more examples of these two effects are given by Lapworth and Robinson (loc. cit.) and they undoubtedly prove the existence of a field effect associated with the nucleus.

Lapworth and Robinson in the same paper also draw attention to the nature of the substituting agent as a factor bearing on the o/p ratio. They refer to the work of Gatterman and Liberman on the formation of azo compounds from δ-naphthol and its 3- and 5- sulphanic acids. These naphthols were coupled with dianisidine salts from sulphanilic acid, p-chloro-aniline, 2:5-dichloroaniline, 2:4:5 trichloroaniline, o-,m- and p-nitroanilines, 4 chloro-3-nitroaniline, 2:4-dinitroaniline, and p-nitroaniline-p-sulphonic acid. The earlier members of this series attacked the 2-positions, and the later attacked the 4-positions to a dominating extent. It is seen that the dianisidine salts of this series constitute a series of increasingly energetic kations from the earlier to the later members, and hence Lapworth and Robinson have suggested that the degree of activation in position 4- is smaller than in position 2-, but that the frequency of activation in 4- is greater than that in 2-. The more energetic kations can take advantage of the position having the higher frequency of activation. Bromine which is undoubtedly a more energetic kationoid re-agent than nitric acid would therefore be expected, according to this explanation, to be a more
powerfully seeking re-agent than nitric acid, as in fact it is.

The above hypothesis has been applied to the case of 4-ace-
tamido diphenyl, which on bromination gives the 4'- derivative,
whilst nitration gives the 3-nitro derivative (Kenyon and P.H.
Robinson, J., 1936, 3050). Because of this, Bell (J, 1931, 2339, 2)

\[ Br \rightarrow \text{Br} \quad \text{NHAc} \]

\[ \text{NO}_2 \]

has suggested that position 4' might have a higher frequency
and lower degree of activation than position 3-. Other develop-
ments of the electronic theory, mainly due to Robinson, have led
to the idea that a shift of electrons, or field effect is not
sufficient to cause substitution, but that an actual increment of
electrons on a carbon atom is necessary. Unlike the inductive
effect, this effect is regarded as being temporary in nature,
arising at the call of the re-agent. This second type of elec-
ron displacement, termed electromeric (E), or tautomeric (T),
occurs in its simplest form in the saturation of olefines and in
additive reactions of carbonyl compounds. The simplest reaction
in the second case is the cyanhydrin formation of formaldehyde.
Lapworth has shown that this type of reaction is essentially due
to the attack of the carbon of a carbonyl group by a cyanidion,
the process being completed as shown below:

\[ \text{R}_2\text{C} = 0 \quad \text{CN} \quad \text{R}_2\text{C} - \text{CN} \quad ; \quad \text{R}_2\text{C} - \text{CN} \quad \text{H}_2\text{O} \quad \text{OH} \quad \text{R}_2\text{C} - \text{CN} \quad \text{DH} \]
It is clear that we must postulate as an intermediate stage in the reaction the actual transference of electrons from the double bond to the oxygen atom, giving the latter a negative charge, and the carbon atom a positive charge. Thus we have the following scheme (each line represents two electrons).

\[ \text{H}_2\text{C} = 1 \rightarrow \text{H}_2\text{C} \overset{0}{\underset{1}{\text{O}}} \quad \text{or} \quad \text{H}_2\text{C} \overset{+}{\underset{0}{\text{C}}} \]

The positive carbon, which has a deficiency of two electrons will restore its octet by,

(a) reversing the original electromeric charge 
or (b) receiving electrons from an external source — in this case from CN.

This type of effect, (electromeric), conveniently written \( \text{H}_2\text{C} \overset{0}{\underset{0}{\sim}} \), is regarded by Robinson as necessary for a reaction to take place. The inductive effect, though not sufficient to cause reaction, can render the electromeric effect more probable in one direction than another, e.g. in the addition of hydrogen bromide to olefines:

\[ \text{CH}_3 \rightarrow \text{CH} = \overset{5}{\underset{5}{\text{CH}}} - \text{H} \text{ is more likely than } \text{CH}_3 \rightarrow \overset{5}{\underset{5}{\text{CH}}} = \text{CH} - \text{H} \]

and hence the B-bromo compound \( \text{CH}_3\text{CHBr}\cdot\text{CH}_2\cdot\text{H} \) is formed.

The reactions of ethylene indicate that it is anionoid in character. It is readily attacked by halogens, nitric acid, and other kationoid reagents, but is unaffected by such strong anionoid reagents as ammonia, Grignard reagents, and amines. Hence ethylene (and olefines in general) is anionoid, and obviously benzene must be placed in the same category. The electronic theory does not afford much assistance in solving the
question of the constitution of the benzene molecule, but assuming the Kekulé formula, facts are readily interpreted by the theory. The ring as a whole is therefore to be regarded as a conjugated electromeric system, the characteristic of which is that the valency of the carbon atoms appears to be equalised along the chain, thus: \[ C \equiv C \equiv C \equiv C \equiv C \equiv C \]. Hence with a group such as \(-\text{CH}_3\), exerting a \(-I\) effect, a \(-E\) effect will be induced according to the following scheme. (Fig. 3).

![Fig. 3](image)

Two alternative processes a and b can take place, activating \(\sigma\) and \(\pi\) carbon atoms. With a group belonging to the \(+I\) type the opposite process will occur (fig. 4).

If a substituent attached to the benzene rings has lone pairs of electrons, these may come under the influence of the ring giving rise to a \(-E\) effect. This process is illustrated by fig. 5. (Each line represents one electron).

\(\text{C}_\sigma\) has an increment of two electrons. The octet of electrons will be restored by the transference of two electrons to \(\text{C}_\rho\) (a) or alternatively by a series of changes to \(\text{C}_\sigma\) (b). Hence \(\text{C}_\rho\) and \(\text{C}_\sigma\) receive temporary negative charges and substitution will take place in these positions. This process explains the \(\sigma-\pi\) directing power of the halogens, in spite of their \(+I\) effect.

See Note Page 6.
Since the halogens are \(\sigma-\pi\)-directive and since dipole moments of halogens benzenes are in the same direction as those of nitro benzenes, it must be assumed that electromeric displacements cannot be otherwise than momentary. Considerations of this type point to Ingold's contention, that there are two effects, different in character, an inductive effect, which is permanent, and an electromeric effect which is temporary and probably excited by the electron seeking nature of the reagent.

Although the benzene ring generally behaves as a donor of electrons, it may also exhibit the opposite effects. The Kationoid reactivity of benzene is well illustrated by the o/p substitution of nitro benzene by negative ions. The reversal of the usual effects is apparent in these reactions:

\[
\begin{align*}
\text{NO}_2^- & \rightarrow \text{NO}_2^- \\
\text{C}_6\text{H}_5\text{O}^- & \rightarrow \text{C}_6\text{H}_5\text{O}^-
\end{align*}
\]

(Wohl Ber., 1899, 33, 3486)

1901, 34, 2414

(Bradley & Robinson J., 1932, 1254)

The amphoteric nature of benzene has also been illustrated in a recent paper by Grieve & Hey (J., 1934, 1797) in which it is shown that sodium benzene diazotate and N-nitro acetanilide reacts with an aromatic compound \(\text{C}_6\text{H}_5\text{R}\), so that the phenyl group undergoes substitution invariably ortho and para to \(\text{R}\) irrespective of the nature of \(\text{R}\). For this type of reaction to take place it is highly probable that a transient formation of free phenyl radicals occurs, the latter being capable of acting as a potential donor or acceptor of electrons.

Recent work of Sutton has shown that a small permanent
effect is associated with the electromeric effect. He found the differences in dipole moments between compounds C₆H₅-X, and Alk - X (where Alk = tertiary butyl - chosen because the symmetrically arranged methyl groups would be in such a position that their individual dipole moments cancel each other and hence a measure of the dipole between Bu - X would be a true indication of the dipole produced by X alone). This difference would give the dipole moment produced by the electromeric effect. Some of the results are tabulated below:

<table>
<thead>
<tr>
<th>X</th>
<th>μ(Ar-X)</th>
<th>μ(Alk-X)</th>
<th>μ(Ar-X) - μ(Alk-X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>+0.145</td>
<td>±0.0</td>
<td>+0.145</td>
</tr>
<tr>
<td>O</td>
<td>-1.26</td>
<td>-1.29</td>
<td>+0.23</td>
</tr>
<tr>
<td>NH₂</td>
<td>+1.55</td>
<td>+1.23</td>
<td>+0.32</td>
</tr>
<tr>
<td>Cl</td>
<td>-1.56</td>
<td>-2.15</td>
<td>+0.59</td>
</tr>
<tr>
<td>CH₂Cl</td>
<td>-2.03</td>
<td>-2.06</td>
<td>±0.0</td>
</tr>
<tr>
<td>COCH₃</td>
<td>-2.97</td>
<td>-2.79</td>
<td>-0.18</td>
</tr>
<tr>
<td>CO</td>
<td>-3.04</td>
<td>-3.76</td>
<td>-0.72</td>
</tr>
<tr>
<td>C≡N</td>
<td>-3.89</td>
<td>-3.46</td>
<td>-0.43</td>
</tr>
<tr>
<td>NO₃</td>
<td>-3.93</td>
<td>-3.05</td>
<td>-0.88</td>
</tr>
</tbody>
</table>

It is to be noted that the top four substituents which are o–p– directive give a positive difference, whilst the last four which are m– directive give a negative difference. This permanent effect associated with the electromeric effect has been termed "mesomeric" by Ingold, who has conveniently classified the effects in the benzene ring. The permanent effect is associated with energy inside the molecule and is a polarisation...
The temporary effect is associated with the energy outside the molecule and is a polarisability. This is summed up below:

- **General Inductive** \((\rightarrow)\) **Tautomeric** 

<table>
<thead>
<tr>
<th>Energy inside molecule</th>
<th>Polarisation</th>
<th>Inductive</th>
<th>Mesomeric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy outside molecule</td>
<td>Polarisability</td>
<td>Inductomerio</td>
<td>Electromeric</td>
</tr>
</tbody>
</table>

It is to be observed also that Ingold has introduced a temporary effect "Inductomerio" associated with the general Inductive effect. However, for general purposes, it will be sufficient to divide these effects into two classes only:--

- **Inductive** (permanent) and **Electromeric** (temporary).

The actual process of substitution has been described by Ingold & Ingold (J., 1926, 1315). Generally, substituting reagents are Kationoid i.e. they will seek negative centres. If a carbon atom in the benzene ring has a relatively high electron density compared with the other carbon atoms, then there will be a preliminary attachment of the Kationoid part of the reagent to this point followed by the elimination of a simple molecule (HgO, HBr, etc.,), according to the following scheme:

\[
\begin{align*}
\text{Br}_2 & \overset{\text{S}^+}{\rightarrow} \text{Br} + \text{Br} \\
\text{NO}_2 & \overset{\text{S}^-}{\rightarrow} \text{NO}_2^+ - \text{OH} \\
N & \equiv N = N, \text{Ar} \\
\end{align*}
\]
In the latter case, of course, the reagent $\text{ArN}_2^+$ has a large positive charge.

**SUMMARY OF CONCLUSIONS.**

Effects may be propagated in these distinct ways:

1. By a Direct or Field effect, which falls off as $\text{O}^\ominus \text{m/p}$.

2. Inductively in aromatic nuclei, the effect centering on $\text{o}$- and $\text{p}$- carbon atoms.

3. By electromeric displacements. The group $R$ increases its covalency with the nucleus and resulting displacements lead to development of a negative charge on $\text{o}$- and $\text{p}$- carbon atoms. These displacements are temporary in nature but exceed in magnitude those produced by (1) and (2).

**ORIENTING POWERS OF VARIOUS GROUPS.**

Substituents have been conveniently classified by Ingold & Shaw (J., 1927, 2918). Starting from the idea that two effects $I$ and $E$ are mainly responsible for direct substitution, it has been found that any substituent belongs to one of the following four classes:

1. \( \gamma \rightarrow R \)  
2. \( \gamma \rightarrow +R \)  
3. \( \gamma \rightarrow E \)  
4. \( \gamma \rightarrow E +I \)

Class 1, of which the methyl group is an example, favours $\text{o}$/$\text{p}$ substitution, e.g., halogenation and nitration of toluene.

Class 2 favours $\text{m}$-substitution. Groups such as $-\text{NO}_2$, $-\text{NMe}_3$, $-\text{COOH}$, fall under this heading.

Most substituents belong to the 3rd class. Here $E$ and $I$ effects are conflicting. Hence this type of group is of a
more complicated nature. It is possible from a study of velocity of reaction to construct a series of substituents having increasing $-E$, and decreasing $+I$ effects e.g.,

$$-	ext{NR}_{2} > -	ext{OR} > -	ext{I} > -	ext{Br} > -	ext{Cl} > -	ext{F} \quad (R = \text{alkyl})$$

$-E$ decreases $\rightarrow$ $\rightarrow$ $+I$ increases

At a certain point in this series, the velocity of reaction will become less than that of unsubstituted benzene, but o/p substitution will continue to take place.

Class 4, is essentially o/p directing. Owing to the Inductive and Electromeric effects both working in the same direction, there is a great activation of all positions in the ring, the phenoxide ion being an example of this type.
II. ELECTRONIC CONSIDERATIONS APPLIED TO NAPHTHALENE.

A. Configuration.

Several constitutions for the naphthalene molecule have been put forward. Formulae of the centric type (I & II) can have no meaning in the light of modern electronic ideas. Of the two formulae (III & IV) the former due to Erlenmeyer is generally accepted.

This structure explains the existence of two and two only mono-substituted products e.g., α- and β-naphthols; α- and β-naphthylamines. Formula (IV) would require four isomeric mono-substituted derivatives. However, the possibility of full interchange between (III) and (IV) should be borne in mind as this would also explain the existence of only two monosubstitution products.

Stereochemical considerations have been applied by Mills and Nixon (J., 1930, 2520) to the case of tetrahydro naphthalene.
Starting from the idea that the angle $\alpha$ between two singly bound carbons is of the order 109° (i.e. the angle at the centre of a regular tetrahedron), then angle $\beta$ (V) is of the order 126°, assuming that the benzene ring is a regular hexagon. Owing to the presence of the double bond this deduction may not be correct but it is reasonable to assume that $\beta > \alpha$. Hence the outer valency bonds of the carbon atoms are not prolongations of the axes (the internal angle of the ring being 120°). Writing the two alternative formulae for tetrahydro naphthalene (VI) and (VII) it is seen that the former corresponds with a configuration of least strain, since this structure requires an internal angle $\beta$ corresponding more closely with the internal angle 120° of a regular hexagon, than structure (VII) in which the internal angle $\alpha$ differs from 120° more than $\beta$. This conclusion has been borne out by experimental evidence, since substitution of tetrahydro aceto-2-naphthalide and tetrahydro-2-naphthol results in 1- substitution. The unsymmetrical structure would require 3- substitution (VII). Since tetrahydro naphthalene has been shown to exist in the symmetrical form, it is reasonable to suppose that naphthalene itself largely exists in the symmetrical form. However, Thompson (J. Soc. Chem. Ind., 1933, 52, 61) points out that owing to the facts that hydrogen is smaller than carbon, and the distance between doubly bound carbon atoms is shorter than that between singly bound carbons, a valency angle of type $\beta$ in structure would tend to be larger than 120° when in an unstrained condition. Consequently he has argued that the unsymmetrical phase is in a condition of less strain than the symmetrical, but although the
latter form does best explain the reactions of naphthalene, its existence is to be related to the strong tendency of both rings to possess an aromatic structure, rather than to steric factors. Therefore either on Mills & Nixon's or Thompson's view, naphthalene should exist largely in the symmetrical form.

The few physical measurements which have been made on naphthalene have thrown some light on its structure. Intra-molecular distances between adjacent carbon atoms in the molecule have been determined by X-ray measurements by Robertson (Proc. Roy. Soc., 1933, (A), 142, 674) and the value 1.41Å for the C-C linkage corresponds to an aromatic structure. Robertson has also established that the naphthalene system forms a flat rigid molecule, a conclusion which has been supported by its zero dipole moment. The following data are taken from Trans. Farad. Soc., 1934, 30. Appendix, page XXX).

<table>
<thead>
<tr>
<th>Investigators</th>
<th>( \mu ) (10^{-18} \text{e.s.u.})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Williams</td>
<td>0.69</td>
</tr>
<tr>
<td>Williams &amp; Ogg</td>
<td>0.72</td>
</tr>
<tr>
<td>Parts</td>
<td>0</td>
</tr>
<tr>
<td>Williams &amp; Fogelberg</td>
<td>0</td>
</tr>
<tr>
<td>Fuchalico</td>
<td>0</td>
</tr>
<tr>
<td>Brieglieb</td>
<td>0.34 ± 0.05</td>
</tr>
</tbody>
</table>

The discussion on the dipole moments of dichlor-naphthalenes (ibid, 887) supplies further information on the constitution of the naphthalene molecule. The zero dipole moments of 1:5- and 2:6-dichloronaphthalenes indicate the naphthalene system to be planar and not folded. Absorption spectra of naphthalene have
been investigated by Morton & de Gouveia (J., 1934, 924) and it is found that two maxima occur in the absorption bands corresponding to an ethylenic linkage \( \text{C} = \text{C} - \text{C} = \text{C} \), and to the chromophore \( \text{C}_6\text{H}_5-\text{C} = \text{C} - \).

The peri-positions in naphthalene are of interest in that they are somewhat analogous to ortho positions in the benzene ring. That these positions are near to each other is illustrated by the ease of condensation of groups in the 1:8 positions to form ring systems such as the formation of naphthalic anhydride from 1:8 naphthalic acid and the ready formation of naphthalene-1:8-sultone (IX) from 1:8-hydroxy-naphthalene sulphonic acid (VIII). (Cumming & Muir, Journ. of the Roy. Glasgow Tech. Coll., 1934, 228).

\[ \text{OH} \quad \text{SO}_3\text{H} \quad \rightarrow \quad \text{SO}_2\text{H} \]

(VIII) (IX)

The peri positions are also near enough to allow of restricted rotation of groups sufficiently large in these positions, and the consequent exhibition of optical activity. Evidence of optical activity exhibited by compounds (X) and (XI) has been obtained by Mills & Elliott (J., 1928, 1291) and Mills & Breckenbridge (J., 1932, 3209).

\[ \text{NO}_2 \quad \text{SO}_2\text{Ph} \quad \text{CH}_2\text{COOH} \quad \text{N} \quad \text{S}_2\text{Ph} \quad \text{Et} \]

(X) (XI)

In the latter case, the corresponding \( \text{N}:\text{N}' \) dimethyl derivative was not active, indicating that the 1:8 positions in
naphthalene are not sufficiently near for the restriction of rotation round a small group like methyl.

That the 1:8- positions allow of considerable interaction has been furnished by dipole moment measurements of 1:8- dichloronaphthalene (Trans. Farad. Soc., loc. cit.). This value like that of 1:2-dichloronaphthalene has been found to be smaller than that calculated on the basis of non-interference between the chlorine group.

Further evidence for the nearness of the peri-positions has been furnished by a study of migration reactions in 1:8-amino-naphthol. From investigations of the migration of acyl groups in ortho amino phenols, Bell (J., 1931, 2346, 2964) has suggested that hydrolytic migration involves the intermediate formation of compounds of the benzoxazole type (XIII), (XV), e.g. in the interchange of 2-acetamidophenyl benzoate (XII) to 2-benzamidophenyl acetate (XVI).

\[
\begin{array}{c}
\text{(XII)} \\
\text{(XIII)} \\
\text{(XIV)} \\
\text{(XV)} \\
\text{(XVI)} \\
\end{array}
\]

Although such compounds (XIII), (XIV) and (XV), were not isolated, probably owing to their unstable nature, sufficient experimental evidence was obtained of their existence. Similar experiments on the migration of acyl groups in 1:8-amino naphthol have provided indications of the stable existence of an oxazole type. Contrary to the statement of Raiford
(J. Amer. Chem. Soc., 1926, 48, 483) it has been found that acetylation of 1-benzamino-8-naphthol (XVI) gave a different product from that obtained by the benzylation of 1-acetamino-8-naphthol (XIX), since a mixture of (XVI) and (XX) produced a large depression in melting point (although their individual melting points were almost the same).

\[ \text{NHB}_2 \quad \text{OH} \quad \rightarrow \quad \text{NHB}_2 \quad \text{OAc} \]

\[ \text{XVI} \quad \rightarrow \quad \text{XVII} \]

\[ \text{NHB}_2 \quad \text{OAc} \quad \rightarrow \quad \text{NHB}_2 \quad \text{OB}_2 \]

\[ \text{XX} \quad \rightarrow \quad \text{XXII} \]

1-Acetamino-8-naphthyl benzoate (XXI) was partially converted by melting to an isomeric compound which it is suggested has the constitution represented by (XXII), since it gave large depressions in melting point with (XVI), (XVII), (XIX) and (XX).

\[ \text{XXI} \quad \rightarrow \quad \text{XXII} \]

It seems therefore that the peri-positions in naphthalene favour the formation of a stable six member oxasole ring system, whereas in the case of benzene such a five membered system appears to be unstable.

B. Active Phases of Naphthalene.

The vigour with which naphthalene undergoes monosubstitution in the \( \alpha \)-positions shows that this position is highly activated. A reactive phase must therefore be postulated to account for the much greater reactivity of the \( \alpha \)- than the \( \beta \)-position.

The naphthalene molecule can be regarded as a combination of
two benzene rings, the amphoteric nature of which has been discussed (pages 6 & 7). At the moment of substitution one ring (B) may be acting as an electron attractor, giving rise, by an electromeric process, to activation of the position in ring A. Comparison with the case of diphenyl would indicate

![Diagram](image1)

that this explanation is not entirely satisfactory. A similar mechanism in this case would require some substitution to occur in the 3- position, which is not realized experimentally. However, reference to dipole moment measurements of 1:3-dichlor- and 1:4-dichlor-naphthalene, (Trans.Farad.Soc.XXX,387), appears to support this view. The experimental values are found to be larger than the theoretical, calculated on the assumption that the naphthalene molecule is planar and that the dipole moment of α-chloronaphthalene is $1.59 \times 10^{-18}$ e.s.u. and that of the β-isomer is $1.72 \times 10^{-18}$ e.s.u. (Parts, Z.physik.Ch.1930,108,264). This difference ($\mu_{1:3} = 1.8, \mu_{\text{calc}} = 1.6; \mu_{1:4} = 0.5, \mu_{\text{calc}} = 0.0 \times 10^{-18}$ e.s.u.) has been attributed by Weissberger, Sängewald & Hampson (Trans.Farad.Soc.loc.cit.) to a small component of polarisation of the order (0.2) as shown in (XXIII) and (XXIV).

![Diagram](image2)

Assuming this value, the calculated values will then agree closely with the experimental
An alternative view is to regard naphthalene as a derivative of styrene. As is well known, an ethylenic side chain is powerfully \( p_- \) and \( p_- \) activating, the substitution of cinnamic acid, for example, proceeds ortho and para, in spite of the deactivating influence of the carbonyl group. However, to regard substitution in naphthalene as being the result of an activation by an ethenoid system, it is necessary to postulate an intermediate unsymmetrical phase. The electromeric change "a" in (XXV) may give rise to a temporary tautomeric unsymmetrical modification (XXVI) which can then allow of substitution in the \( \alpha_- \) positions (XXVII); the resulting substituted derivative then reverting to the original symmetrical structure (XXVIII).

The familiar conjugated addition of bromine to butadiene is somewhat similar, only here the conjugated system has been destroyed, whereas in the case of naphthalene, the double bonds are free to revert to their former positions.

\[
\text{CH}_2 = \text{CH} \rightleftharpoons \text{CH} = \text{CH}_2 \quad \text{BrCH}_2 - \text{CH} = \text{CH} \cdot \text{CH}_2 \cdot \text{Br}
\]

This explanation is more in harmony with the similar one for diphenyl, the reactive phase of which may be represented by (XXIX). This phase requires monosubstitution to occur in the 2 and 4 positions, which does in fact take place, (Bell, Kenyon & Robinson J., 1926, 1239) (Snell & Turner J., 1929, 491).
The possibility of tautomeric forms may be applied to mono-substituted derivatives, but here complications arise because instead of the two possible forms as in unsubstituted naphthalene, there are now three. Experimental evidence, however, can decide which of these two forms are likely or not likely, to exist. The least complicated case is that of α-nitro naphthalene, where the nitro group is powerfully deactivating. The further nitration of this substance occurs in the unoccupied ring, and 1:5- and 1:8- dinitro derivatives are formed, in approximately equal amounts. (Friedländer, Ber., 1899, 32, 3531).

\[
\text{\[XXXa\]} \quad \text{\[XXXi\]}
\]

If the unsymmetrical form (XXXi) is capable of being produced as the result of the +E effect arising from the nitro group (XXXa), then it might be expected that in spite of the deactivating effect of the nitro group, a certain amount of \(\tau\)-substitution should take place, owing to the powerful ethenoid effect at this position. This phase must therefore be rejected on experimental grounds.

The phase (XXXii), although capable of explaining hetero-

\[
\text{\[XXXb\]} \quad \text{\[XXXii\]}
\]

nuclear substitution, is improbable owing to this being formed in opposition to the +E effect of the nitro group (XXXb).
Therefore on theoretical and experimental grounds, \( \alpha \)-nitro naphthalene must be regarded as having a fixed symmetrical structure. On this basis, 5- and 8- substitution must be regarded as due to an ethenoid effect (b or c) arising from the attraction of electrons (a) by the ring containing the nitro group. These considerations apply also to 2- nitro naphthalene.

Bromination and chlorination of 1-nitro naphthalene follow a similar course to nitration (Guartèschi, Ann., 1884, 222, 291; Ullmann & Consonno, Ber., 1902, 35, 2807; Scheufelen, Ann., 1885, 231, 185).

Groups of a similar type to the nitro (+E), are the carboxy and sulphonie acid groups. Substitution reactions of naphthoic and naphthalene sulphonie acids are comparable to those of nitro naphthalene, although in the latter case, a sulphonie acid group in the \( \alpha \)-position has a tendency to be replaced by the substituting group. (Kerkhoff, Rec. Trav. Chim., 1932, 51, 739; Zelkind & Belikov, Ber., 1931, 64B, 955). Nitration and halogenation of \( \alpha \)-naphthoic acid furnish the 5- and 8- derivatives, (Ekstrand, J. Pr. Chem. (2) 1888, 38, 139, 155, 38; Rule & Barnett J., 1932, 177: Kerkhoff, loc. cit.). Bromination of 2- naphthalene sulphonie acid (Zelkind & Belikov, loc. cit.) is also heteronuclear, occurring in the 5- and 8- positions.

A compound more closely analogous to naphthalene than diphenyl, is \( \alpha \)-diphenylene which was discovered by Dobbie, Fox & Gauge (J., 1911, 1617). On the basis that the benzene rings are regular hexagons and that the four membered system between them is a square then \( L_a, p, q, r \) are 120°, 90°, and 150° respectively (XXXVI)
Owing to the considerable distortion produced, however, this deduction is unlikely to be accurate, but it is reasonable to assume that \( r > p > q \). On Mills' & Nixon's view, a configuration of least strain should be that indicated by (XXXIV) (\( \alpha \) of the order 109° and \( \beta \) of the order 125°). The configuration represented by (XXXV) would be out of harmony with the views of Thompson (page 120) and adopting the arguments of this author, \( o \)-diphenylene should be capable of existing as an equilibrium mixture of (XXXIII) and (XXXIV) and which would correspond respectively with the symmetrical and unsymmetrical phases of naphthalene.

It seemed of importance to compare the properties of diphenylene with those of naphthalene, but unfortunately it has not proved possible to prepare this hydrocarbon. The method of Dobbie, Fox & Gauge (loc. cit.) proved to be unsuitable for the preparation of diphenylene in sufficient amount, owing to the poor yields of \( 2 \):\( 2' \)-diamino- and \( 2 \):\( 2' \)-dibromodiphenyl.

\[
2 \quad \text{O} \quad \text{N}=\text{N} \quad \rightarrow \quad \text{O} \quad \text{N} \quad \text{N} \quad \rightarrow \quad \text{N} \quad \text{N} \quad \rightarrow \quad \text{N} \quad \text{N}
\]

An alternative method of preparation, by the elimination of iodine from \( o \)-di-iodobenzene by means of the Grignard reaction gave a hydrocarbon, m.p. 189 - 192°, which was probably impure \( 9 \):\( 10 \)-bensphenanthrene (described by Mannich, *Ber.* 1907, 40, 160;
Recently, Mascarelli & Gatti (Gazzetta 1933, 63, 654-660, 661-665) have also attempted to obtain o-diphenylene. Employing Dobbie, Fox & Gauge’s method (loc.cit.) they find that 2:2'-di-bromo-diphenyl is unaffected by sodium in ether. Negative results were also obtained with 2:2'-diochloro- and 2:2'-di-iodo diphenyl, and the Ullmann reaction upon o-bromo-iodobenzene gave diphenylene oxide.

C. The Anionoid Reactivity of Naphthalene – Chemical Evidence for Symmetrical Structure.

The ease with which naphthalene undergoes substitution indicates that it is powerfully anionoid – far more so than benzene, which undergoes substitution with difficulty. This is to be attributed to the operation of mechanisms which have been discussed in the previous section. Further illustrations of electron accession in the naphthalene molecule are to be found in the ease with which the diazo hydroxides of nitro naphthylamines undergo internal diazo-oxide formation in aqueous solution. Thus, Morgan & Evens (J., 1919, 115, 1127) have described the preparation of 4-nitro-1-naphthalene diazo-2-oxide (XXXVII) from 2:4-dinitro-1-naphthylamine.
It has now been found that 1:6:8-trinitro-2-naphthylamine (XXXVIII) undergoes easy internal diazo oxide formation (XXXIX), and that like compound (XXXVII) it is stable, gives an intense blue colouration with alkaline resorcinol, and is slowly reduced by boiling alcohol.

The mechanism of this type of reaction must depend upon the ease with which the nitro group adjacent to the amino group can take up electrons and leave the molecule in the form of nitrous acid. Morgan & Evans (loc. cit.) have shown that nitro amines of the benzene series do not undergo internal diazo oxide formation. Hence in the naphthalene molecule there must be factors present, enabling facile electron accession, which are absent in benzene. The first factor may be due to an effect (b) arising from one ring to the other, and the second factor, which is regarded as being more important, is due to the fixed double bond between the nitro and amino groups giving rise to the electromeric mechanisms (a):—
The mechanism (b) is, of course, absent in the benzene series, and the mechanism (a) in benzene can only take place to a small extent owing to the freedom of the double bonds to oscillate in the benzene nucleus. The fixation of the double bond between the amino and the nitro groups, giving rise to the neutralised electromeric system HO - N = N - C = C - N = O is regarded as being the main factor causing internal diazo oxide formation. On the basis of this argument it would be expected that 3-nitro-2-naphthylamine (XLIII) would not give rise to an internal diazo oxide, owing to the arrangement of the double bonds.

![Diagram of chemical structures](image)

However, no convenient method for the preparation of this compound has been found. Nevertheless, this argument can be applied to the cases of 1-bromo- and 3-bromo-2-naphthylamines (XLIII) and (XLIV). Both these compounds show a marked difference in physical and in some chemical properties. 1-Bromo-2-naphthylamine has m.p. 63°, is easily soluble in cold benzene and volatile in steam. On the other hand 3-bromo-2-naphthylamine (which can now be conveniently prepared), has m.p. 172°, is sparingly soluble in cold benzene, and non-volatile in steam. This difference of physical properties suggests that the 1-bromo compound is chelated, whilst the 3-bromo compound is either feebly or not chelated.

It has been observed by Bell (J., 1929, 2787; 1930, 1072; 1931, 2345) that some amines having bromine or nitro groups ortho to amino undergo facile disulphonamidile formation, but even
with two molecular proportions of sulphonyl chloride, the yield of disulphonanilide is not quantitative, showing that the velocity with which the latter is formed must be high compared with the velocity of formation of the monosulphonanilide. Moreover, amines which show this type of behaviour cannot be acetylated with acetic anhydride alone. Acetylation will only take place in the presence of acid. These peculiarities have been associated by Bell (loc. cit.) to the presence of a chelate ring (e.g. XLV) and the velocity of disulphonanilide formation is attributed to the tendency of the imino hydrogen atom to ionise, and this in turn depends on the electron absorbing power of groups such as NO₂, Br, adjacent to it.

The reactions described above have now been applied to 1-bromo- and 3-bromo-2-naphthylamines and a marked difference in behaviour has been observed. The former amine can be recovered unchanged from boiling acetic anhydride but acetylates readily if a small quantity of concentrated sulphuric acid be present. On the other hand, 3-bromo-2-naphthylamine is acetylated by acetic anhydride alone, no acid being necessary. There can be no doubt therefore that the first amine is chelated and the second either feebly or not chelated.

3-Bromo-2-naphthylamine, with one molecular proportion of sulphonyl chloride in pyridine, gave only the mono anilide (XLVI), whereas, under the same conditions 1-bromo-2-naphthylamine gave a mixture of mono- and di-sulphonanilides (XLVII) and (XLVIII)
This difference in properties must be due to the fixed arrangement of the double bonds in the molecule. No other reason for this difference appears to be possible. It seems that a double bond can facilitate chelation between bromine and amino hydrogen, and that the strength of such chelation depends on electron accession towards the bromine atom, as shown below:

\[
\begin{align*}
\text{Br} & \rightarrow \text{Br} \\
\text{C} & \rightarrow \text{H}
\end{align*}
\]

The powerful inductive effect of the bromine atom causes a depletion of electrons on the carbon atom to which it is attached, and this depletion may be made up by an electromeric transfer of the lone pair of electrons from the nitrogen atom. The resultant development of a unit negative charge between carbon and bromine will then facilitate chelation. Provided that the chelate ring can be broken down, this mechanism will also explain the disulphonanilide formation exhibited by 1-bromo-2-naphthylamine. Electron recession from the nitrogen atom will aid the ionisation of the amino hydrogen atoms.

A third characteristic can be explained on this basis, and that is the ease with which a halogen atom occupying the 1-position in brominated \( \beta \)-naphtols and \( \beta \)-napthylamines is replaced by hydrogen. Reduction of such compounds has been
shown by Fransen & Stauble (J. pr. Chem. 1920, (2), 101, 58 – 74; 1921, 103, 352) to result in removal of halogen in position 1—other halogens being unaffected. It has now been found that 1:3-dibromo-2-naphthylamine under the same conditions is converted to the 3-bromo derivative:

It is therefore apparent that the bromine atom in position 1— is held more loosely than bromine atoms in other positions. During the process of reduction, the bromine atom must leave the molecule with its full octet of electrons, i.e. negatively charged. Electron accession to the halogen must be partly due to the electron donating power of the amino group; but since bromine in position 3— is unaffected, the double bond mechanism outlined above must be brought into consideration. In addition, the effect (b) may to some extent facilitate removal of bromine.

An interesting application of the double bond mechanism may be found in the reactions of 1-nitroso-2-naphthol and 1-benzene-azo-2-naphthol. Bradley & Robinson, (J., 1934, 1484) have shown that these substances react with potassium cyanide to form 4-cyano derivatives. These workers regard these reactions as being essentially an addition of a cyanidion to the katio-enoid systems in their quinonoid forms. It is now further suggested that these quinonoid forms (L) and (LII) can be formed only through the symmetrical structures (XLIX) and (L1),
and not through the unsymmetrical phases (XLIXa) and (Ila).

The mechanism of these transformations can therefore be brought into line with the formation of internal diazo-oxides, the difference in properties between 1-bromo- and 3-bromo-2-naphthylamines, and the reduction of 1:3-dibromo-2-naphthylamine as accounting for the symmetrical structures of these compounds.

The double bond mechanism has been applied by Baker (p., 1934, 1684) to account for the difference of physical and chemical properties exhibited between 2:4-diacyetyl- and 4:6-diacyetyl resorcinols. The former has the properties of a fully chelated compound, whereas the latter is only partially chelated, and Baker argues that chelation of a hydroxyl group with an o-carbonyl is only possible because of the necessity of the neutralized system HO - C = C - C = O:
Baker has applied this chelation theory to 4-0-acetyl resacetophenone. On the basis of this theory this compound should have the constitution shown below, and the Fries migration, should result in the formation of 2:4-diacetyl-resorcinol, which was actually found to take place:

![Chemical structures](image)

The double bond mechanism put forward for naphthalene is similar to these ideas of Baker, but in a sense it is different. Whereas, according to Baker, the tendency for doubly bound oxygen to chelate fixes the position of the double bonds in the nucleus, the fixed symmetrical structure of the naphthalene molecule determines the chelation of bromine in the 1- position.
III. ORIENTING INFLUENCES IN THE NAPHTHALENE SYSTEM

ORIENTING POWERS OF VARIOUS GROUPS.

In a discussion of the orienting effects in the naphthalene molecule, it is necessary to bear in mind not only the effect of a substituent itself, but also the effect of one benzene ring (acting as an ethenoid group) upon the other. This has already been referred to in the discussion of the substitution of nitro naphthalene, naphthoic and naphthalene sulphonic acids. If a substituent is sufficiently powerfully orienting, it will determine all positions of substitution, whereas if it is a weaker system it may determine one or perhaps two positions of substitution, but further substitution will be governed by the ethenoid effect in the naphthalene molecule. A discussion of the influence of different groups will illustrate these ideas.

A. The Directing Power of the Hydroxyl group and the Lowering of its orienting influence on Conversion to Alkosy, and m-Nitro benzene Sulphonoxy groups.

Section 1. Substitution of α- and β-naphthols.

Owing to the ease with which phenolic hydrogen can assume a positive charge, the high activating power of a phenolic group is due to the reactive phase Ar- in which the oxygen can exert a -I effect on the nucleus. In addition the lone pairs of electrons surrounding the oxygen nucleus will give rise to a -E effect, and the combined -E-I effects will result in strong o- and p- activation. This effect is so powerful that trisubstitution in phenol can occur with ease (Llll). In the case of α- naphthol, electromeric changes indicate substitution in
positions 2:4:7:5 (shown by single headed arrows in (L1V)).

It is to be expected that positions 2:4- will be the first to be attacked since activation of these positions is a simple and direct process, whereas activation of the 7:5- positions is indirect. The latter are sufficiently powerfully activated however, for further substitution to take place in these positions, and owing to the ethenoid effect at position 5-, it would be expected that the 2:4:5- trisubstituted derivative should be formed in greater amount than the 2:4:7-. Experimental evidence fully bears out these expectations. Nitration of 2:4-dinitro-α-naphthol gives a mixture of 2:4:5- and 2:4:7- α-naphthols (Ekstrand, Ber., 1878, 11, 162; Kermann, Haberkaut, ibid. 1898, 31, 2420; Steiner, ibid., 1900, 33, 3285). An improvement on the method of previous workers has been found which furnishes a convenient method for the separation of the isomers. The ratio of 2:4:5- to 2:4:7- was found to be of the order 5:2.

An additional point of interest may be mentioned. If the direct effect (page 7) is sufficient to cause substitution, then the negative field surrounding the oxygen in α-naphthol in close proximity to the 8- position should cause substitution here. The facts that the nitro group does not enter the 8- position but attacks the 7- lends considerable support to Robinson's contention that substitution takes place only through electro-
emic disturbances (page 2).

In the case of β-naphthol two alternatives are theoretically possible, either 1:6:8- or 1:3- substitution (LV). Nitration of B-naphthol gives the 1:6- dinitro derivative (Bell, J., 1932, 2732) and attempts to nitrate this substance further results in decomposition. There is no doubt that the 1:6- positions are highly activated, but the failure of 3-substitution is surprising, since this seems to be an even simpler process than 6- substitution. Position 1- must be much more highly activated than other positions owing to the high o/p ratio of the hydroxyl group and to activation by the unoccupied ring. Hence it is reasonable to assume that this must be the first position taken up by the entering group. The nitro group will deactivate positions in its own ring and hence it might be expected that further substitution will proceed 6- rather than 8-.

Hence in β-naphthol, the 6- position seems to function similarly to a para position in phenol.

Section 2. Substitution of α- and β- naphthyl ethers.

Methoxy and ethoxy groups are somewhat similar to the hydroxyl group although their orienting power is less. However, the nitration of the methyl and ethyl ethers of β-naphthol proceeds 1:6:8, showing that these groups are still powerfully activating. Gaess' work on the nitration of 2-naphthyl-ethyl ether (J. pr. Chem. 1891, (2) 43, 22; 1892, 45, 615; 1892, 46, 160) showed that the first products of nitration consisted of a mixture of 1-, 6-, and 8- nitro derivatives, the 1- compound being produced in comparatively large amount, whilst only very small quantities of the latter two isomers were obtained. Nitration
of 1-nitro-2-naphthyl ethyl ether, leads to a mixture of 1:6-dinitro (main product) and a small amount of 1:8-dinitro compound. Nitration of the methyl ether follows the same course (Davies, Chem. News 1896, 74, 302). It appeared of interest to supplement these results by nitrating 1-nitro-2-naphthyl ethyl ether. If the nitro group already in position 1- sufficiently lowers the orienting power of the ethoxy group, some 5- substitution would be expected. With fuming nitric acid, however, this substance gave a mixture of 1:6:8 trinitro and 1:6- dinitro derivatives, showing that the ethoxy group is still fairly powerfully activating and that the 8- position is less activated than the 6-. So for β-naphthol and its methyl and ethyl ethers, activation is according to the following order 1⁻ → 6⁻ → 8⁻.

Nitration of α-naphthyl ethers gives, in the first instance a mixture of 4- and 2- mono nitro derivatives (the former in greater amount) (Heermann, J., Pr. Chem. (2), 1891, 44, 240). Dinitration furnishes a mixture of 2:4 and 4:5- derivatives (Heermann, loc. cit.); the formation of the latter may be attributed to the decreased orienting power of the alkoxy group, with the corresponding entry of the 2nd nitro group in the unoccupied ring. (Contrast nitration of β-ethers). Trinitration proceeds 2:4:5-. (Talen, Rec. trav. chim. 1928, 47, 329, 346). This apparent decrease in orienting power of the α-alkoxy group compared with that of the β-alkoxy group, is illustrated also by the substitution of halogeno-naphthalenes. Whereas 2-chlor and 2-bromo-naphthalenes are nitrated successively at positions 1:6:8- (Scheid, Ber., 1901, 34, 1815; van der Kam, Rec. trav. chim. 1926, 45, 564) the α-compounds are substituted in positions 4:5:8 (Talen, loc. cit).
Hence for α-naphthol and its methyl and ethyl ethers activation is as follows: 4\(\overset{2}{\to}\)5\(\overset{2}{\to}\)7. These results are summarised below:

<table>
<thead>
<tr>
<th></th>
<th>First</th>
<th>Second</th>
<th>Third</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-naphthol</td>
<td>4</td>
<td>2:4</td>
<td>2:4:5; 2:4:7</td>
</tr>
<tr>
<td>α-naphthyl ether</td>
<td>2&amp;4</td>
<td>2:4 &amp; 4:5</td>
<td>2:4:5</td>
</tr>
<tr>
<td>β-naphthol</td>
<td>1</td>
<td>1:6</td>
<td>1:6:8</td>
</tr>
<tr>
<td>β-naphthyl ether</td>
<td>1,6,8</td>
<td>1:6; 1:8</td>
<td></td>
</tr>
</tbody>
</table>


It has been seen that protection of the hydroxyl group by an alkyl radical lowers its orienting power. The orienting power can be lowered still further by conversion to the sulphonyloxy group \(-\text{OS}^\ominus\text{R}\). Here sulphur is joined to two oxygen atoms by semi-polar linkages and as a result carries a large positive charge, and will therefore exert a powerful attraction upon the electrons which surround it. An inductive effect will be set up between the sulphur atom and the adjacent phenolic oxygen or group R (aryl or alkyl). This powerful effect is shown by the large dipole moment of the sulphonyloxy group, which is of the same sign as that of the nitro group and considerably larger (Todd & Shrirer J. Amer. Chem. Soc. 1934, 1382; \(\mu = 5.05 \times 10^{-18}\text{e.s.u.}\)). Hence an aryl sulphonyloxy group should be expected to have a large +I effect, and since there are lone pairs of electrons surrounding the phenolic oxygen, a small -E effect. In this respect, the group as a whole will be somewhat similar to a halogen. In both cases, although there will be de-activation of the nucleus by the inductive effect, substitution can still occur by virtue of the electromeric effect.
Combined with the ethenoid effects (b and c), positions available for substitution should be 4:5 or 4:8 in the a- compound, and 1:5 or 1:8 in the b-. Experimental results fully bear out these expectations.

Nitration a- and b- m-nitro benzene sulphonates has been shown by Bell (J., 1933, 286) to proceed according to the following schemes:

\[
\begin{align*}
4: \text{nitro} & \rightarrow 4:5 \text{ dinitro} \\
8: \text{nitro} & \rightarrow 1:8 \text{ dinitro}
\end{align*}
\]

The similarity to a halogen substituent is shown by the fact that nitration of 8-nitro-1-chloronaphthalene gives the 4:8- dinitro derivative and nitration of 5-nitro-1-bromonaphthalene gives the 4:5-dinitro derivative (Guareschi, Annalen, 1884, 222, 291; Ullmann & Consonno, Ber., 1902, 35, 2807). It has also been found that 4:5-dinitro-1-bromonaphthalene can be directly prepared by dinitration of the bromonaphthalene. (The method
of preparation given by Ullmann & Consonno — *loc.cit.*— consisted in brominating nitro naphthalene, and nitrating the resulting nitro-brom naphthalene).

4:5-Dinitro-1-bromonaphthalene, and 4:8-dinitro-1-chloronaphthalene were used to orient compounds (LV1) and (LVII) above. It was found that these nitrohalogen naphthalenes gave principally the ethoxy derivatives and not the naphthols, as stated by Ullmann & Consonno (*loc.cit.*), by the action of alcohol and sodium carbonate at 130° - 135° in a sealed tube. 4:5- and 4:8-1-ethoxy-naphthalenes were identical with the ethylated naphthals from (LV1) and (LVII).

An attempt was made to brominate the α- and β- sulphonates to ascertain whether analogous positions were substituted, but little information could be obtained, since not more than one bromine atom could in each case be introduced. The α- compound underwent bromination fairly readily and the resulting mono-bromo product was resistant to further bromination. This compound was identified as 4-bromo-α-naphthyl-α-nitro-benzene sulphonate by scission with piperidine to give 4-bromo-1-naphthol. The β-sulphonate underwent bromination extremely slowly giving a small yield of a mono bromo derivative. The slowness of the reaction probably indicates that substitution takes place in the unoccupied ring and the resulting compound may have been 5- or 8- substituted or a mixture of both. Nevertheless, bromination, like nitration of α- and β- naphthyl sulphonates shows definitely that the sulphonyl groups has a much feebler orienting power than the hydroxyl and the alkoxy group.

This conclusion is supported by reference to the reactions
of phenyl-\(p\)-toluene sulphonate (Bell, J., 1928, 2771). Vigorous nitration leads to formation of \(p\)-nitro-phenyl-\(o\)-nitro-\(p\)-toluene sulphonate (LVIII), while under less vigorous conditions, 4-nitrophenyl-\(p\)-toluene sulphonate is formed (LIX). Further

\[
\text{CH}_3 - \overset{\text{OSO}_2}{\text{O}} - \overset{\text{CH}_3}{\text{CH}_3} \xrightarrow{\text{N}_2 \overset{\text{OSO}_2}{\text{O}}} \text{CH}_3 - \overset{\text{N}_2}{\text{CH}_3} - \overset{\text{OSO}_2}{\text{C}_5 \text{H}_7} \quad (\text{LVIII})
\]

\[
\text{CH}_3 - \overset{\text{OSO}_2}{\text{O}} - \overset{\text{N}_2}{\text{CH}_3} \quad (\text{LIX})
\]

\[
\text{CH}_3 - \overset{\text{OSO}_2}{\text{O}} - \overset{\text{N}_2}{\text{CH}_3} \quad (\text{LXI})
\]

evidence is supplied by the fact that nitration of \(\mu\)-tolyl-\(p\)-nitrobenzene sulphonate (LX) leads to the introduction of a nitro group ortho to the methyl (LXI), showing that the sulphonoxy group, like a halogen, has a low o/p ratio, which is to be expected since this system represents a powerful B effect superimposed upon an A type (page 9).

\[
-\text{OH} \quad -\overset{\text{O}}{\text{SO}_2 \text{R}}
\]

A type \quad B superimposed on A.


It is not possible to obtain direct evidence of the orienting influence of the amino group, but indirect evidence indicates that this substituent is powerfully o/p directive. In spite of the fact that nitration of amines are conducted in strong acid solutions, in which medium the amine is largely converted to the salt, yet considerable quantities of para nitro derivatives are formed. For example, nitration of aniline in concentrated sulphuric acid was shown by Holleman, Hartogs, van der Linden,
(Ber., 1911, 44, 716) to give an \( \frac{n}{m} : \frac{p}{n} \) ratio of the order 1:50:50. Addition of aniline nitrate to concentrated sulphuric acid gave a value of the order 4:39:60 (ibid). Even under these condi-

tions, therefore, where much of the activity of the amino group is destroyed, there is a great deal of \( p \)-substitution. This suggests an activating power comparable to that of the hydroxyl group. The small proportion of ortho derivative is in accordance with Lapworth & Robinson's view (page 9); salt formation may be regarded as a superposition of type B effect upon type A.

In the bromination of amines, intermediate additive compound formation must be taken into account (Fries, Annalen, 1906, 346, 128), yet ortho and para positions are attacked. Aniline, for example, readily gives the trisubstituted 2:4:6-tribromo derivative with bromine.

Salt formation of \( \alpha \)- and \( \beta \)-naphthylamines in concentrated sulphuric acid will produce a similar deactivating effect as with aniline, so that positions of substitution would be governed by the ethenoid effects in both \( \alpha \)-positions in the unoccupied ring. This is supported by experimental evidence. Addition of \( \beta \)-naphthylamine nitrate to concentrated sulphuric acid produces a mixture of 5- and 8- nitro derivatives, (Friedländer & Szymanski, Ber., 1892, 25, 2078).
Nitration of \( \alpha \)-naphthylamine in concentrated sulphuric acid (Meldola, Streetfield, J., 1896, 63, 1055; Morgan, Micklethwaite, J., 1906, 89, 7) also gives the 5- and 8- nitro derivatives together with a small amount 4-. It is not possible to determine accurately the proportions of isomers formed since a considerable amount of decomposition occurs, but there can be no doubt that the 5- nitro derivative is formed in greater amount than the 8-.

Bromination of \( \beta \)-naphthylamine is an indirect process, but the ultimate product, claimed by Claus, Philipson (Ber., 1891, 24, 263) and Claus, Jack (J. pr. Chem. (2), 1898, 57, 13) to be the 1:4:6 tribromo derivative, has been shown by Fransen & Stauble (J. pr. Chem. 1921, (2), 103, 352) to be the 1:3:6- tribromo derivative. There is no mention in the literature of the direct action of bromine on \( \alpha \)-naphthylamine. This reaction has therefore been investigated, and it has been found that a solution of the amine in chloroform absorbs only one molecular proportion of bromine, the resulting product being a complex mixture of hydrobromides. From this mixture there was obtained \( \alpha \)-naphthylamine indicating that the hydrogen bromide produced during the bromination combined with some of the unchanged amine rendering it inactive to bromine. To avoid complications, therefore, a solution of \( \alpha \)-naphthylamine was added to a solution of bromine. In this way 2:4-dibromo-1-naphthylamine hydrobromide was formed, and the intermediate formation of an unstable additive compound was noticed. This reaction is therefore comparable to the bromin-
ation of α-naphthol which also gives an unstable intermediate, the ultimate product being the 2:4- dibromo derivative (Meldola, Hughes, J., 1890, 57, 395).

It was found that 4-nitro-1-naphthylamine could also, like naphthylamine, be brominated direct, but the reaction follows a curious course. In chloroform suspension, addition of bromine produced an unstable green compound which finally changed to an orange substance. The ease with which this latter compound lost bromine and nitrogen to give 1:2:4- tribromonaphthalene (LXIII) together with its analytical data, suggested that it was 2:4- dibromo-1-naphthalene diazo perbromide (LXII). Consequently it was compared with authentic diazo perbromide, whose preparation has been described by Meldola (J., 1883, 43, 4) and in their reactions both compounds were identical.

Since no hydrogen bromide is produced during the reaction, it is suggested that bromine first adds on to the 1:2- double bond and by a series of changes, nitrous acid is produced which diazotises the amino group. The following scheme is put forward as a likely mechanism of the reaction:

![Mechanism Diagram]

The action of bromine upon 4-nitro-1-naphthylamine follows a different course in acetic acid medium. Here the main product
is the 2-bromo derivative (LXIV) together with a small quantity of diazo bromide.

\[
\begin{align*}
\begin{array}{c}
\text{NO}_2 \\

\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{NO}_2 \\

\end{array}
\end{align*}
\]

(LXIV) \quad + \quad (\text{Small})

No suggestion can be made as to why bromination should follow the normal course in acetic acid and not in chloroform.

The tendency for double bond addition to take place with halogens is a characteristic property of naphthalene. For example Cleve (Ber., 1888, 21, 891) showed that either 1-keto-2:4-trichloro-1:2-dihydro- or 1-keto-3:4:4-trichloro-1:4-dihydro-naphthalene (LXV) and (LXVI) is formed when chlorine is passed into \( \alpha \)-naphthol, and Zincke (Ber., 1880, 13, 1036) isolated 1-keto-2:2:3:4:4-pentaclilor-1:2:3:4-tetrahydronaphthalene (LXVII) from a similar reaction. The opening of the 1:2-double bond

\[
\begin{align*}
\begin{array}{c}
\text{H} \\
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{H} \\
\end{array}
\end{align*}
\]

(LXV) \quad \begin{align*}
\begin{array}{c}
\text{Cl} \\
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{Cl} \\
\end{array}
\end{align*}
\]

(LXVI) \quad \begin{align*}
\begin{array}{c}
\text{Cl} \\
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{Cl} \\
\end{array}
\end{align*}
\]

(LXVII)

with resulting ketonisation, in the case of 2:4-dibromo-1-naphthol is suggested as a mechanism for its conversion to an indigotin type of derivative under the influence of alkali (Willstätter & Schuler, Ber., 1938, 61B, 362).

\[
\begin{align*}
\begin{array}{c}
\text{Br} \\
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{Br} \\
\end{array}
\end{align*}
\]

In a comprehensive investigation upon the bromination of
**β-naphthol**, Fries & Schimmelschmidt (*Annalen*, 1930, 434, 245) have shown that addition to double bonds and ketonisation takes place, an example of which is shown below.

The replacement by bromine of the nitro group in 4-nitro-1-naphthylamine may be compared with the replacement by bromine of the aldehyde group in 1-hydroxy-4-naphthaldehyde (Kerkhoff, *Rech. trav. chim.*, 1932, 51, 739).

The examples cited above not only illustrate the tendency for double bond addition in naphthalene but also the tenacity with which the molecule retains its symmetrical character.

### C. The Directing Influence of Amino Derived Substituents.

**Section 1. The directing influence of the acetamido group.**

The acetamido group constitutes a system which has been described as "neutralised" by Robinson. Here we have two opposing forces upon the unshared electron pair of the nitrogen atom - one into the nucleus and the other towards the doubly bound oxygen atom. Compared with the amino group therefore, it should have a smaller orienting power and since this group consists of a type B (acetyl) combined with a type A (amino), mono-substitution should be expected to...
Extensive investigations of nitration and bromination of acetanilide have shown that the o/p ratio varies very much according to experimental conditions. Moreover, bromination proceeds para to a far larger extent than does nitration, and it appears that in both cases acetanilide tends to substitute para to a greater extent thanortho.

With α-acet naphthalide, it might be expected that substitution would proceed para to a larger extent than with acetanilide owing to the additional ethenoid effect at position 4-. Nitration with concentrated nitric acid gave an o/p ratio which varied from 0.33 to 0.48 according to the quantity nitrated. Moreover the yield of nitrated products varied within wide limits (55 - 69%) and hence it was not possible to gain any precise information. Nevertheless the o/p ratio is surprisingly high.

α-Acet-naphthalide like acetanilide can be easily dinitrated to the 2:4-dinitro derivative (Morgan, Evens, J., 1919, 115, 1127) so that both these positions are strongly activated.

Bromination offers an interesting contrast to nitration. Monobromination of α-acetnaphthalide gives only the 4-bromo compound, no 2- being produced (Meldola, Ber., 1878, 11, 1904). 4-bromo-1-acet naphthalide reacts with a further molecule of bromine with difficulty to give the 2:4-dibromo derivative (Meldola, J., 1883, 48, 4; Ber., 1889, 12, 1961). It is evident therefore, that the nature of the substituting agent is an important factor bearing on the ortho-para ratio (pp. 10 -11).

In view of the facts that α-acet naphthalide is dinitrated much more easily than it is dibrominated, it appears that the acetamido group is more effective in nitration than in bromi-
nations, a conclusion which is true also of acetamido-diphenyl (Bell, J., 1931, 2339).

That the acetamido group does undoubtedly activate positions fairly powerfully is shown by the production of the 1-6- and 8- mono nitro derivatives when β-acet-naphthalide undergoes nitration (Jacobson, Ber., 1881, 14, 805; Vesely & Jakes, Bull. soc. chim., 1923, 23, 942), the 1- nitro preponderating. Further substitution of the 1- nitro derivative shows that the acetamido group is less powerfully activating than an alkoxy or amino group, since the nitro group overcomes to some extent the influence of the acetamido group and further substitution takes place in position 5-. Substitution of 6- and 8- nitro acet naphthalides takes place in unoccupied 1- position. (Bell J., 1929, 2785). These processes are represented below:

The nitration of 1-nitro-2-acet naphthalide is comparable to the nitration of 3-nitro-4-acetamido diphenyl, the second nitro group entering the 41-position, heteronuclear substitution taking place because of the deactivating effect of the nitro
The failure of the acetamido group to direct substitution into position 3- is illustrated also by analogous results by Groeneveld (Rec. trav. chim., 1932, 51, 783 - 811) on the nitration of \( \beta \)-naphthyl urethane and N-(\( \beta \)-naphthyl)-N-ethyl urea. The former undergoes nitration first to give the 1:6- and 1:3- dinitro derivatives and then the 1:6:8- trinitro derivatives. The latter gives the 1:6:8- trinitro derivative.

Although the acetamido group is fairly powerfully orienting comparison of nitration of 2-acet naphthalide and 2-naphthyl ethers indicates that the alkoxy substituent has a greater activating power. This conclusion is to be contrasted with the nitration of 2-methoxy 1-acet naphthalide which occurs in position 4. (LXVII). - (Bradley & Robinson, J., 1934, 1484) and with the nitration of o-methoxy acetanilido (Ingold & Ingold, J., 1926, 1310) - (LXIX) indicating a reversal of the orienting powers of methoxy and acetamido substituents.

Section 2. The directing influence of the aryl sulphonamido group and the exceptional behaviour of \( \alpha \)-naphthalides towards bromination.

With regard to the substitution of \( \alpha \)- and \( \beta \)-naphthalides comparatively little has been done, but the results obtained indicate that the sulphonamido group has an activating power
comparable to that of a phenolic group. Under mild conditions, p-toluene sulphon-1-naphthalide gives the 2:4-dinitro derivative (Morgan & Evens, J., 113, 1127), whilst the β-naphthalide is nitrated in positions 1:6 (idem.). Morgan & Evens (loc. cit.) have also succeeded in mono-nitrating this compound in position 1-, although conditions have to be carefully regulated to prevent 1:6- disubstitution occurring. By employing the β-nitrobenzene sulphonyl derivative Bell (J., 1929, 2784) has shown that β-naphthalides are capable of trinitration, substitution proceeding 1:6-, then 1:6:8 (LXX) and (LXXI).

The similarity in behaviour between a naphthol and a naphthalide is further shown by the facts that α- and β- p-toluene sulphonnaphthalides couple with diazotised aniline and p-nitraniline as readily as do the corresponding naphthols (Witt, Ber., 1894, 27, 2370).

The high orienting power of the sulphonamido group is illustrated by the results of attempts to mono-nitrate p-toluene sulphon-1-naphthalide. Under very mild conditions (warming with dilute nitric acid) it was found impossible to prevent dinitration taking place. This result has been confirmed in a memoir which appeared at the time these experiments were being carried out (Hodgson & Walker, J., 1934, 180). These workers, however, have isolated 40% of the 4-nitro derivative by nitrination in nitro-benzene solution, the remainder being 2:4- dinitro. A further attempt to mono nitrate this substance, using the method which Morgan & Micklworthwaite (J., 1912, 148) adopted for
the mono nitration of the β-naphthalide again resulted in a mixture of dinitro- and unchanged product, but a very small amount of 2-nitro-naphthalide was obtained, which was oriented by hydrolysis to 2-nitro-1-naphthylamine — identical with an authentic specimen from 2-nitro-1-acet naphthalide.

These results combine to show that the 2 and 4 positions in α-naphthalides are highly activated, the 4- to a greater extent than the 2-.

Using μ-nitro benzene sulphon-1-naphthalide, it has been found that trinitration could be brought about. The 2:4-di-nitro derivative (LXXII) was easily formed and this on further nitration yielded uniformly 2:4:5- trinitro μ-nitro benzene-sulphon-1-naphthalide (LXXIII), which was found to be identical with that produced by the mild nitration of 5-nitro-μ-nitro-benzene-sulphon-1-naphthalide (LXXIV), thus its constitution is proved.

The absence of 2:4:7- trinitro derivative is to be contrasted with the trinitration of α-naphthol, but there is no doubt that the 5- position is activated by the sulphonamide group in position 1- since the conditions for trinitration are mild. The marked difference between the orienting powers of the sulphonamido and acetamido groups and the great similarity between
the sulphonamido and phenolic groups are from these experiments apparent. In the case of \( \beta \)-naphthalides (and like \( \beta \)-naphthol, \( \beta \)-ethers, and \( \beta \)-acetanaphthalides) it is again noteworthy that no 3- substitution occurs. It must therefore be concluded that the 3- position either suffers no activation or is less activated than the 8- position, a conclusion difficult to reconcile with the ordinarily accepted formula for naphthalene. Since other evidence is favourable to such a formula, it might be concluded that electromeric charges brought about by a group \( X \) can for some unknown reason, only follow the course indicated in (LXXV).

The powerful activating influence of the sulphonamido group is also illustrated in the benzene series. Early experiments by Everest & Flurschheim (D.R.P.243079) have shown that this group powerfully activates positions ortho and para to it. Two nitro groups are easily introduced into the following compounds:

Three nitro groups can be introduced even in the case of \( m \)-nitro-\( m \)-nitrobenzene sulphonanilide:

It would appear remarkable that such a group, \( \text{NH}_2\text{SO}_2\text{C}_2\text{H}_5 \), having a highly positively charged sulphur atom in close proximity to the nucleus should so powerfully activate ortho and
para positions. It has been shown that replacement of a phenolic hydrogen by the sulphoxy group lowers the activating power enormously and yet replacement of an amino hydrogen by this group brings about an activating power comparable to that of the phenolic group. It appears, therefore, that the sulphonamide group must acquire a reactive phase somewhat similar to a phenoxide ion. That sulphonanilides give salts with alkalis shows that the amino hydrogen is capable of acquiring a positive charge having the nitrogen atom negative, this process being facilitated by the sulphonyloxy group. The reactive phase of a sulphonanilide may therefore be represented by (c), and this is compared with a phenol (a) and an acetamido substituent (d).

\[
\begin{align*}
\text{(a)} & \quad \text{(b)} & \quad \text{(c)} & \quad \text{(d)} \\
\begin{array}{c}
\text{O}^+ \text{H}^+ \\
\end{array} & \begin{array}{c}
\text{S}^+ \text{R}^+ \\
\end{array} & \begin{array}{c}
\text{N}^+ \text{O}^+ \\
\end{array} & \begin{array}{c}
\text{C}^+ \text{Me}^+ \\
\end{array}
\end{align*}
\]

Evidence for such a form (c) has been provided by Von Braun & Weissbach, (Ber., 1930, 63, 2836) who have shown that some sulphonanilides, e.g., n-butyl-sulphon-ethylanilide react with phosphorus pentachloride to give a stable chloro body:

\[
\text{Bu}^- \text{S}^- \text{N}^- \text{Et}^- \rightarrow \text{Bu}^+ \text{S}^+ \text{N}^+ \text{Et}^+
\]

Moreover, replacement of the amino hydrogen in p-toluene sulphon-2-naphthalide lowers the orienting power of the group (Morgan & Mickieithwaite, loc.cit.) and analogous results have been obtained in the benzene series by Bell (J., 1928, 2772), so that now the orienting power is comparable to the methoxyl substituent

\[
-\text{OMe} \quad -\text{N}^+ \text{S}^+ \text{R}^+
\]

The low o/p ratio of the sulphonamide group is illustrated by the formation of p-nitro derivatives from the mild nitration
of sulphonalides (A.G.F.A., D.R.P., 157859; 163516) and Bell (J., 1929, 2877; 1928, 2771) has shown that although the o/p ratio is low, the ortho positions are highly activated.

It has been observed that in the case of α-acet naphthalide, there is a marked difference in the o/p ratio for nitration and bromination and that the acetamido group is more effective in the former than the latter. This has been found to be true also of the sulphonamido group, and here the difference is even more marked. It was thought that an easy method of preparation of 2:4-dibromo-1-naphthylamine would be to brominate an α-naphthalide and hydrolyse the product. The surprising result emerged that m-nitro-benzene sulphon-1-naphthalide gave only a mono bromo derivative in chloroform solution even with two molecules of bromine. It was identified as the 4-bromo derivative (LXXVI) by hydrolysis to give 4-bromo-1-naphthylamine. It has been shown by Bell (J., 1931, 2340) that the reactivity of a sulphonamido group is enhanced by salt formation in pyridine with the production of a negative nitrogen pole, due to the removal of the incipiently ionised hydrogen:

\[ \text{N-SO}_2 R \xrightarrow{R_b} \text{H}_2 \text{N}_2 \text{C}_5 \text{H}_5 \text{SO}_2 R \]

Bromination by this method was therefore tried and it was found that 4-bromo-m-nitro benzene sulphon-1-naphthalide in pyridine gave an almost theoretical yield of the 2:4-dibromo-1-naphthalide (LXXVIII) which was identical with the product from the interaction of m-nitro-benzene sulphonyl chloride and 2:4-dibromo-1-naphthylamine in pyridine.
This failure of \( \alpha \)-naphthalides to undergo bromination in the 2- position by ordinary means is further exemplified by the fact that 4-nitro-\( \alpha \)-toluene sulphon-1-naphthalide was unaffected upon by bromine in chloroform solution, whereas in pyridine, it gave the 2-bromo-derivative, which was obtained also from the interaction of \( \alpha \)-toluene sulphonyl chloride and 2-bromo-4-nitro-1-naphthylamine in pyridine.

The bromination of \( \alpha \)-naphthalides is therefore in marked contrast to nitration. Whereas three nitro groups can be introduced with ease, only di-bromination can occur and special conditions are necessary for the entry of one bromine into the 2- position. Steric factors cannot account for the failure of \( \alpha \)-naphthalides to undergo bromination in the 2- position by ordinary methods, since nitration takes place easily in this position. Moreover, the present results on the bromination and nitration of disulphonyl derivatives of \( \alpha \)-phenyldiamine, (where steric factors might be thought to play an even greater part), show conclusively that the ortho positions are far from blocked. Nitration of di-\( \alpha \)-toluene-sulphonyl- and di-\( \alpha \)-nitro benzene-sulphon-\( \alpha \)-phenylene diamines (LXXVIII) and (LXXXI) gave first the 4:6- dinitro derivatives (LXXIX) and (LXXXII) and...
These compounds underwent further nitration to give 2:4:6-trinitro di-$\alpha$-nitro-$m$-toluene sulphonyl- and 2:4:6-trinitro di-$m$-nitrobenzene sulphonyl-$m$-phenylene diamines (LXXX) and (LXXXIII).

\[
\begin{align*}
\text{(LXXVIII)} & \quad \text{(LXXXI)} \\
\text{(LXXIX)} & \quad \text{(LXXX)} \\
\text{(LXXXII)} & \quad \text{(LXXXIII)}
\end{align*}
\]

Bromination of compound (LXXVIII) gave analogous results. In chloroform or pyridine, with two molecular proportions of bromine, the 4:6-dibromo derivative (LXXXIV) was produced, and bromination of this by either of these methods gave the 2:4:6 tribromo derivative (LXXXV).

\[
\begin{align*}
\text{(LXXXIV)} & \quad \text{(LXXXV)}
\end{align*}
\]

The differences between bromination and nitration of $\alpha$-naphthalides have an interesting analogy in the reactions of 2-$m$-nitro benzene sulphonamido diphenyl. Bell has shown (J., 1930, 1071) that this substance undergoes facile trinitration, whereas 2-$p$-toluene sulphonamido diphenyl, in chloroform solution, undergoes monobromination only, to give the 5-bromo
derivative, and the latter in pyridine furnishes the 3:5-dibromo derivative (Bell, J., 1931, 2340).

The bromination of \( \text{\(\beta\)}\)-toluene sulphon-2-naphthalide offers no departure from anticipation. This compound gives the \( 1\)-bromo- derivative (LXXXVI) with one molecular proportion of bromine in chloroform solution, and Bell (J., 1932, 2732) has recorded the formation of the \( 1:6\)-dibromo derivative (LXXXVII) by this method, using two molecular proportions of bromine.

Bromination in pyridine however follows a different course. Bell (loc. cit.) found that by this method the \( 1:3\)-dibromo compound (LXXXVIII) was formed, and that \( 1:6\)-dibromo-\( \text{\(\beta\)}\)-toluene sulphon-2-naphthalide by bromination in pyridine formed the \( 1:6:3\)-derivative (LXXXIX).
This type of reaction has been extended to 1-nitro-\(p\)-toluene sulphon-2-naphthalide. It has now been found that this compound gives the analogous 3-bromo derivative (XC). The amine (XC1) obtained by hydrolysis of this was deaminated by the method of Hodgson & Walker (J., 1933, 1620) to give 1-nitro-3-bromo-naphthalene, which was identical with that given by the deamination of 2-bromo-4-nitro-1-naphthalmine. This substance has been described by Vesely & Chudezilow (Chem. Listy 1923, 19, 260).

1-Nitro-3-bromo-\(p\)-toluene sulphon-2-naphthalide was further oriented by the fact that it was identical with the nitration product of 3-bromo-\(p\)-toluene-sulphon-2-naphthalide (XC11), the latter being obtained from 3-bromo-2-naphthylamine, the preparation of which has been described (page 32).

\[
\begin{align*}
\text{(XC)} & \\
\text{(XC1)} & \\
\text{(XC11)} & 
\end{align*}
\]

It is possible therefore to introduce a substituent in position 3- to a reactive group in position 2-; bromination in pyridine being a homonuclear process. It is remarkable that the effect of the negative pole cannot be transmitted from one ring to another.

To gain further information upon the mechanism of this reaction the bromination of \(p\)-toluene-sulphon-anilide in pyridine was investigated. It was found that a mixture of bromo deri-
vatives resulted, which could not be separated, but hydrolysis of this mixture gave 2:4- dibromo- and 2:4:6- tribromo aniline. Hence it appears probable that bromination in pyridine can occur through electromeric mechanisms and if this be so the negative pole facilitates the operation of such mechanisms, so that in β-naphthalides the normal 1:6:8 activation are now converted to 1:3- activations:

\[
\begin{align*}
\text{It is noteworthy that bromine in pyridine is of little use as a brominating agent, unless such a group as } & \text{-NHSO}_2R \text{ is present. } \\
\text{2-Naphthyl-} & \text{p-toluene sulphonate and even 2-acet naphthalide were recovered unchanged after such treatment. Therefore it is possible that this type of substitution may be brought about through the agency of an additive effect.}
\end{align*}
\]

Just as α-naphthalides, in their reactions with nitric acid and bromine, are closely comparable to 2-diphenyl anilides, so β-naphthalides are very similar to 4-diphenyl anilides. 4-p-toluene sulphon amido diphenyl brominates by ordinary methods first in the 3- position and then in the 4-, and the latter in pyridine brominates further, in the 5- position to give 3:5:4-tribromo-4-p-toluene sulphonamido diphenyl (Bell, J., 1928, 2778; 1930, 1076).
As in the naphthalene series this type of reaction is homo-nuclear, as the following show (Bell, loc. cit.):

\[
\begin{align*}
\text{Ph} - \text{NHT} & \xrightarrow{\text{Br}_2} \text{Ph} - \text{NHT} \\
\text{NO}_2 - \text{NHT} & \xrightarrow{\text{Br}_2} \text{NO}_2 - \text{NHT} \\
\text{NHT} & \xrightarrow{\text{Br}_2} \text{NHT}
\end{align*}
\]

Like 2-\text{m}-nitrobenzene-sulphonanaphthalide, 4-\text{m}-nitrobenzene-sulphonamido-diphenyl is capable of trinitration (Bell, loc. cit.)

\[
\begin{align*}
\text{Ph}-\overset{\text{NHT}}{\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4}\text{NO}_2 & \xrightarrow{\text{Br}_2} \text{Ph}-\overset{\text{NHT}}{\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4}\text{NO}_2 \\
& \xrightarrow{\text{N}_2} \text{Ph}-\overset{\text{NHT}}{\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4}\text{NO}_2 \\
& \xrightarrow{\text{N}_2} \text{Ph}-\overset{\text{NHT}}{\text{NH}_2\text{SO}_2\text{C}_6\text{H}_4}\text{NO}_2
\end{align*}
\]

The enhanced reactivity of the sulphonamido group in pyridine is further illustrated by the formation of iodo derivatives. It has been found that \text{p}-toluene sulphon-2-naphthalide in pyridine gives the 1-iodo derivative with iodine, iodine chloride, or iodine trichloride. This compound readily reacts with sodium nitrite in acetic acid to give the 1-nitro-naphthalide, a reaction which serves to determine its constitution.
6-Toluene-sulphon-\textit{p}-toluidide; 2-\textit{p}-toluene sulphonamido-diphenyl and 4-\textit{p}-toluene sulphonamido-diphenyl also gave iodo derivatives by any of these methods:

\[
\begin{align*}
\text{CH}_3 & \quad \text{NH}_2\text{SO}_2\text{C}_7\text{H}_7 & \rightarrow & \text{CH}_3 & \quad \text{I} \\
\text{Ph} & \quad \text{NH}_2\text{SO}_2\text{C}_7\text{H}_7 & \rightarrow & \text{Ph} & \quad \text{I} \\
\text{Ph} & \quad \text{NH}_2\text{SO}_2\text{C}_7\text{H}_7 & \rightarrow & \text{Ph} & \quad \text{I}
\end{align*}
\]

In all these cases there was no indication of the presence of chloro derivatives with iodine chloride and trichloride showing that these reagents react as \( I \rightarrow Cl \) and \( I \rightarrow Cl_5^- \) and that the feeble activating influence of the disulphonamide group.

Replacement of the amino hydrogen in the sulphonamide group by a further sulphonyl residue should enormously decrease the orienting power of the group, and the disulphonamide group should have an orienting power of the same order as the sulphonyoxy group. Each group may be considered as a combination of A and \( A \rightarrow S_2R \) types and the lone pair of electrons of the nitrogen atom will still be able to give rise to electromeric displacements in the nucleus; moreover, owing to the cumulative effect of the two sulphonyl residues it might be expected that this group, like the sulphonyoxy group should be feeble para directive.
In other words the total effect is $+1 - E$ where $I$ is very large and $E$ small.

The orienting power of this substituent has now been compared with that of methyl and it is shown that the latter governs the position of substitution.

Nitration of di-$m$-nitro benzene sulphonanilide under vigorous conditions yielded a mixture of $p$ and $m$-nitro derivatives (XCIII) and (XCIV), whilst nitration of disulphon-$o$- and $p$-toluidines resulted in the nitro group entering a position $o$- or $m$- to the methyl group (XCV) (XCVI) and (XCVII). These results are comparable with those of Brady, Quick & Wellig (J., 1925, 127, 2364) on the nitration of the corresponding phthalanils.

It was thought that di-$m$-nitro-benzensulphon-$\alpha$- and $\beta$-naphthalides would give on nitration analogous results to the nitration of the corresponding naphthyl-sulphonates. These compounds reacted only slowly with a mixture of fuming and nitric acids at water-bath temperature, but no method was found
to hydrolyse the very insoluble products, which on account of their indefinite melting points were probably mixtures. Analyses of these products showed that they were mononitro derivatives. Hence the disulphonamido group is shown to be very feebly orienting in the naphthalene as well as the benzene series.

Except for the anomalous behaviour of α-naphthalides on bromination, the sulphonamido, acetamido and disulphonamido substituents may be placed in the following order of decreasing orienting power.

\[-\text{NHSO}_2R > -\text{NHCOR} > -\text{N(SO}_2R)_2\,\text{.}\]

D. Substitution in 1:5- Amino Naphthol.

The naphthalene molecule appears to be peculiarly suitable for a comparison of orienting effects exerted by two different substituents each in a different nucleus, but there are few examples of this type of work in the literature. Rule, Pursell & Brown (J., 1934, 168) have shown that 8-bromo- and 8 chloro-α-naphtholic acids nitrate and brominate in the 4-position, indicating that a halogen exerts an orienting power superior to that of a carboxyl group:
Fichter & Gageur (Ber., 1909, 42, 4748) have nitrated 1-acetamino-8-naphthyl acetate and have shown that with concentrated nitric acid the 4-nitro derivative (XCVIII) is obtained. The methods they employed for orienting this compound are outlined below:

\[
\begin{align*}
&\text{NHAc} \quad \text{OAc} \\
&\quad \rightarrow \\
&\quad \text{N}_{\text{HCl}} \quad \text{OAc}
\end{align*}
\]

(XCVIII)

It appears somewhat surprising that no 2-nitro derivative was isolated, since the conditions of nitration were the same as those which give a good proportion of 2-nitro-1-acet naphthalide from \(\alpha\)-acet naphthalide. The absence of a nitro group in the acetate containing ring is to be expected since Fichter & Kuhnel (Ber., 1909, 42, 4751) have shown that vigorous conditions are necessary to nitrate \(\alpha\)-naphthyl acetate.

Substitution reactions in naphthalene derivatives, where the same substituent is in each ring, indicate that the naphthalene rings function as separate benzene nuclei, as the following examples show.

The nitration of acenaphthaquinone to give the 4-nitro and then the 4:5-dinitro derivatives (Rowe & Davies, J., 1920, 117, 1349; Matyer & Kaufman, Ber., 1920, 53, 296) has been confirmed by Rule & Brown (J., 1934, 171). The latter workers (loc.cit.) repeating the investigations of Graebe & Briones (Annalen, 1903, 327, 84) have shown that an alteration of the peri-carbonyls to
an anhydride gives an interesting change in orienting power, so
that nitration of peri-naphthalic anhydride takes place in the
3- and 6- positions.

\[ \text{CO} \quad \text{CO} \quad \rightarrow \quad \text{CO} \quad \text{CO} \quad \rightarrow \quad \text{CO} \quad \text{CO} \]

It appeared of interest to nitrate a number of derivatives
of 1:5- amino naphthol since the latter is now a cheap commercial
product, but unexpected difficulties arose during the
course of this investigation owing to the very high insolubilities
of some of the derivatives and the ease of decomposition of
others.

The first product to be investigated was the di-\( m \)-nitro
benzenesulphonyl derivative (XCLI). This, under mild conditions
easily gave a dinitro derivative, which undoubtedly was 2:4-
dinitro-1-\( m \)-nitro-benzene-sulphonamido-5-naphthyl-\( m \)-nitro ben-
zenesulphonate (C). This compound was so insoluble that no

\[ \text{NO}_2 \quad \text{NO}_2 \quad \rightarrow \quad \text{NO}_2 \quad \text{NO}_2 \]

method of hydrolysing to the amine could be devised.

The nitration of the dibenzoyle derivative (Cl) was next
attempted. This compound has been described by Sachs (Ber.,
1906, 39, 3026) and is fairly insoluble, in marked contrast to
1-benzamine-3-naphthyl benzoate. It was found that the 1:5-
compound gave a dinitro derivative (CII) when warmed with
acetic and nitric acids. This dinitro derivative was exceptionally insoluble, but it was found possible to remove the o-benzoyl group with aqueous caustic soda to give the naphthol (Cl III), although a fair amount of decomposition takes place. Attempts to hydrolyse the N-benzoyl group were unsuccessful. It is believed that both nitro groups are in the same ring since the benzamino group is much more powerfully orienting that the benzoate group, and conditions for nitration were fairly mild.

This suggestion is supported by results obtained from the nitration of 1-acetamino-5-naphthyl benzoate (CIV), which was found to be a more convenient substance to work with on account of its easier solubility. Nitration in acetic acid again furnished a dinitro derivative (CV) together with a small quantity of dinitro-1-amino-5-naphthyl benzoate (CVI), some hydrolysis of the N-acyl group having taken place, during nitration. The former was hydrolysed by sodium hydroxide to the naphthol (CVII) in rather poor yield, ammonia being readily evolved as a result of decomposition. It was also found that some of the N-acetyl group had been removed resulting in the formation of dinitro amino naphthol (CVIII). The latter was obtained also by treating compound (CVII) with alcoholic hydrochloric acid. This dinitro amino naphthol gave with two molecular proportions of m-nitro-benzene sulphonyl chloride a compound identical with (CIX); hence it is almost certain that both nitro groups are
in the same ring as the acetamino substituent, and by analogy the dinitro compound (CII) has the similar constitution.

It was further found that compound (CVI), on acetylation, regenerated compound (CV), hence nitration was uniform.

The compound (CIV) was obtained by the following method:-

An attempt was made to nitrate compound (CLX) by the method that Fichter & Gageur (loc.cit.) employed for the 1:8-compound, but curiously enough this substance was recovered unchanged after solution in cold concentrated nitric acid, whilst warming with dilute nitric acid led to decomposition. It was also not found possible to nitrate compound (CX) owing to decomposition. However, compound (CIV) did give an apparently uniform mono-nitro derivative under both these conditions, but this compound, unfortunately could not be oriented, owing to the ease with which it decomposed with alkali. So its constitution could not be definitely established.
In spite of the scanty results obtained from the nitration of derivatives of 1:6- amino naphthol, it appears fairly certain that a feebly orienting group in position 5-, such as -O$_2$N, -OCO$_2$H, does not modify the positions of substitution governed by sulphonamido, or acyl-amino substituents in position 1-, and in this case the molecule as a whole functions as two separate benzene nuclei.

CONCLUSION.

Although prediction with the aid of the Electronic Theory, of chemical reactions in the naphthalene series is a more unsafe process than with benzene, there is no doubt that interpretation in terms of electron behaviour is satisfactory in many cases. More light will have to be thrown on the constitution of the naphthalene molecule itself and upon the mechanisms of the different types of substitutions. It is too early to expect a completely satisfactory explanation from the electronic theory, but there is no doubt that the development of this theory which is now taking place with the aid of the physicist will inevitably lead to a great advance and systematisation of organic chemical knowledge.
EXPERIMENTAL.

The experimental work is arranged under the following headings:—

Reactions of 1:8-amino naphthol
Attempts to prepare diphenylene
Chemical evidence for symmetrical structure of naphthalene
Orientation of nitration products of $\alpha$- and $\beta$-naphthyl-$m$-nitrobenzenesulphonates
Nitration of $\alpha$-naphthol
Nitration of $\beta$-naphthol
Bromination of $\alpha$- and $\beta$-naphthyl-$m$-nitrobenzenesulphonates
Bromination of 4-nitro-1-naphthylamine
Preparation of 2-nitro- and 4-nitro-1-naphthylamines
Nitration and bromination of $\alpha$-napthalides
The bromination of $\beta$-napthalides
Iodination of some sulphon-anilides in pyridine
Substitution of $m$-phenylenediamine
Nitration of disulphonanilides
The nitration of 1:5-amino naphthol

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REACTIONS OF 1:8 - AMINO NAPHTHOL.

1:8- Amino naphthol was prepared from peri-amino naphthalene-sulphonic acid by the method of Raiford (J. Amer. Chem. Soc. 1926, 48, 483). Potassium hydroxide (30g.) and sodium hydroxide (30g.) were melted together with water (50c.c.) and peri acid (10g.) added. The mixture was gradually heated to 250 - 260° and kept at this temperature for 1 hour. After cooling, the solid was extracted with hot water and the filtered alkaline solutions of 1:8- amino naphthol used to prepare the following derivatives:

8-Benzamino-1-naphthyl benzoate by the Schotten-Baumann reaction. It formed light brown oblong plates from alcohol, or needles from acetic acid, m.p. 208° - 210°. (Raiford gives m.p. 207 - 208°).

8-Benzamino-1-naphthol from the dibenzoyl derivative (above) by hydrolysis with sodium hydroxide solution, formed plates from aqueous alcohol m.p. 208°. (Raiford gives m.p. 216°).

8-Benzamino-1-naphthyl acetate, obtained from the above compound, by the action of acetic anhydride formed plates, from aqueous alcohol, m.p. 182 - 183°. (Raiford gives m.p. 180°).

8-Acetamino-1-naphthol was obtained by shaking the alkaline solution of amino-naphthol with acetic anhydride. Presumably the diacetyl derivative so formed was immediately hydrolysed in the alkaline medium. Acidification of the solution precipitated a white solid which after crystallisation from aqueous alcohol formed long colourless rods m.p. 180° (dec). (Raiford gives m.p. 181°).

8-Acetamino-1-naphthyl benzoate by benzyolisation of the above compound in alkaline solution was obtained as needles
from aqueous alcohol, m.p. 179° - 183°. (Found: N, 4.6% C_{19}H_{15}O_3N requires N, 4.6%). A mixture of this and 8-acetamino-1-naphthalbenzoate melted indefinitely between 155 and 165°. Therefore, benzoylation of 8-acetamino-1-naphthol and acetylation of 1-benzamino-8-naphthol give two different substances. (Aaiford states that benzoylation of 1-acetamino-8-naphthol gives 1-benzamino-8-naphthyl acetate).

1-Acetamino-8-naphthyl benzoate was maintained at its melting point (180° - 190°) for 1 hour. The resultant gum was extracted with boiling alcohol from which there separated crystals m.p. 194° - 196°. This substance was insoluble in cold alkali and gave large depressions in melting point with the following:

(i) with 1-acetamino-8-naphthyl benzoate m.p. 165° - 170°
(ii) " 1-benzamino-8-naphthyl acetate m.p. ca 150°
(iii) " 1-benzamino-8-naphthol m.p. ca 170°
(iv) " 1-acetamino-8-naphthol m.p. ca 160°

and was probably compound (XII - page 24).
(Found: N, 4.5%, C_{19}H_{15}O_3N requires N, 4.6%).

ATTEMPTS TO PREPARE DIPHENYLENE.


Several methods for the preparation of 2,2'-dinitro diphenyl were attempted. That of Ullmann & Frenzel (Ber, 1905, 38, 725) by the diazotisation of o-nitroaniline and the action of cuprous chloride on the diazonium solution gave very poor yields. Large amounts of o-chloro nitro benzene were formed.
A 33% yield was obtained by the method of Niementowski (Ber., 1901, 34, 3325), which consists of treating diazotised o-nitraniline with freshly precipitated copper.

The method finally adopted was that of Ullmann (Ber., 1901, 34, 2176) i.e. by heating o-chloro-nitro benzene with copper bronze. In this way 2-2-dinitro diphenyl m.p.123 - 126° was obtained in ca.34% yield.

By the reduction of this with tin and hydrochloric acid (Niementowski, loc.cit.), 2:2-diamino-diphenyl m.p.78 - 80° was obtained in ca.37% yield.

For the preparation of 2:2-dibromo diphenyl the method of Dobbie, Fox & Gauge (loc.cit.) was employed, which consists of treating a hot solution of cuprous bromide and 2:2-diamino diphenyl in hydrobromic acid with sodium nitrite. The yield of 2:2-dibromo diphenyl, m.p.80°, was too small to serve for the preparation of o-diphenylene.

11. Stages

\[
\begin{align*}
\text{NH}_2 & \quad \rightarrow \quad \text{I} \\
\text{NO}_2 & \quad \rightarrow \quad \text{I} \\
\text{I} & \quad \rightarrow \quad \text{I}
\end{align*}
\]

o-Nitraniline was diazotised and converted to o-iodo-nitro benzene in the usual way and this was reduced in the cold with stannous chloride to give o-iodo-aniline m.p.55 - 57°.

o-Di-iodobenzene was obtained from this by diazotising and treating with potassium iodide solution. After purification it was a rather dark oil which when strongly cooled froze and then had m.p.24 - 27°, and boiled with slight elimination of iodine at 280 - 286° (Korner, Jahresbericht, 1875, 313; 1887, 711 records m.p.27° and b.p.286.5° for this substance).
Elimination of Iodine by means of the Grignard Reaction.

Diiodo benzene (15g.) magnesium powder (1g.) and anhydrous cuprous chloride was refluxed in dry iso-propyl ether. The reaction was slow and was left to proceed for twelve hours. The mixture was poured on to ice, and after filtering, extracted with ether. The aqueous washings were also extracted with ether. After washing the combined etherial solution with this solution to remove iodine, it was dried over calcium chloride. After removal of ether, a dark viscous product remained, which was extracted with hot benzene. On dilution with ligroin a solid was thrown down, which contained no iodine (sodium fusion) and had m.p.189°. No diphenylene was obtained by this method. (Mannich, Her., 1907, 40, 160; Schmidt, Schultz, Annalen, 1880, 203, 135, record m.p.194° for 9:10-benz-phenanthrene).

CHEMICAL EVIDENCE FOR SYMMETRICAL STRUCTURE OF NAPHTHALENE.


m-Nitro-benzene-sulphon-ß-naphthalide was converted to the dinitro and then the trinitro derivative, according to the method of Bell (J., 1929, 2784).

1:6:8-Trinitro-m-nitrobenzenesulphon-2-naphthalide (16g.) was mixed with sulphuric acid (96c.c.) and water (13c.c.) and warmed on the water bath. The substance slowly dissolved and after complete solution, cooled below 10° and sodium nitrite (3.2g.) in concentrated sulphuric acid (10c.c.) added. Ice was added till a sample of the liquid no longer gave a precipitate of the amine on further dilution. After addition of more ice, the liquid was filtered into ca. one litre of water. After a short time the clear solution deposited a reddish brown precipitate of 6:8-dinitro-2-naphthalene diazo-1-oxide, which after
filtering and drying had a decomposition point of ca.110°.  
(Found: N, 20.4  C_{10}H_{4}O_{5}N_{4} requires N, 21.5%). It under­
grew the reactions of a diaco-oxide e.g.,
(a) Dissolved in cold sodium hydroxide solution with evolution of nitrogen.

(b) Evolved acetaldehyde with boiling alcohol in the presence of aluminium powder.

(c) Gave intense blue colouration with resorcinol.

2. Acetylation of 1-bromo- and 3-bromo-2-naphthylamines.  1-Bromo-
2-naphthylamine was recovered unchanged after boiling with acet-
ico anhydride. It readily acetylated, however, when a drop of concentrated sulphuric acid was added to a warm solution of the amine in acetic anhydride. The resulting acetyl derivative had m.p.140°, alone or mixed with authentic 1-bromo-2-acet-naph-
thalide.

3-Bromo-2-naphthylamine (page 98) reacted slowly with cold acetic anhydride. It partly dissolved with evolution of some heat and was thereafter precipitated as the acetyl derivative. Acetylation was made complete by boiling with acetic anhydride. On cooling 3-bromo-2-acetnaphthalide separated in the form of colourless parallelopipeds m.p.177°. (Unchanged after recrys-
tallisation from alcohol.) (Found: N, 5.4  C_{12}H_{10}O_{5}NBr requires N, 5.3%). A mixture of this substance and original amine (m.p.172°) melted ca.135°.

3. The action of p-toluenesulphonyl chloride on 1-bromo and 3-bromo-
2-naphthylamines. To 1-bromo-2-naphthylamine (1 mol.) in pyri-
dine solution, was added p-toluenesulphonyl chloride (1 mol.) and the solution allowed to stand for a week. After removal of pyridine with dilute hydrochloric acid, the residue was ex-
traced with boiling alcohol. From the solution, 1-bromo-p-
toluenesulphon-2-naphthalide, m.p.100°, crystallised. The insoluble residue, which was 1-bromo-di-p-toluenesulphon-2-naphthalide crystallised from alcoholic pyridine in long prisms m.p. 182 - 184°. (Found: N, 2.66 C_{24}H_{20}O_4NS_2Br requires N, 2.64%). This substance was prepared also from the interaction of 1-bromo-p-toluenesulphon-2-naphthalide and p-toluenesulphonyl chloride in pyridine.

3-Bromo-2-naphthylamine under the same conditions as above, gave only 3-bromo-p-toluenesulphon-2-naphthalide, fine needles from alcohol, m.p.127 - 129°. (Found: N, 3.8 C_{17}H_{14}O_2NSBr requires N, 3.7%).

4. Reduction of 1:3-dibromo-2-naphthylamine. (See page 98).
ORIENTATION of NITRATION PRODUCTS of α- and β- NAPHTHYL-M-NITRO BENZENE SULPHONATES. (In collaboration with Dr. F. Bell).

1. 4-Nitro-β-naphthol.

**Stages:**

\[ \text{p-Toluenesulphon-α-naphthalide} \rightarrow \text{p-Toluenesulphonyl chloride} \rightarrow \alpha-\text{naphthylamine} \rightarrow \text{presence of fused sodium acetate} \rightarrow \text{dinitro derivative} \]

\[ \text{Dinitro naphthalide} \rightarrow \text{Hydrolysed in strong sulphuric acid} \rightarrow \text{converted to 4-nitro-1-naphthalene diazo-2-oxide} \]

\[ \text{Alcohol and aluminium powder} \rightarrow \text{4-nitro-2-naphthol} \rightarrow \text{m.p.116 - 120°} \]

\[ \text{4-Nitro-2-naphthol} \rightarrow \text{m-nitro benzene sulphonate} \rightarrow \text{fuming nitric acid} \rightarrow \text{4:5-dinitro derivative, m.p.212°} \]

\[ \text{This was identical with the product from the nitration of 5-nitro-2-naphthyl-m-nitro-benzene sulphonate in fuming nitric acid.} \]
II. 4:5- and 4:8-Dinitro-α-Naphthols. Two methods of preparation were tried. The first, due to Graebe & Oser (Annalen, 1904, 335, 154) consists of converting 1:5-dinitro and 1:8-dinitro naphthalenes to 8-nitro-4-nitroso and 5-nitro-4-nitroso-α-naphthols respectively by fuming sulphuric acid, but although good yields of the nitroso compounds were obtained, repeated attempts to oxidise these with potassium ferri-cyanide produced negative results. Oxidation with other oxidising agents failed also.

1:5 and 1:8 dinitro naphthalenes were obtained by nitration of α-nitro-naphthalene in concentrated sulphuric acid and separation of the isomers by means of sulphuric acid according to the method of Friedlander (Ber., 1899, 32, 3531; D.R.P., 117368). The bulk of 1:5 dinitro naphthalene m.p. 211°, crystallised from the sulphuric acid, whilst 1:8-dinitro naphthalene, m.p. 169-170°, remains in solution. The ratio of the two isomers was approximately 1:1.

The second method adopted for the preparation of the dinitro naphthols was by replacement of halogen in 1:5 and 1:8-dinitro halo naphthalenes according to the method of Ullmann & Consonno (Ber., 1902, 35, 2807):
5-Nitro-α-brom-naphthalene, m.p.119 – 120°, was prepared by bromination of α-nitronaphthalene (Guaracchi, Annalen, 1884, 222, 291). This was converted to the 4:5:1-bromo-naphthalene, m.p.169 – 171°, by nitration with fuming nitric acid. It was found that this could be obtained also by the direct nitration of α-brom-naphthalene itself. 10 c.c. was added drop by drop to fuming nitric acid (20 c.c.) cooled in ice, and the oily liquid treated with a further quantity of nitric acid (20 c.c.). After standing for ½ hour at room temperature, acetic acid (20 c.c.) was added, when the dinitro compound crystallised out. After recrystallisation from acetic acid it had m.p.169 – 171° identical with above.

4:5-Dinitro-1-napthol. Contrary to Ullmann & Consonna (loc. cit.), the action of 50% alcohol on the dinitro brom-napthalene in the presence of sodium carbonate at 135° for 5 hours gave mostly 4:5-dinitro-1-ethoxy naphthalene, m.p.182°. This was also formed under less drastic conditions viz., by refluxing the dinitro brom naphthalene with alcohol and potassium carbonate for several hours.

4:5-Dinitro-1-ethoxy naphthalene was identical with the ethylated dinitro naphthol from the nitration of 4-nitro-1-naphthyl-α-nitrobensensulphonate. The latter with fuming nitric acid gave the 4:5-dinitro derivative, m.p.174°. This was severed by piperidine to 4:5-dinitro-1-naphthol, m.p.198°, and ethylated with ethyl sulphate in xylene solution to give the ethoxy derivative.
4:8-Dinitro-1-Naphthol. Chlorination of $\alpha$-nitro naphthalene, $\textit{gave}$ 3-chloro-$\alpha$-nitro-naphthalene, m.p. 88 – 91° (Ullmann, \textit{loc.cit}) and this on nitration with fuming nitric acid furnished 4:8-dinitro-1-chloro naphthalene, m.p. 132 – 134°. Like dinitro-bromo-naphthalene, heating with alcohol in a sealed tube gave mostly the ethoxy body, and a small amount of 4:8-dinitro-$\alpha$-naphthol, m.p. 230°(dec.).

8-Nitro-1-naphthyl-m-nitrobensenesulphonate with fuming nitric acid furnished the 4:8-dinitro derivative and this on scission with piperidine gave the naphthol, m.p. 230° alone or mixed with that described above.
NITRATION of α-NAPHTHOL.

2:4-Dinitro Naphthol. (Morgan, Evens, J., 115, 1128). Finely powdered α-naphthol (20g.) was added to concentrated sulphuric acid (40c.c.) with stirring and the dark solution heated on the water bath for 15 mins., during which time separation of the disulphonic acid took place. The cooled solidified mass was mixed with water (80c.c.) and the solution added slowly to concentrated nitric acid (24c.c.) below 10°. The mixture was then stirred for ½ hour on the water bath and the yellow solid filtered.

Crystallised from alcohol 2:4-dinitro-α-naphthol formed orange needles 135 - 137°. (M. gives m.p. 138°).

Nitration of 2:4-Dinitro-α-Naphthol. (a). 5g. were introduced into ice cold fuming nitric acid (10c.c.). Towards the end of the addition, crystals appeared. After standing for 5 minutes, the mixture was diluted with acetic acid (10c.c.) and after ½ hour, the almost pure 2:4:5-trinitro-1-naphthol was filtered and washed with acetic acid, (m.p. 183°). Recrystallised from acetic acid it then formed yellow prisms, m.p. 189°. The mother liquor was poured into water and the gummy precipitate crystallised twice from acetic acid. The 2:4:7-trinitro-α-naphthol so obtained formed yellow needles, m.p. 145°(dec.). This method suffices, therefore, to separate completely the two isomers.

The yields of purified products were 2:4:5 - 2g. 2:4:7 - 0.8g.

(b) Dinitro naphthol (5g.) was added in small quantities to a mixture of fuming nitric acid (10c.c.) and acetic acid (10c.c.) in the cold. Partial dissolution took place.
After standing at room temperature for 12 hours, the yellow crystalline material was filtered and crystallised from acetic acid, m.p. 190°, and was therefore 2:4:5 trinitro naphthol (yield 2g.). The nitric-acetic acid mother liquor gave 2:4:7-trinitro-α-naphthol on dilution with water, yield 0.9g. (m.p. 143°) after crystallisation from acetic acid.

Methods (a) and (b) above, therefore, suffice to separate conveniently the isomerides produced, and in each case the ratio of the isomers is approximately the same. Previous methods of nitrating 2:4-dinitro-α-naphthol have been given by Ekstrand (Ber., 1878, 11, 162) and Kehrman, Haberkant (ibid., 1898, 31, 2430) and Steiner (ibid., 1900, 33, 3285). These workers used sulphuric acid as the nitration medium and the separation of the resulting isomers is a somewhat tedious process.
**NITRATION of **\(\beta\)-**NAPHTHOL.**

\(\beta\)-Naphthol was nitrated in acetic acid to the 1:6-dinitro derivative, (Bell, J., 1932, 2732) and no pure compound was obtained from the action of fuming nitric acid upon this.

**Nitration of 1-nitro-2-naphthyl ethyl ether.** This (m.p. 99 - 102°) was obtained by nitrating naphthyl ethyl ether in acetic acid according to the method of Gaess (J., Pr. Chem. (2), 43 22; 45,615; 46,160).

1-Nitro-2-naphthyl ethyl ether (6.5g.) was added to fuming nitric acid (100 c.c.) at 0°. After standing for ½ hour, the solution was poured into water and the yellow precipitate filtered and warmed with sodium carbonate solution. After filtering and drying the crude product weighed 7.5g. This consisted of a mixture of 1:6-dinitro and 1:6:8-trinitro-2-naphthyl ethyl ethers. The former was removed by extraction with boiling benzene from which it crystallised on cooling, m.p.144°.

The insoluble portion, m.p.183 - 185°, was mainly the 1:6:8-trinitro ether. Its m.p. was 186 - 187°, after crystallisation from acetic acid (light yellow flakes).

**Bromination of \(\alpha\)- and \(\beta\)-Naphthyl-m-Nitrobenzenesulphonates.**

\(\alpha\)-Naphthyl m-nitrobenzenesulphonate (10g.) was mixed with chloroform (20c.c.) and bromine (5.4g.) in chloroform (5c.c.) was added. On heating under reflux, hydrogen bromide was evolved and the sulphonate dissolved. After about two hours, evolution of hydrogen bromide had ceased, and on cooling, crystals of 4-bromo-1-naphthyl m-nitrobenzenesulphonate separated m.p.148° (8.5g.), unchanged after recrystallisation from acetic acid. (Found: Br, 19.2 \(\text{C}_16\text{H}_{10}\text{O}_5\text{NSBr}\) requires Br, 19.6%). The chloroform mother liquor was evaporated, and the residue
crystallised twice from acetic acid. In this way a further
2.5g. of bromo derivative were obtained.

Orientation. The bromo compound (3g.) was added to piperidine and left for one hour on the water bath. The solution was diluted with water, filtered from the precipitated m-nitrobenzenesulphonyl piperidine (m.p.124°), and the filtrate neutralised with hydrochloric acid. The gummy precipitate, after desiccation was crystallised twice from benzene from which it separated as needles, m.p.126°. It was therefore 4-bromo-α-naphthol.

β-Naphthyl-m-nitrobenzenesulphonate (3g.) was mixed with chloroform 25 c.c. and bromine (4.4g.) and heated under reflux. Hydrogen bromide was very slowly evolved. After three hours the solution was diluted with petrol and the crude product fractionally crystallised from acetic acid.

First crop: plates m.p.117°. (No depression with original).
Second crop: plates m.p.110 - 112° (No depression with original).
Third crop: This was obtained after leaving the mother liquor to stand for 12 hours. A small amount of crystals separated, m.p.119 - 125°, which gave a large depression with original substance, and had m.p.128° after recrystallisation from alcohol. This was a mono-bromo derivative. (Found Br: 19.4  C_{16}H_{18}O_5NSBr requires Br, 19.6%), but was too small in quantity for further investigation.
BROMINATION of 4-NITRO-1-NAPHTHYLAMINE.

Summary.

(a) To a finely powdered suspension of the nitro amine (2g.) in chloroform (15c.c.) was added bromine (1.5c.c. - 2.5 mols.) in chloroform (5c.c.) drop by drop. Heat was evolved, and a green suspension was formed. The mixture was then refluxed for half an hour, during which time the colour changed from green to orange. No hydrogen bromide was evolved during the course of bromination. The crystallised suspension was filtered and washed with chloroform till the washings were colourless.

The substance formed short orange needles with a sharp decomposition point between 123° and 136° depending upon the rate of heating. It was compared with authentic 2:4-dibromo-1-naphthalene diazo perbromide (page 90) and shown to be identical with it.
Analyses.

1. Found Br: 69.9, N: 5.2  
   \( \text{C}_{10}\text{H}_5\text{N}_2\text{Br}_5 \) requires Br, 72.3% and N, 5.06%.

2. Heated to decomposition point and liberated nitrogen collected and measured in a nitrometer (over 50% KOH).
   8.837 m.g. gave 0.38 c.c. \( \text{N}_2 \) at 777.5 m.m. and 16°.
   \( \text{N}_2 \) evolved = 5.03.
   \( \text{C}_{10}\text{H}_5\text{N}_2\text{Br}_5 \) requires loss of \( \text{N}_2 \) : 5.06%.

3. Warmed with potassium iodide solution and liberated iodine titrated against N/10 thio.
   0.5339 g. required 18.80 c.c. N/10 thio.
   \( \%\text{Br}_2 \) liberated = 28.1
   \( \text{C}_{10}\text{H}_5\text{N}_2\text{Br}_5 \) requires loss of \( \text{Br}_2 \) : 28.8%.

Reactions. Both this and authentic diazo perbromide underwent the following reactions to give 1:2:4-tribromo naphthalene m.p.112 - 113°. (No nitrogen present. Found: Br, 64.5  
\( \text{C}_{10}\text{H}_5\text{Br}_3 \) requires Br, 65.75%).

1. Heated to decomposition point and residue crystallised from alcohol or acetic acid.
2. Reacted violently with pyridine. Latter was removed and residue crystallised.
3. Dissolved slowly in boiling acetic acid or acetic anhydride. On cooling tribromonaphthalene was obtained.

The substances from (1) (2) and (3) above gave no depression in m.p. with each other or with authentic tribromo naphthalene.
(b) To a suspension of 4-nitro-α-naphthylamine (10g.) in acetic acid (50c.c.) was gradually added, with agitation, bromine (3.4c.c.) in acetic acid (30c.c.). The pasty reaction mixture was repeatedly shaken during 30 mins., and thereafter filtered. The precipitated material separated from alcoholic pyridine in orange-red, dagger-shaped needles (7g.) m.p. 249° (dec.). This was 2-bromo-4-nitro-α-naphthylamine. (Found: N, 10.2; C_10H_7O_2N_2Br requires N, 10.5%). From the acetic acid mother liquor there was deposited, after standing for 12 hours, a small quantity of the diazo perbromide, identical with that from (a).

2-Bromo-4-nitro-1-acetanaphthalide was obtained by acetylation of the amine with acetic anhydride and a drop of sulphuric acid. Crystallised from acetic acid it formed yellow needles, m.p. 235 - 236°. (Found: N, 8.9; C_12H_9O_3N_2Br requires N, 9.1%).

1-Nitro-3-bromo naphthalene. The bromo nitro amine above was diazotised and deaminated according to the method of Hodgson & Walker (J., 1933, 1620). A suspension of the amine (10g.) was added to a solution of sodium nitrite (3g.) in concentrated sulphuric acid (20c.c.). Alcohol (100c.c.) was added and the solution warmed on the water bath. Nitrogen and acetaldehyde were evolved, and then all volatile liquids were distilled off. The red gummy mass remaining was extracted with alcohol and gave red needles of 1-nitro-3-bromo naphthalene, m.p. 93° and m.p. 95 - 97° after recrystallisation from alcohol (yield 3.5g.) (Vesely & Chudomilow, Chem. Listy., 1925, 19, 360, give m.p. 97 - 98°).
2:4-Dibromo-\(\alpha\)-Naphthylamine. The preparation of 2:4-dibromo-\(\alpha\)-naphthylamine from the corresponding acetonaphthalide is described by Meldola (J., 1882, 43, 4; Ber., 1878, 11, 1904). The latter is obtained by bromination of 4-bromo-acetonaphthalide with bromine in acetic acid, but this reaction is very slow, taking a week for completion. By the following method 2:4-dibromo-1-naphthylamine can be very conveniently prepared.

\(\alpha\)-Naphthylamine (28 g.) dissolved in acetic acid (100 c.c.) was added in the cold to a solution of bromine (22 c.c.) in acetic acid (200 c.c.). A pasty green mass was formed, and little hydrogen bromide was evolved. The mixture was warmed on the water bath with addition of a further quantity of acetic acid (100 c.c.). Hydrogen bromide was evolved and the precipitate became white. When no more hydrogen bromide was given off, the hydrobromide of 2:4-dibromo-\(\alpha\)-naphthylamine was collected and washed with acetic acid. Yield 75 g. (100%).

The salt (75 g.) was refluxed with alcohol (250 c.c.) and a solution of sodium hydroxide (10 g.) in a minimum quantity of water added. Dissolution soon occurred, and after filtering hot, 2:4-dibromo-\(\alpha\)-naphthylamine, m.p. 116 - 118°, crystallised as brownish plates (acetyl derivative, from acetic anhydride and a drop of sulphuric acid, m.p. 226°). Meldola (loc. cit.) gives m.p. 118 - 119° and 225° respectively.

2:4-Dibromo-1-naphthalene diazo perchloride. A modification of Meldola's method (loc. cit.) was tried. The amine (5 g.) was dissolved in hot acetic acid (30 c.c.) cooled rapidly and the cold suspension added to a solution of sodium nitrite (1.2 g.) in concentrated sulphuric acid (8 c.c.) cooled in ice. Ice was then added and the solution filtered. To the diazo solution
was added a solution of bromine in hydrobromic acid till a filtered sample gave no further precipitate with bromine. The yellow diazo perbromide was filtered and purified by refluxing with chloroform. It decomposed at 138°. Yield 7g. The diazo perbromide underwent the reactions described on page 82.

PREPARATION of 2-NITRO- and 4-NITRO-1-NAPHTHYLAMINES.

1. Nitration of p-toluenesulphon-α-naphthalide. (a) A mixture of naphthalide (20g.), acetic acid (100c.c.) and concentrated nitric acid were shaken together. The naphthalide rapidly dissolved with evolution of heat and after about 20 mins. yellow crystals appeared. These were filtered and crystallised from acetic acid. The melting point was low (ca.130°).

Several recrystallisations from acetic acid raised the melting point to 140 - 145°. Mixed with authentic 2:4-dinitro naphthalide (m.p.162 - 165°), the melting point was elevated.

All the mother liquors were combined and diluted with water. The gummy material was dissolved in boiling alcohol and the cold solution filtered from crystals (m.p.ca.140°).

The mother liquor after twelve hours deposited deep yellow plates (ca.0.5g.) of 2-nitro-p-toluenesulphon-α-naphthalide m.p.154°. (Found: N,8.2  C_{17}H_{14}N_{2}O_{4}S requires N, 8.2%). This constitution was confirmed by hydrolysis with sulphuric acid to give 2-nitro-1-naphthylamine m.p.133° alone or mixed with an authentic specimen.

(b) Nitration of the α-naphthalide with dilute nitric acid yielded a mixture of 2:4-dinitro derivative and unchanged original.

2. Nitration of α-acetanaphthalide and the o/p ratio therefrom.

The best method after several trials was found to be by
nitrating the naphthalide with concentrated nitric acid, hydro-
lysing one of the isomers by Hellmann & Remy's method (Ber., 1886,
19, 802) and separating the products according to the directions
of Morgan & Micklethwaite (J., 1905, 37, 928). The following is
a typical procedure.

The naphthalide (26g.) was added in small quantities to
concentrated nitric acid (170°C.) at 0 - 10°C, and during the
addition the nitration product began to crystallise. After the
addition, the mixture was allowed to stand for 3 hour and then
poured into ice water. The yellow precipitate (30g.) was col-
lected and dried. This was dissolved in ca. 500°C. warm alco-
hol and heated under reflux for 2 hours with addition of potas-
sium hydroxide (4.5g.) in a little water. The solution was
poured into water and the brown precipitate filtered and dried
(23g.). This was dissolved in just sufficient boiling ethyl
acetate which on cooling, deposited almost pure 2-nitro-α-naph-
thalide (6g.), pale yellow needles, m.p. 198°C, from alcohol.
Most of the ethyl acetate from the mother liquor was evaporated
off and on cooling almost pure 4-nitro-α-naphthylamine (14g.)
was obtained. It crystallised from acetic acid in orange need-
les m.p. 192 - 193°C.

**Nitration at 0 - 10°C.**

<table>
<thead>
<tr>
<th>Amount</th>
<th>2-Nitro</th>
<th>4-Nitro</th>
<th>Total Yield</th>
<th>o/p</th>
</tr>
</thead>
<tbody>
<tr>
<td>22g.</td>
<td>4g. = 15%</td>
<td>11g. amine = 50%</td>
<td>65%</td>
<td>0.33</td>
</tr>
<tr>
<td>26g.</td>
<td>6g. = 19%</td>
<td>14g. &quot; = 50%</td>
<td>69%</td>
<td>0.38</td>
</tr>
<tr>
<td>38g.</td>
<td>8g. = 17%</td>
<td>15g. &quot; = 38%</td>
<td>55%</td>
<td>0.47</td>
</tr>
<tr>
<td>50g.</td>
<td>12g. = 19.4%</td>
<td>20.5g. &quot; = 40.5%</td>
<td>60%</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Hydrolysis of 2-nitro-α-acetanaphthalide was effected by heating 10g. with 60% sulphuric acid at 100° till complete solution. 2-Nitro-1-naphthylamine crystallised from alcohol in orange needles, m.p.143°. With p-toluene sulphonyl chloride in pyridine it gave 2-nitro-p-toluenesulphon-α-naphthalide, m.p.154° (page 91).

4-Nitro-p-toluenesulphon-α-naphthalide from 4-nitro-α-naphthylamine and p-toluenesulphonyl chloride in pyridine solution formed yellow plates from acetic acid m.p.186 - 190°.

**NITRATION and BROMINATION of α-NAPHTHALIDES.**

Reactions described.

\[ \text{m-Nitrobenzenesulphon-α-naphthalide from the interaction of α-naphthylamine and m-nitrobenzenesulphonyl chloride in pyridine formed plates m.p.162 - 164° from acetic acid. (Found:} \]
Nitration. (a) The naphthalide (3.0g.) was suspended in acetic acid (240c.c.) and warmed gently with addition of concentrated nitric acid (18c.c.) in acetic acid (18c.c.). Nitration occurred with dissolution of the naphthalide. After cooling the yellow crystalline precipitate was collected and crystallised from acetic acid in needles (21g.) m.p.185 - 188°. This was 2:4-dinitro-α-nitrobenzenesulphon-α-naphthalide. (Found: N, 13.4%
\[\text{C}_16\text{H}_{12}\text{O}_4\text{N}_2\text{S}\text{ requires N, 13.4%}
\]) since hydrolysis with concentrated sulphuric acid furnished 2:4-dinitro-α-naphthylamine, m.p.235°.

(b) The dinitro naphthalide (5g.) was added slowly to fuming nitric acid (15c.c.) cooled in ice. The solution was left to stand for ½ hour, and then diluted with acetic acid (20c.c.) and filtered from 2:4:5-trinitro-α-nitrobenzenesulphon-α-naphthalide, which was sparingly soluble in boiling acetic acid from which it separated as yellow plates m.p.215°(dec.). (Found: N, 14.3
\[\text{C}_16\text{H}_{10}\text{O}_8\text{N}_4\text{S requires N, 15.1%}
\]) Apart from a further small quantity of this substance, no other compound was obtained from the dilution of the mother liquor.

(c) The dinitro naphthalide (5g.) was heated gently with a mixture of acetic acid (10c.c.) and fuming nitric acid (10c.c.). Nitration occurred with dissolution of the naphthalide and on cooling the 2:4:5-trinitro derivative separated identical with that from (b) above. 5-Nitro-α-nitrobenzenesulphon-α-naphthalide from the interaction of α-nitrobenzenesulphonyl chloride and 5-nitro-α-naphthylamine in pyridine solution formed plates, m.p.208 -210°, from acetic acid or alcoholic pyridine. (Found: N, 11.5
\[\text{C}_16\text{H}_{11}\text{O}_6\text{N}_3\text{S requires N, 11.3%}
\]).
(5-Nitro-α-naphthylamine was obtained by two alternative methods. That by the reduction of 1:5-dinitro naphthalene with ammonium sulphide - Beilstein, Kuhlberg, Annalen, 1873, 169, 87 - gave poor yields. The method ultimately adopted was by nitrating α-naphthylamine in concentrated sulphuric acid solution - Meldola, Streatfeild, J., 1893, 63, 1058; Morgan, Micklethwaite, J., 1906, 89, 7).

Nitration of 5-nitro-α-nitrobenzenesulphon-α-naphthalide.
A mixture of naphthalide (2g.) in acetic acid (150 c.c.) and nitric acid (20 c.c.) were warmed gently. The naphthalide dissolved and was thereafter precipitated as the 2:4:5-trinitro derivative, m.p. 215° (dec.) alone or mixed with that from (b) or (c) above. This substance on solution in hot pyridine and dilution with alcohol separated as the pyridine salt, m.p. 170 - 175°. (Found: N, 15.2; C₁₆H₉O₁₀N₃ requires N, 15.5%).

Bromination of m-nitrobenzenesulphon-α-naphthalide. (a) To this (6g.) in chloroform (250 c.c.) was added bromine (20 c.c. - 2 mols.) in chloroform (50 c.c.). After the initial vigorous reaction, accompanied by evolution of hydrogen bromide, the solution was refluxed for 1 hour. The crystalline precipitate of 4-bromo-m-nitrobenzenesulphon-α-naphthalide after cooling was collected and recrystallised from acetic acid from which it formed colourless plates (7g.) m.p. 174 - 176°. (Found: Br, 19.3; C₁₆H₁₁O₁₄N₂Br requires Br, 19.7%). Its identity was established by hydrolysis with concentrated sulphuric acid to give 4-bromo-α-naphthylamine m.p. 102° (Acetyl derivative, m.p. 193°).
(b) To a solution of the 4-bromo naphthalide (2.5g.) in pyridine was added bromine (0.3c.c.) drop by drop. After standing for 12 hours, the semi-solid mass was rubbed with hydrochloric acid and the residue crystallised from a large bulk of acetic acid from which it separated as short fine needles (2.6g) m.p.232 - 233°. This was identical with the compound obtained from the interaction of 2:4-dibromo-α-naphthylamine (5g.) and m-nitrobenzenesulphonyl chloride (3.7g.) in pyridine and therefore was 2:4-dibromo-m-nitrobenzenesulphon-1-naphthalide. 

(Found: N, 5.9. C_{16}H_{10}O_{4}N_{2}SBr_{2} requires N, 5.8%).

Bromination of 4-nitro-p-toluenesulphon-1-naphthalide.
This substance was recovered unchanged after heating with a mixture of bromine and chloroform, but was brominated as follows.

To 1g. in pyridine was added bromine (0.3c.c.) drop by drop and the mixture left for 12 hours. After removal of pyridine by hydrochloric acid, the oil remaining partly solidified on rubbing with alcohol. This was separated and was unchanged original (m.p.186 - 190° after recrystallisation from alcohol; no depression with original). The remaining oil slowly solidified on standing in alcohol in a strong freezing mixture. After two crystallisations from acetic acid it formed orange rhombohedra, m.p.298 - 296° alone or mixed with authentic 2-bromo-4-nitro-p-toluenesulphon-1-naphthalide. (Found: N, 6.7, C_{17}H_{13}O_{4}N_{2}SBr requires N, 6.65%). The latter was obtained by interaction of p-toluenesulphonyl chloride and 2-bromo-4-nitro-1-naphthylamine in pyridine.
Bromination of p-toluenesulphon-2-naphthalide. To a mixture of naphthalide (15g.) and chloroform (50c.c.) was added bromine (2.8c.c.) in chloroform (10c.c.). After the initial reaction, the solution was heated under reflux for 1½ hours. After cooling, the solution deposited white needles (3g.) of the hydrobromide of 1-bromo-2-naphthylamine, m.p.228° (dec.) (converted to the amine m.p.63° by alkali). After filtration, most of the chloroform was distilled off and the solution diluted with ligroin. The oil which separated was rendered solid by rubbing
and cooling, and was then crystallised from alcohol, from which it formed stout needles (15g.) m.p.100° alone or mixed with an authentic specimen of 1-bromo-p-toluenesulphon-2-naphthalide. (Bell, loc. cit., 1932, 2782)

1:3-Dibromo-p-toluenesulphon-2-naphthalide. Bell (loc. cit.) describes the preparation of this substance from the bromination of the α-naphthalide in pyridine. This was repeated and the yield found to be small. Much better results were obtained by brominating the 1-bromonaphthalide in pyridine. Bromine (1.4cc) was added drop by drop to a solution of this (10g.) in pyridine. After the addition, the mass was warmed gently for 1 hour to effect complete solution. After 12 hours the mixture was rubbed with hydrochloric acid and the residue crystallised twice from acetic acid. Yield - 7g. m.p.160°. (Bell, loc. cit. gives m.p.163°).

3-Bromo-2-naphthylamine. 1:3-dibromo-2-naphthylamine from the hydrolysis of the naphthalide with concentrated sulphuric acid was reduced as follows:-

A mixture of the amine (5g.), alcohol (40c.c.), concentrated hydrochloric acid (40c.c.) and granulated tin (5g.) was heated under reflux for 2 hours. The cooled filtered solution deposited crystalline 3-bromo-2-naphthylamine hydrochloride, which was decomposed with hot alcoholic sodium hydroxide to yield the free base, which formed lustrous plates m.p.173° (3g.) from alcohol. (Found: N, 6.2  C10H10NBr requires N, 6.3%) (Acetyl derivative is described on page 77).

1-Nitro-3-bromo-p-toluenesulphon-2-naphthalide. 1-Nitro-p-toluenesulphon-β-naphthalide was prepared according to the method of Morgan & Micklethwaite (J., 1912, 101, 148). p-Toluene-
sulphon-β-naphthalide (20g.), acetic acid (100c.c.), and concen-
trated nitric acid (7c.c.) were shaken together and the clear solution, soon formed, deposited crystals on continued agitation. The 1-nitro derivative so obtained had m.p.159° after recrystallisation from acetic acid.

To this compound (10g.) in pyridine solution was added bromine (1.6c.c.) drop by drop. After 12 hours, the mass was triturated with dilute hydrochloric acid and the solid product crystallised from alcoholic pyridine from which it separated as pale yellow plates (7g.), m.p.237 - 239° (dec.). This compound was obtained also by warming a mixture of 3-bromo-2-toluenesulphon-2-naphthalide (1g.) (described page 78), acetic acid (5c.c.) and nitric acid (0.3c.c.) and was therefore 3-bromo-1-nitro-p-tolu enesulphon-2-naphthalide. (Found: N,6.6  C_{17}H_{19}O_{2}N_{2}BrS requires N, 6.05%).

Reduction either with tin and hydrochloric acid or zinc and acetic acid furnished 2-p-toluenesulphon-3-bromo-1:2-naphthylene diamine, which crystallised from acetic acid in needles, m.p.185°. (Found: N, 7.0  C_{17}H_{15}O_{2}N_{2}Br requires N, 7.2%).

1-Nitro-3-bromo-2-naphthylamine. Careful addition of the 1-nitro-3-bromo naphthalide to ice cold concentrated sulphuric acid furnished the amine which formed orange needles, m.p.105°, from alcohol. (Found: N,10.2  C_{10}H_{7}O_{2}N_{2}Br requires N, 10.5%).

This was converted by boiling with N-sodium hydroxide solution for 6 hours to 1-nitro-3-bromo-2-naphthol, which crystallised from alcohol in yellow plates m.p.131° (dec.). (Found: N, 5.1  C_{10}H_{6}O_{3}NBr requires N, 5.2%).

To a hot solution of the amine in acetic anhydride was added a drop of concentrated sulphuric acid. On cooling 1-nitro-3-bromo-2-acetanaphthalide separated and recrystallised from alcohol it formed yellow needles, m.p.136°.
It was thought of interest to ascertain whether reduction of 1-nitro-3-bromo-2-naphthylamine would remove the nitro group as in the case of the bromine in 1:3-dibromo-2-naphthylamine, but reduction with tin and hydrochloric acid proceeded no further than 3-bromo-1:2-naphthylene diamine, which formed needles m.p. 86° (dec.) from aqueous alcohol. (Found: N, 11.5 \( \text{C}_{10}\text{H}_9\text{N}_2\text{Br} \) requires N, 11.3%). This substance was identified as an ortho diamine by giving the quinoline derivative with benzil in hot alcoholic solution. This formed yellow plates m.p. 195 - 199° from acetic acid. (Found: N, 6.8 \( \text{C}_{24}\text{H}_{15}\text{N}_2\text{Br} \) requires N, 6.8%) and gave an intense violet colouration with concentrated sulphuric acid.

1-Nitro-3-bromo naphthalene. A solution of 1-nitro-3-bromo-2-naphthylamine (1g.) in hot acetic acid (12c.c.) was rapidly cooled and the mixture added to a solution of sodium nitrite (0.3g.) in concentrated sulphuric acid (4c.c.). To the solution was added alcohol (15c.c.) and on warming on the water bath, nitrogen and acetaldehyde was evolved. After removal of volatile liquids and extracting with alcohol 1-nitro-3-bromo-naphthalene m.p. 97 - 99° was obtained identical with that from 2-bromo-4-nitro-1-naphthylamine (page 89).

Bromination of p-toluenesulphon anilide. To this compound (9g.) in pyridine was added bromine (4c.c. - 2 mols.) drop by drop. The mixture after standing for 12 hours was rubbed with hydrochloric acid and the solid crystallised from alcohol in plates m.p. 124 - 127°. This was a mixture for on hydrolysis with concentrated sulphuric acid two amines were obtained which were separated by fractional crystallisation from alcohol.
The less soluble had m.p. 118° alone or mixed with 2:4:6-tribrom aniline. The more soluble had m.p. 77 - 80° alone or mixed with 2:4-dibrom aniline (acetyl derivative m.p. 144 - 146°). Attempts to separate the brominated anilide were not successful.

IODINATION OF SOME SULPHON-ANILIDES IN PYRIDINE.

1-iodo-p-toluenesulphon-β-naphthalide. p-Toluenesulphon-β-naphthalide was iodinated by the following methods.

(a) To the naphthalide (5g.) in pyridine was added powdered iodine (4.5g.); some heat was evolved and the solution after the addition was allowed to stand for 12 hours. Trituration with hydrochloric acid produced an oil. Excess iodine was removed by sulphur dioxide and the oily residue was made solid by rubbing with alcohol. 1-iodo-p-toluenesulphon-β-naphthalide formed stout prisms (3.5g.), m.p. 126 - 127° after two crystallisations from alcohol. Mixed with the original naphthalide an large depression in m.p. was obtained. (Found: N, 3.3, C_{17}H_{14}O_2SNI requires N, 3.4%).

(b) To the naphthalide (5g.) in pyridine was slowly added iodine chloride (3g.). A vigorous reaction took place and after treatment as described in (a), the iodo naphthalide was obtained.

(c) Treatment of the naphthalide in pyridine with iodine trichloride also furnished the iodo derivative.

Orientation. The constitution was proved by warming the iodo naphthalide (1g.) in acetic acid on the water bath with addition of sodium nitrite (0.2g.). The naphthalide dissolved to give a deep brown solution. After 3 hours the yellow crystals which separated on cooling were recrystallised from acetic acid and had m.p. 160° alone or mixed with authentic 1-nitro-p-toluenesulphon-2-naphthalide.
Attempts were made to convert the iodo naphthalide to the amine (a) by concentrated sulphuric acid and (b) by refluxing with alcoholic hydrochloric acid. In each case the product of hydrolysis was unstable, rapidly liberating iodine with decomposition. This confirms Meldola's observation (J., 1885, 47, 520) on the instability of 1-iodo-2-naphthylamine.

The following iodo derivatives were obtained by methods (a) (b) and (c).

3-Iodo-2-p-toluenesulphonamido diphenyl (0.4g.), prisms, m.p. 114 - 115° from alcohol (found: N, 3.1 \( \text{C}_{19}\text{H}_{16}0_{2}\text{NSI} \) requires N, 3.1\%) from 2-p-toluenesulphonamido diphenyl (5g.). The iodo derivative gave a large depression in m.p. with original substance.

3-Iodo-4-p-toluenesulphonamido diphenyl (m.p. 109 - 115°) from 4-p-toluenesulphonamido diphenyl. (Found: N, 3.1 \( \text{C}_{19}\text{H}_{16}0_{2}\text{NSI} \) requires N, 3.1\%).

2-Iodo-p-toluenesulphon-p'-toluidide m.p. 127 - 132° from p-toluenesulphon-p'-toluidide. (Found: N, 3.4 \( \text{C}_{14}\text{H}_{14}0_{2}\text{NSI} \) requires N, 3.6\%).
SUBSTITUTION of m-PHENYLENE DIAMINE.

Reactions described.

1:3-Di-p-toluenesulphonamido benzene. (a) Prepared by interaction of p-toluenesulphonyl chloride (49g.) and m-phenylene diamine in pyridine (llg.) a poor yield was obtained (25g.).

(b) A more satisfactory method was found to be as follows:- The diamine (5g.) was ground together with p-toluenesulphonyl chloride and anhydrous sodium acetate (9g.). No reaction set in, but gentle warming caused the reaction to start. The solid was then filtered and washed with hot water and then crystallised from alcohol, from which it separated as pink needles m.p.170°.

1:3-Di-m-nitrobenzenesulphonamido benzene. The product of interaction of m-phenylene diamine and m-nitrobenzenesulphonyl chloride in pyridine was an oil. This was warmed with dilute sodium hydroxide and the filtered solution introduced slowly into dilute hydrochloric acid. The resultant solid after recrystallisation from acetic acid gave plates m.p.195°. (Found: N,11.9 C_{18}H_{12}O_8N_4 requires N, 11.7%).
Nitration of 1:3-Di-p-toluenesulphonamido benzene.

(a) 10 g. were heated on the water bath with a mixture of acetic acid (40 c.c.) and nitric acid (50 c.c., d. 1.4) for two hours. On cooling 4:6-dinitro-1:3-di-p-toluenesulphonamidobenzene separated and after recrystallisation from acetic acid formed pale yellow plates, m.p. 208-210° (7 g.). (Found; N, 11.4 \( \text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_8\text{S}_2 \) requires N, 11.1%). Apart from a further small quantity of the 4:6-dinitro compound, no pure product could be isolated from the mother liquor. On solution in sulphuric acid this compound furnished 4:6-dinitro 1:3-phenylenediamine m.p. 303° (acetyl derivative, m.p. 228°).

(b) Addition of the 4:6-dinitro derivative to fuming nitric acid converted it to 2:4:6-trinitro-di-o-nitro-p-toluenesulphonamidobenzene, which formed rhombohedra, m.p. 223°, from acetic acid. (Found; N, 15.2 \( \text{C}_{20}\text{H}_{15}\text{O}_{14}\text{N}_7\text{S}_2 \) requires N, 15.3%). This was hydrolysed by sulphuric acid to 2:4:6-trinitro-1:3-phenylenediamine, m.p. 285° (acetyl derivative, m.p. 300°).

Nitration of 1:3-Di-m-nitrobenzenesulphonamidobenzene.

(a) To 10 g. in acetic acid (100 c.c.) at 70° was added fuming nitric acid (100 c.c.) in acetic acid (100 c.c.). On cooling 4:6-dinitro-1:3-di-m-nitrobenzenesulphonamidobenzene separated and formed needles, m.p. 235°, after recrystallisation from acetic acid. Yield 4 g. (Found; N, 15.0 \( \text{C}_{19}\text{H}_{12}\text{O}_{12}\text{N}_6\text{S}_2 \) requires N, 14.8%). No other pure product could be isolated from the mother liquor. Sulphuric acid converted this to 4:6-dinitro-1:3-phenylene diamine.

(b) The dinitro compound (2 g.) was dissolved in fuming nitric acid (40 c.c.) and the resultant solution diluted with acetic acid. The precipitate after recrystallisation from acetic acid gave 2:4:6-trinitro-di-m-nitrobenzenesulphonamidobenzene as stout.
prisms, m.p.218°. (Found: N, 15.6 \( \text{C}_{15} \text{H}_{11} \text{O}_{14} \text{N}_{9} \text{S}_{2} \) requires N, 16.0%). On solution in sulphuric acid this compound furnished 2:4:6-trinitro-1:3-phenylenediamine, m.p.285°.

**Bromination of 1:3-Di-p-toluene sulphonamidobenzene.** (a) To a mixture of this substance 5g. in chloroform (20c.c.) was added bromine (1.3c.c.) in chloroform (5c.c.). After refluxing for two hours, the solution after filtering deposited 2:4:6-tribromo-1:3-di-p-toluene sulphonamidobenzene, needles m.p.239°, after re-crystallisation from acetic acid. (Found: N, 4.4 \( \text{C}_{30} \text{H}_{17} \text{O}_{4} \text{N}_{2} \) \( \text{Br}_{3} \text{S}_{2} \) requires N, 4.3%). Its constitution was confirmed by hydrolysis to 2:4:6-tribromo-1:3-phenylenediamine, m.p.162° (acetyl derivative, m.p.300°). From the mother liquor after distilling off most of the chloroform there separated 4:6-dibromo-1:3-di-p-toluene sulphonamidobenzene, stout needles, m.p.209°. (Found: N, 5.0 \( \text{C}_{20} \text{H}_{13} \text{O}_{4} \text{N}_{2} \text{Br}_{2} \text{S}_{2} \) requires N, 5.0%). This constitution was confirmed by hydrolysis with cold concentrated sulphuric acid to the corresponding base, m.p.134° (acetyl derivative, m.p.257 - 260°).

(b) 10g. of the powdered material were introduced into pyridine and then bromine (7.7g.) added drop by drop to the thick mass of the pyridine salt. After standing 12 hours, the mixture was agitated with hydrochloric acid and the resultant solid filtered off, boiled with alcohol and filtered hot. The residue (7g., m.p.207°) after re-crystallisation from acetic acid furnished pure 4:6-dibromo-di-p-toluene sulphonamidobenzene, m.p.209°. The alcoholic mother liquor gave a further small yield of the same compound and some of the 2:4:6-tribromo derivative.

(c) With excess of bromine in pyridine the 4:6-dibromo compound gave the 2:4:6-tribromo derivative.
The following disulphonanilides were prepared by allowing the amine and m-nitrobenzenesulphonyl chloride (2 mol.) to interact in pyridine solution for several days. The products were repeatedly boiled with acetic acid until all the more soluble sulphonanilide had been eliminated.

**Di-m-nitrobenzenesulphonanilide**, needles m.p.189°. (Found; N, 9.0 %, C_{18}H_{13}O_{2}N_{3}S_{2} requires N, 9.1%).

**4-Methyl-di-m-nitrobenzenesulphonanilide**, m.p.199° (Found; N, 8.7 %, C_{19}H_{15}O_{2}N_{3}S_{2} requires N, 8.8%).

**3-Methyl-di-m-nitrobenzenesulphonanilide**, m.p.226° (Found; N, 8.8%).
The following were prepared by heating an alkaline solution of the mono naphthalide with m-nitrobenzenesulphonyl chloride (1 mols). for several hours.

**Di-m-nitrobenzenesulphon-α-naphthalide prisms, m.p.252° from alcoholic pyridine.** (Found: N, 8.2 requires N, 8.2)

**Di-m-nitrobenzenesulphon-β-naphthalide, colourless rods, m.p.255° from alcoholic pyridine.** (Found; N, 8.1).

**Nitration of di-m-nitrobenzenesulphonanilide.** 10g. were added slowly to fuming nitric acid (30c.c.) and the resultant solution poured on to ice. The precipitate (11g., m.p.195 - 205°) could not be purified by boiling with acetic acid or by fractional precipitation from pyridine by means of ethyl alcohol. 5g. were left with sulphuric acid for several hours and the mixture poured into water. The product on extraction with acetic acid left 3-nitro-di-m-nitrobenzenesulphonanilide, m.p.235° (0.8g.) (Bell, J., 1930, 1077), and 4-nitro-m-nitrobenzenesulphonanilide, m.p.180° (J., 1929, 2788) was isolated from the filtrate. Both were identified by comparison with authentic specimens and in the case of the former by scission with warm piperidine, when m-nitrobenzenesulphonyl piperidine, m.p.124°, and 3-nitrobenzenesulphonanilide, m.p.151°, were obtained.

**Nitration of 4-Methyl-di-m-nitrobenzenesulphonanilide.** 3g. were added to nitric acid (10c.c.) and the solution poured on to ice. The precipitate (3.3g., m.p.ca 205°) after boiling with acetic acid gave pure 3-nitro-4-methyl-di-m-nitrobenzenesulphonanilide, m.p.208° (Found; N, 10.8 C_{19}H_{14}O_{10}N_{4}S_{2} requires N, 10.7°) It was left with sulphuric acid for several hours and the clear solution poured into water. The precipitate after crystallisation from acetic acid formed prisms, m.p.136°, alone or mixed with an authentic specimen of 3-nitro-4-methyl-m-nitrobenzenesulphonanilide.
(from the interaction of m-nitro-benzenesulphonyl chloride and 3-nitro-p-toluidine) (Found; N, 12.6 C_{13}H_{11}O_6N_3S requires N, 12.5%).

Nitration of 2-Methyl-di-m-nitrobenzenesulphonanilide. 3g. as above gave a product readily separable by acetic acid into a less soluble part, m.p. 221°, and a more soluble part, needles, m.p.ca. 95°, or after heating to remove acetic acid, m.p. 185°.

The less soluble part on hydrolysis with sulphuric acid gave 2-methyl-5-nitro-aniline; it must therefore be 2-methyl-5-nitro-di-m-nitrobenzenesulphonanilide. (Found: N, 10.9 C_{19}H_{14}O_9N_4S_2 requires N, 10.7%). The other which was not identical with the already described 4 and 6-nitro compounds (‡, 1930, 1077) must be 2-methyl-3-nitro di-m-nitrobenzenesulphonanilide. (Found: N, 10.9%). By solution in piperidine it was severed to give 2-methyl-3-nitro-m-nitrobenzenesulphonanilide, (found N, 12.4%) which crystallised from acetic acid in needles m.p. 148°.

Nitration of α- and β-di-m-nitrobenzenesulphon-naphthalides.

Both these compounds dissolved slowly in a hot mixture of equal parts fuming and nitric acids and dilution with acetic acid furnished the nitro derivatives. No method was found for hydrolysing the very insoluble products. The product from the α-compound after recrystallisation from boiling pyridine softened at 205° and melted between 231 - 227° (dec.). (Found: N, 10.1 C_{22}H_{14}O_9N_4S_2 requires N, 10.0%). The product from the β-compound after crystallisation from pyridine softened at 185° and melted between 190 and 196° (found N, 10.2).

Analysis therefore indicates mono nitration in both cases.
Purification of 1:5-Amino naphthol. The starting material was 1:5-amino naphthol sulphate which was supplied by Imperial Chemical Industries Ltd., (Dyestuffs Group). The best method of purification was by dissolving it in boiling dilute hydrochloric acid with addition of animal charcoal, filtering and neutralising the filtrate with 880 ammonia. The 1:5-amino naphthol so obtained was practically colourless and had m.p. 185 - 190° (dec.). The hydrochloride, somewhat sparingly soluble in cold water formed colourless needles, which blackened at ca. 230° and melted with decomposition at ca. 300°.

Nitration of Di-m-nitrobenzenesulphonyl-1:5-amino naphthol. To 1:5-amino naphthol (10g.) in pyridine was added m-nitrobenzenesulphonyl chloride. The mixture was left to stand for two hours and then rubbed with dilute hydrochloric acid. The solid powder was collected, and dried. The di-m-nitrobenzenesulphonyl derivative was an extremely insoluble compound and was purified by suspending in boiling glacial acetic acid and filtering. It was thus obtained as a grey powder, m.p. 239 - 241°. (Found: N, 8.0 C_{22}H_{15}S_{2}O_{9}N_{3} requires N, 7.9%).

This substance was suspended in a mixture of acetic acid (70c.c.) and concentrated nitric acid (10c.c.) and warmed on the water bath. Nitration took place, the solid going into solution and shortly afterwards being precipitated as the dinitro body. After all visible reaction had ceased, the mixture was filtered hot and the substance washed successively with boiling acetic acid, till the washings were colourless. 2:4-dinitro-di-m-nitrobenzenesulphonyl-1:5-aminonaphthol, (found N, 11.5 C_{22}H_{13}S_{2}O_{13}N_{5} requires N, 11.1%), was so obtained as reddish brown plates, m.p.
No pure product was isolated from the mother liquor. This compound was resistant to further nitration and dissolved in hot caustic soda to give a deep red solution. No method could be found to hydrolyse this very insoluble substance. It was unaffected by cold concentrated sulphuric acid or by 60% sulphuric acid at 100°.

Nitration of Dibenzoyl-1:5-aminonaphthol. This was obtained by shaking an alkaline solution of 1:5-aminonaphthol with benzoyl chloride. It crystallised from a large bulk of acetic acid in plates, m.p. 274°. (Ber., 1906, 39, 3026).

A mixture of dibenzoyl 1:5-aminonaphthol (25g.) acetic acid (400c.c.) and concentrated nitric acid (16c.c.) was heated on the water bath. After a short time the substance dissolved with evolution of brown fumes, and was thereafter precipitated as a brownish yellow crystalline precipitate. This was filtered hot and washed with boiling acetic acid. It had m.p. 269 - 271° (dec.) and the yield was 10g. The nitric acid mother liquor deposited a further small quantity (1g.) after 12 hours. This dinitro compound was sparingly soluble in boiling acetic acid (ca.1g. in 300c.c.) and crystallised in yellow needles, m.p. 270 - 272° (dec.). (Found: N, 9.0. C_24_H_15_0_7_N_3 requires N, 9.0%)

Hydrolysis. The O-benzoyl group was removed by warming with dilute sodium hydroxide solution (ca.1 N.) on the water bath. The substance gradually passed into solution forming a deep red colour. The liquid, after filtering, was acidified when a greenish yellow precipitate was thrown down. This was collected, washed with hot water to remove benzoic acid, and dried. The dinitro compound had m.p. 275 - 280° (dec.) and after crystallisation from boiling acetic acid, in which it was
very sparingly soluble, formed yellow plates, m.p. 280 - 285° (dec)
(Found: N, 11.6. C₁₇H₁₁O₆N₃ requires N, 11.8%).

Attempts to hydrolyse the N-benzoyl group were unsuccessful. The substance was recovered unchanged after (a) heating
with 60% sulphuric acid to 100° and (b) heating with concentrated hydrochloric acid in a sealed tube to 135 - 140° for 3½ - 4
hours. It was decomposed by heating with 15% ammonia at 130°
for 1 hour.

Acetylation of 1:5-Amino naphthol. A number of methods
were tried and the most convenient found to be as follows:-

To the amino naphthol sulphate (20g.) mixed with fused
sodium acetate (20g.) was added excess of acetic anhydride, with
agitation. Heat was evolved and the diacetyl compound crystallised out. The mixture was heated for ½ hour on the water bath
and then warmed for a further period with addition of water.
The reddish brown solid was filtered and crystallised from alcohol (charcoal). 1-Acetamino-5-naphthyl acetate was so obtained
as plates, m.p. 194°. (Found: N, 5.8. C₁₄H₁₃O₃N requires N, 5.8%).
It was unattacked by cold concentrated nitric acid, and was
decomposed with warm dilute nitric acid.

N-Acetyl-1:5-amino naphthol was obtained from the diacetyl
compound by hydrolysing with sodium hydroxide. It crystallised
from aqueous alcohol in needles, m.p. 177° (found: N, 7.0
C₁₂H₁₁O₂N requires N, 7.0%).

Attempts to nitrate this compound led to much decomposition.

1-Acetamino-5-naphthyl benzoate was obtained from the above
compound by benzoylation of the alkaline solution with benzoyl
chloride. It crystallised from alcohol in needles, m.p. 208°
(Found: N, 4.6. C₁₉H₁₅O₃N requires N, 4.6%).
Nitration. (a) The substance was added in small quantities to ice cold concentrated nitric acid. After the addition, the solution was poured on to ice and the yellow precipitate, after crystallisation from alcohol formed pale yellow prisms, m.p. 228 - 230°. This was obtained also by warming the 1-acetamino-5-naphthyl benzoate with dilute nitric acid. It was a mono-nitro derivative. (Found: N, 8.2 % requires N, 8.0 %). With hot dilute sodium hydroxide solution ammonia was evolved and no pure product was obtained on acidification, of the solution.

(b) 10g. were warmed on the water bath with a mixture of glacial acetic acid (50c.c.) and concentrated nitric acid (10cc.) Solution took place with evolution of brown fumes. 2:4-Dinitro-1-acetamino-5-naphthyl benzoate (found; N, 10.9 % requires N, 10.6 %) was soon after precipitated as lustrous yellow flakes (7g.). Crystallised from a very large bulk of acetic acid it was obtained as pale yellow needles, m.p. 280°(dec)

The nitric acid mother liquor on standing for 12 hours deposited a small quantity of orange needles (0.7g.) which decomposed sharply at 154° (after recrystallisation from acetic acid), were insoluble in sodium hydroxide solution and with acetic anhydride and a drop of sulphuric acid were reconverted to 2:4-dinitro-1-acetamino-5-naphthyl benzoate. The compound was therefore 2:4-dinitro-1-acetamino-5-naphthyl benzoate. (Found: N, 12.2 % requires N, 11.9 %).

Hydrolysis of 2:4-dinitro-1-acetamino-5-naphthyl benzoate. This dissolved slowly in warm very dilute sodium hydroxide solution. Even under these mild conditions, however, ammonia was evolved and some decomposition set in. The deep red solu-
after filtering, was acidified and the dark yellow precipitate collected. Benzolic acid was removed by hot water and the product after crystallisation from acetic acid formed yellow rods, m.p. 253 – 259° (dec.). The yield of 2:4-dinitro-1-acetamino-5-naphthol so obtained was about 50% theory. (Found: N, 14.5 C12H9O6N3 requires N, 14.4%). The aqueous washings containing benzoic acid were neutralised in the cold with sodium bicarbonate. A small quantity of orange precipitate remained which after recrystallisation from hot water formed light red plates, with indefinite m.p. (ca. 250° with decomposition). This was obtained also by hydrolysis of the dinitro-N-acetyl naphthol (above) with alcoholic hydrochloric acid and its constitution as 2:4-dinitro-1-amino-5-naphthol (found: N, 16.3 C10H7O5N3 requires 16.9%) confirmed by giving 2:4-dinitro-di-m-nitro-benzenesulphonyl-1:5-amino naphthol (page 109) with m-nitrobenzene sulphonyl chloride in pyridine solution.

Summary.
APPENDIX.

SUMMARY of NEW COMPOUNDS OBTAINED in the EXPERIMENTAL WORK.

(All compounds with the exception of those marked (s) were analysed by the author. The latter were analysed by Schoeller, Berlin. Numbers in brackets refer to the pages in which the compounds are described.).

Derivatives of \( \alpha \)- and \( \beta \)-napthalols.

1. 4-Bromo-1-naphthyl-\( \bar{\alpha} \)-nitrobenzenesulphonate (s) (85)
2. 2-Bromo-2-\( \bar{\alpha} \)-nitrobenzenesulphonate (s) (86)
3. 1-Nitro-3-bromo-2-naphthol (99)

Derivatives of \( \alpha \)-napthylamine.

4. 2-Bromo-4-nitro-1-naphthylamine (89)
5. " " acetonaphthalide (89)
6. " " 2-toluenesulphon-1-naphthalide (96)
7. 2-nitro-" " (91)
8. \( \bar{\alpha} \)-nitrobenzenesulphon-1-naphthalide (93)
9. 2:4-dinitro-\( \bar{\alpha} \)- " " (94)
10. 5-nitro-" " (94)
11. 2:4:5-trinitro-" " (94)
12. Pyridine salt of above (95)
13. 4-Bromo \( \bar{\alpha} \)-nitrobenzenesulphon-1-naphthalide (s) (95)
14. 2:4-Dibromo-\( \bar{\alpha} \)- " " (96)

Derivatives of \( \beta \)-napthylamine.

15. 3-Bromo-2-naphthylamine (98)
16. 3-Bromo-2-acetonaphthalide (77)
17. 3-Bromo-\( \bar{\alpha} \)-toluenesulphon-2-naphthalide (78)
18. 1-Nitro-3-bromo-2-naphthylamine (99)
19. 1-Nitro-3-bromo-2-acetonaphthalide (99)
<table>
<thead>
<tr>
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<tr>
<td>20.</td>
<td>1-Nitro-3-bromo-(p)-toluenesulphon-2-naphthalide</td>
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<td>1-Iodo-</td>
<td>(101)</td>
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<td>22.</td>
<td>Di-(m)-nitrobenzenesulphon-1-naphthalide</td>
<td>(107)</td>
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<td>23.</td>
<td>(?)-Nitro-</td>
<td>(108)</td>
</tr>
<tr>
<td>24.</td>
<td>Di-(m)-</td>
<td>(107)</td>
</tr>
<tr>
<td>25.</td>
<td>(?)-Nitro-</td>
<td>(108)</td>
</tr>
<tr>
<td>26.</td>
<td>1-Bromo-di-(p)-toluenesulphon-2-naphthalide</td>
<td>(78)</td>
</tr>
<tr>
<td>27.</td>
<td>Di-(m)-nitrobenzenesulphon-(p)-toluidide</td>
<td>(106)</td>
</tr>
<tr>
<td>28.</td>
<td>&quot;</td>
<td>(106)</td>
</tr>
<tr>
<td>29.</td>
<td>&quot;</td>
<td>-anilide (106)</td>
</tr>
<tr>
<td>30.</td>
<td>3-Nitro-</td>
<td>(107)</td>
</tr>
<tr>
<td>31.</td>
<td>5-Nitro-</td>
<td>(108)</td>
</tr>
<tr>
<td>32.</td>
<td>3-Nitro-</td>
<td>(108)</td>
</tr>
<tr>
<td>33.</td>
<td>2-(p)-Toluenesulphon-3-bromo-1:2-naphthylene diamine</td>
<td>(99)</td>
</tr>
<tr>
<td>34.</td>
<td>3-Bromo-1:2-naphthylene diamine</td>
<td>(100)</td>
</tr>
<tr>
<td>35.</td>
<td>Quinoxaline derivative of above</td>
<td>(100)</td>
</tr>
<tr>
<td>36.</td>
<td>Derivatives of (m)-phenylene diamine</td>
<td></td>
</tr>
<tr>
<td>37.</td>
<td>1:3-Di-(m)-nitrobenzenesulphonamido benzene</td>
<td>(103)</td>
</tr>
<tr>
<td>38.</td>
<td>4:6-Dinitro-</td>
<td>(104)</td>
</tr>
<tr>
<td>39.</td>
<td>2:4:6-Trinitro-</td>
<td>(104)</td>
</tr>
<tr>
<td>40.</td>
<td>4:6-Dibromo-1:3-di-(p)-toluenesulphonamido benzene</td>
<td>(105)</td>
</tr>
<tr>
<td>41.</td>
<td>2:4:6-Dinitro-</td>
<td>(104)</td>
</tr>
<tr>
<td>42.</td>
<td>2:4:6-Trinitro-1:3-di-(p)-nitro-(p)-toluenesulphonamido benzene</td>
<td>(104)</td>
</tr>
</tbody>
</table>
Derivatives of 1:5-Amino naphthol.

43. 1-m-nitrobenzenesulphonamido-5-naphthyl-m-nitrobenzenesulphonate. (109)

44. 2:4-Dinitro- " " " " (110)

45. 2:4-Dinitro-1-benzamino-5-naphthyl benzoate (110)

46. " " " -5-naphthol (110)

47. 1-Acetamino-5-naphthyl acetate (111)

48. 1-Acetamino-5-naphthol (111)

49. 1-Acetamino-5-naphthyl benzoate (111)

50. 2:4-Dinitro- " " " (113)

51. " " -1-amino- " " (8) (112)

52. " " -1-acetamino-5-naphthol (113)

53. 2:4-Dinitro-1-amino-5-naphthol (113)

54. 2-Nitro-1-acetamino-5-naphthyl benzoate (113)

Miscellaneous.

55. 3-Nitro-m-nitrobenzenesulphon-p-toluidide (107)

56. " " " " -p-" " (108)

57. 2-Iodo-1-p-toluenesulphon-p-toluidide (102)

58. 3-Iodo-2-p-toluenesulphonamido diphenyl (102)

59. " -4- " " " (102)

60. 6:8-Dinitro-2-naphthalenediazol-1-oxide (77)