FOREWORD

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This constitutes a final summary report of work performed during the period of 1 October 1960 through 31 May 1963.

The experimental work described in this report was carried out by Mr. P. A. Barfield. Dr. J. Lee has given valuable advice, particularly in connection with spectroscopic work.
ABSTRACT

Evidence from nuclear magnetic resonance (N.M.R.) studies for π-bonding between boron and nitrogen in the borazens is presented. Preliminary experiments, by infrared spectroscopy, which indicate that a similar situation might exist between phosphorus (III) and nitrogen in open chain compounds are reported.

The energy barrier to rotation about the BN bond in dimethylamino-phenylchloroborane is calculated, from observations upon three different parameters characterizing the shape of the N.M.R. signal, as 14 ± 0.2 kcal. mole⁻¹. The barrier in the corresponding bromo-compound was evaluated as 21 ± 0.7 kcal. mole⁻¹ by analogous methods.

The interesting features of the N.M.R. spectrum of the recently reported compound, 1,3-di-t-butyl-2,4-di-t-butylamino-1,3-diaza-2,4-borostane, which clearly demonstrate that the compound has more than one steric configuration presumably due to exocyclic π-bonding, are also presented.

This technical documentary report has been reviewed and is approved.

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AF Materials Laboratory
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I. INTRODUCTION

It has been suggested that the search for materials suitable for the synthesis of thermally and hydrolytically stable polymers, might well be pursued among those inorganic compounds in which π-bonding occurs.

One consequence of there being a well developed π-bond between any pair of atoms is that there might be a high degree of restriction to rotation about the bond. We have been investigating the problem of restricted rotation about pairs of inorganic atoms, by spectroscopic methods paying particular attention to systems based upon boron; in the chemistry of which, π-bonding is known to be an important feature.

In particular, nuclear magnetic resonance has been used to study such restricted rotation and from the data obtained barriers to rotation have been evaluated at 14 ± 0.8 kcal. mole⁻¹ in dimethylaminophenylchloroborane, C₆H₅B(Cl)NMe₂, and as 21 ± 0.7 kcal. mole⁻¹ in the corresponding bromo-compound, C₆H₅B(Br)NMe₂. The information obtained in these studies is summarised in tables given at the end of this report and is discussed under appropriate headings.

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II. STUDIES ON OPEN CHAIN BORON-NITROGEN SYSTEMS.

These studies have been based upon the system I, which may evolve contributions from the canonical form II, if delocalisation of the \( p_z \)-nitrogen electrons into the available boron \( p_z \)-boron orbital is significant. This particular system is of great interest since it is both isoelectronic and isosteric with the corresponding ethylenic system III.

Much evidence for the existence of structures of type II has been recorded in the literature and this has been summarised\(^1,2\).

Our studies have been based essentially upon the two systems IV and V, which differ from the systems studied by other authors\(^3,4\), in that in all our cases a phenyl group is attached to the boron atom.

2.
In IV two \( \overset{\text{N}}{\text{N}} \)-methyl groups may occupy chemically different but equally abundant environments, whilst in V a single \( \overset{\text{N}}{\text{N}} \)-methyl group may occupy chemically different but unequally abundant environments, i.e., \textit{cis-trans} isomerism is possible.

The methods for the synthesis of the compounds studied are summarised in an appendix to this report.

\textbf{NUCLEAR MAGNETIC RESONANCE STUDIES.}

Data are summarised in Table I, from which it can be seen that the spectrum of dimethylaminophenylchloroborane, \( \text{C}_6\text{H}_5\text{B}\text{(Cl)}\text{NMe}_2 (X = \text{Cl}) \), consists of two bands at an average \( \Delta = 7.2 \) (fig. 1a). The bands are separated by 8.18 c/s at 40 Mc/s but this increases to 12.86 c/s at 60 Mc/s. This observation is typical of the existence of an internal chemical shift.

At increased temperatures, the bands broaden and merge (fig. 1b, 1d) until at 118°C only a single band can be detected. At still higher temperatures, the single broad band increases in its intensity whilst its width is diminished (1e, 1f).

The two bands can be assigned to the protons of the methyl groups which are attached to the nitrogen atom and owe their origin to a differential shielding of each group. The
Fig. 1. Spectrum of compound type IV, X = Cl, at several temperatures.
TABLE I. N.M.R. DATA FOR COMPOUNDS OF TYPE (I).

<table>
<thead>
<tr>
<th>Compounds I</th>
<th>X = NMe₂</th>
<th>X = OMe</th>
<th>X = F</th>
<th>X = Me</th>
<th>X = Cl</th>
<th>X = Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ(⁻¹NMe₂)*</td>
<td>7.49</td>
<td>7.47</td>
<td>7.35</td>
<td>7.32</td>
<td>7.26</td>
<td>7.18</td>
</tr>
<tr>
<td>ν⁺ - ν⁻ (c/s)†</td>
<td>single band 17.4 ± 0.2 $^\circ$</td>
<td>single band 4.2 ± 0.2 $^\circ$</td>
<td>12.8 ± 0.3 $^\circ$</td>
<td>17.89 ± 0.05 $^\circ$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T°C $^\circ$</td>
<td>&lt; -50</td>
<td>37</td>
<td>&lt; -50</td>
<td>99.5</td>
<td>118</td>
<td>118</td>
</tr>
</tbody>
</table>

* (-NMe₂), average γ-value of absorption maxima due to hydrogen nuclei of -NMe₂ group.
† (ν⁺ - ν⁻), separation of -NMe₂ group band maxima at zero isomeric interconversion rate.

$^\circ$ T°C = "coalescence" temperature.
subsequent observations, which are characteristic of a variable isomeric interconversion process, have also been recorded for three other members of series IV, \( (X = Br, Me, \) and \( OMe) \), and for two members of series V \( (R = C_2H_5 \) and \( C_3H_7) \).

From observations upon the spectra recorded at various temperatures, evaluation of the kinetic constants associated with the process is possible. The underlying details have been given previously \(^6\) (see also section VI of this report).

The barrier to rotation \( (R_a) \) for dimethylaminophenyl-chloroborane, \( C_6H_5B(Cl)NMe_2 \), has been calculated from observations upon three parameters, which characterise the shape of the N.M.R. signal, as \( 14.0 \pm 0.8 \text{ kcal.mole}^{-1} \). The energy barrier to rotation about the BN bond in the corresponding bromo-analogue \( [i.e. C_6H_5B(Br)NMe_2] \) has been evaluated by identical methods as \( 21.0 \pm 0.7 \text{ kcal.mole}^{-1} \). The remaining kinetic constants are summarised in Tables V and VI (Section VI of this report). The higher barrier in the second case can be interpreted in terms of the ability of the halogen itself to \( \pi \)-bond with the boron atom. It is well known that bromine is less efficient in this respect than chlorine. This interpretation would appear to find some confirmation in the fact that when the more efficient fluorine is substituted for chlorine, no doublet was observed even at temperatures...
as low as \(-50^\circ\)C in toluene solution. It is probable also that the size of the halogen atom in the three compounds significantly affects the ease of rotation about the BN bond.

Although we have previously\(^7\) concluded that the observation of a high barrier in the case of dimethylaminophenylchloroborane, \(\text{C}_6\text{H}_5\text{B(Cl)NMe}_2\), could not be due to steric effects alone (our conclusions were based on the observation that when \(X = \text{NMe}_2\), where steric effects would certainly be greater than for \(X = \text{Cl}\), no doublet is observed even at temperatures as low as \(-50^\circ\)C) it would appear that steric effects cannot be ignored in all cases. Thus, in a preliminary experiment on dimethylaminophenylmethoxyborane, a barrier to rotation as high as 16 kcal\(\cdot\)mole\(^{-1}\) was evaluated. This value is particularly surprising in view of the fact that oxygen is usually considered to be a better \(\pi\)-donor to boron than chlorine\(^7\).

Some attempt has been made to correlate the position (relative to tetrasmethylsilane) of the \(-\text{NMe}_2\) absorption with the barrier to rotation. Thus, if the barrier is high, delocalisation of the nitrogen \(\pi\) electrons into the boron \(\pi\) orbital is presumably efficient. This would be expected to correspond to a greater delocalisation of electrons from the \(-\text{NMe}_2\) group (i.e., the \(-\text{NMe}_2\) protons would be less shielded) with a consequent shift to low field (i.e., low \(\gamma\)). The observed behaviour is in general agreement with these arguments, the outstanding exception being the compound

\(^7\)
dimethylaminophenylmethoxyborane, $C_6H_5B(OMe)NMe_2$, where the possibility of steric problems arises.

Table II summarises our essentially preliminary data on two members of the unsymmetrical series V. In ethylmethylaminophenylchloroborane, $C_6H_5B(Cl)N(Me)Et$, the $-N\text{-CH}_3$ absorption consists of two bands of approximately equal intensities at 23°C (fig. 2). By assuming equal populations of the two environments, the values quoted were calculated and are probably reasonable in view of the fact that it has been suggested previously that large nitrogen substituents might lead to a decrease in $\text{N-C} - \text{C-N}$ overlap due to lengthening of the BN bond$^{1,8}$. The methylene absorption in this compound consists of two overlapping 1:3:3:1 quartets giving a 1:3:4:4:3:1 sextet.

In the case of methylisopropylaminophenylchloroborane, $C_6H_5B(Cl)N(Me)Pr^1$, the $-N\text{-CH}_3$ absorption consists of two bands of relative intensities 3:4 at 23°C. In order to calculate the barrier to rotation in this case, a more general analysis will be required.

The case of methylphenylaminophenylchloroborane is interesting. The $-N\text{-CH}_3$ protons show an absorption which is certainly broadened at room temperature. We note that it
Fig. 2. Spectrum of compound type V, $R = C_2H_5$
<table>
<thead>
<tr>
<th>Compound</th>
<th>γ(−NMe₂)</th>
<th>(ν_A − ν_B) c/sec.</th>
<th>Θ°C</th>
<th>Isomer Ratio</th>
<th>Θ Calculated Barrier To Rota. (E_a kcal⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Min/Max</td>
</tr>
<tr>
<td>II, R = Et</td>
<td>7.22 †</td>
<td>11.33 ± 0.2</td>
<td>99.5</td>
<td>1:1</td>
<td>11.5</td>
</tr>
<tr>
<td>II, R = Pr¹</td>
<td>7.20 †</td>
<td>11.56 ± 0.3</td>
<td>103</td>
<td>3:4</td>
<td>-</td>
</tr>
</tbody>
</table>

* E_a derived from Arrhenius Theory
† at 18°C
Ø at 98°C
θ estimated from the relative intensities of the two methylene absorptions.
has been suggested that at lower temperatures the development of a second band might occur\textsuperscript{3a}. We have not been able to detect the development of a second band, neither in the chloro-compound nor in its bromo-analogue, even at temperatures as low as \(-50^\circ\text{C}\). (The compounds were studied in toluene solution). It would certainly appear that a single isomeric form is preferred, a situation which would be analogous to that of the corresponding \(N\)-arylamides\textsuperscript{9}, (e.g. \(N\)-methyl-acetanilide), where only a simple methyl resonance has been observed.

**INFRARED STUDIES.**

The infrared spectra of all members of the series show a strong absorption at about 1500 cm\(^{-1}\), characteristic of the BN stretching fundamental,\textsuperscript{1,10,11} That the band appears at high frequency and is fairly strong, clearly reflects the degree of \(\pi - \pi\) overlap in the boron-nitrogen bond. Full assignments are not so far complete.

The spectra of dimethylaminophenylchloroborane, \(\text{C}_\text{6}\text{H}_\text{5}\text{B(Cl)}\text{NMMe}_\text{2}\) and ethylmethylaminophenylchloroborane vapour have been recorded at temperatures up to \(140^\circ\text{C}\). No major shifts in the vibrations are apparent.
III. STUDIES ON CYCLIC BORON-NITROGEN COMPOUNDS

The first example of a cyclic 3-co-ordinate boron-nitrogen compound, isoelectronic with cyclobutadiene, has recently been isolated\(^ {12}\). The nuclear magnetic resonance spectrum of this compound, systematically named 1,3-di-t-butyl-2,4-di-t-butyl-amino-1,3-diaza-2,4-borostane, has been recorded by us. The results, together with other observations, suggest that exocyclic \(\pi\)-bonding is responsible for stabilization of the molecule, and are of considerable interest.

Investigations were made both for the neat liquid and for a 10\% v/v solution in carbon tetrachloride. The portions of the spectra associated with \(\text{CH}_3\) groups are shown in figs. 3 (neat liquid) and 4 (\(\text{CCl}_4\) solution). The difference in the two spectra is largely attributed to the decreased viscosity of the solution. Because of the additional resolution in the solution spectrum, this was chosen as the most satisfactory for diagnostic purposes. The band positions (on the \(\gamma\)-scale) are summarised in Table III.

<table>
<thead>
<tr>
<th>Band No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.68</td>
<td>8.76</td>
<td>8.80</td>
<td>7.25</td>
<td>7.39</td>
<td>7.50</td>
<td>7.55</td>
<td>7.60</td>
</tr>
</tbody>
</table>

The large differences in \(\gamma\)-values, between the pure liquid and the carbon tetrachloride solution, may be due to preferential "layering" of the planes in solution. This

12.
Fig. 3. Spectrum of compound \( \text{VI} \), neat liquid.
Fig. 4. Spectrum of compound $\text{VI}$, 10\% v/v in carbon tetrachloride
explanation is based on analogy with the benzene $^1H$ nuclear magnetic resonance spectrum and solvent effects thereon$^{13}$. The solution spectrum is more complex than expected from the presence of a single isomer. Two possible structures are VI(a) and VI(b). Isomerism arises from restricted rotation about both the exocyclic BN bonds. This appears to be a reasonable assumption, particularly on the basis, VI(c), that multiple bonding is largely exocyclic rather than cyclic.

VI(a)  
\[ \text{But}^+ \text{NH} \text{But}^+ \text{But}^+ \text{But}^+ \]

VI(b)  
\[ \text{But}^+ \text{But}^+ \text{But}^+ \text{But}^+ \]

VI(c)  
\[ \text{But}^+ \text{NHBut}^+ \]

Assuming ring planarity in each case, structure VI(a) has

15.
three (or even four; the two marked "c" may also differ significantly) distinct butyl groups in abundance ratio 2:1:1 while structure VI(b) has only two butyl environments, these being in equal abundance. On this basis then, and assuming absence of spin-multiplets, we should expect the $^1$H spectrum of VI(a) to consist of three bands in the intensity ratio 2:1:1, while that of VI(b) should comprise of two equally intense bands. The expectation would be in substantial agreement with the observed solution spectrum if an assignment shown in Table IV is accepted coupled with an isomeric abundance ratio trans-/cis- [i.e., VI(b)/VI(a)], of ~2.

**TABLE IV. BAND ASSIGNMENTS**

<table>
<thead>
<tr>
<th>Band No.</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band No.</td>
<td>see Fig. 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Assignment

(see VI(a) "a" or "d" "b" or "c" "c"
and VI(b) "b" "a"

The field order of bands assigned to "a", "d" and "b" groups would be in accordance with expectation. The N-H groups (for both isomers) is associated with a quadrupole broadened absorption centered on $r = 5.42$.

Although some preliminary studies have been made on this compound at various temperatures, quotation of results would be premature. We are proceeding with our investigations and we anticipate that spectral changes will confirm the conclusions given above.

16.
IV. OPEN CHAIN BORON-OXYGEN COMPOUNDS

Thermochemical \(^{14}\) and spectroscopic \(^{15}\) data for \(\pi\)-bonding from oxygen to boron have been reported although this would certainly appear to be less effective than in the corresponding case of a nitrogen atom attached to boron.

The methods used for the synthesis of the compounds studied are given in an appendix to this report.

NUCLEAR MAGNETIC RESONANCE STUDIES.

The compounds studied are all based on the system VII. The \(^1\)H nuclear magnetic resonance spectrum of each of these

\[
\begin{align*}
\ce{C6H5} & \quad \ce{\vert} \\
\ce{\vert} & \quad \ce{\vert} \\
\ce{B} & \quad \ce{\vert} \\
\ce{\vert} & \quad \ce{\vert} \\
\ce{OMe} & \\
\end{align*}
\]

\[X = \text{OMe, Cl, NMe}_2\]

VII

compounds recorded at room temperature is characterised by a single absorption which can readily be assigned to the protons of the methoxy-group. In no case could the existence of a second low intensity band (assignable to a second isomer) be detected. The absence of a second band does not prove that \(\pi\)-bonding from oxygen to boron is inefficient in these compounds, since the possibility of preferred isomeric arrangements arises.
It is possibly significant that absorption occurs at lower field in phenylmethoxychlororoborane, \( \text{C}_6\text{H}_5\text{B(Cl)OMe} \) (\( \gamma = 6.39 \)), than in phenyldimethoxyborane, \( \text{C}_6\text{H}_5\text{B(OMe)}_2 \) (\( \gamma = 6.45 \)) or dimethylaminomethoxyphenylborane, \( \text{C}_6\text{H}_5\text{B(OMe)NMMe}_2 \) (\( \gamma = 6.70 \)). Clearly a greater demand will be made upon the oxygen \( \pi^2 \) -electrons in phenylmethoxychlororoborane, with a consequent shift to low field of the absorption signal, than in either of the other cases. It would be quite reasonable to expect that absorption in dimethoxyphenylborane would occur at lower field than in dimethylaminomethoxyphenylborane, since in the latter we have the presence of the nitrogen atom which is known to be a better \( \pi \) -donor than oxygen.

INFRARED STUDIES.

Details of infrared studies in a large number of compounds of this type have been published previously\(^{15} \). Assignments of the various bands in the compounds prepared by us fit exactly with published data.
V. INVESTIGATIONS INTO OTHER SYSTEMS.

A. THE PHOSPHORUS(III)-NITROGEN SYSTEM.

\( \pi \)-Bonding in the phosphorus nitrogen bond has been invoked in the discussion of a PN compound and its pseudoaromaticity\textsuperscript{16}.

Our studies have been based upon the compound \( \text{N,N-dimethyl-} P\text{-phenylphosphonamidous chloride, } C_6\text{H}_5\text{P(Cl)NMe}_2, \) and the corresponding diamide, \( C_6\text{H}_5\text{P(NMe}_2)_2 \). The \( ^1H \) nuclear magnetic resonance spectrum of both compounds at room temperature consists of a broad low field absorption (phenyl) together with a doublet at higher field. The doublet was shown to arise from electron-coupled spin-interaction between \( ^31P \) and \( ^1H \) nuclei, through measurements at both 60 and 25 Mc/s.

The infrared spectrum of \( \text{N,N-dimethyl-} P\text{-phenylphosphonamidous chloride, } C_6\text{H}_5\text{P(Cl)NMe}_2, \) shows a medium band in the 1600 cm\(^{-1}\) region, characteristic of monosubstituted aromatic compounds. This is accompanied by another band at approximately 20 cm\(^{-1}\) lower and this may be due to the presence of an unsaturated side chain which allows extended conjugation with the aromatic ring. Similar features have been observed in the spectra of borazens\textsuperscript{1}. It is significant that the low intensity band is absent in the diamido, \( C_6\text{H}_5\text{P(NMe}_2)_2 \), where the extent of \( \pi \)-bonding would be expected to be reduced.

19.
Comparison of the spectra of these phosphorus compounds with their boron analogues reveals that PN stretching vibration falls at 986 cm$^{-1}$ for C$_6$H$_5$PClNMe$_2$, and at 971 cm$^{-1}$ (asym.) and 957 cm$^{-1}$ (sym) for C$_6$H$_5$P(NMe$_2$)$_2$.

B. THE PHOSPHORUS(V)-NITROGEN SYSTEM.

As a further extension to our studies, the compound VIII, C$_6$H$_5$POClNMe$_2$, in which contributions from canonical forms of type IX might be important, i.e. the possibility of $p^\pi$-d$^\pi$ bonding occurs) was prepared. The $^1$H nuclear magnetic resonance spectrum recorded at room temperature, consisted of a characteristic low field absorption due to hydrogens of the phenyl ring, together with a doublet at $\gamma = 7.25$. The doublet is almost certainly due to electron-coupled interaction of $^{31}$P and $^1$H nuclei; $J_{PH} = 14.1$ c/s.

C. THE NITROGEN-NITROGEN SYSTEM.

It has recently been shown$^{19}$, by nuclear magnetic resonance methods, that compounds of the type XI can exist in two isomeric forms Xa and Xb. The existence of isomers in such
compounds may possibly be explained on the basis of lone pair repulsions of the phosphorus electrons.

We have recently examined the $^1\text{H N.M.R.}$ spectra of $N,N'$-dimethylhydrazobenzene but cannot detect any signs of isomeric forms being present at room temperature. In a preliminary experiment observations on the spectrum were made whilst the sample was slowly cooled. Although it was not possible to obtain any accurate details, due to instrumental difficulties, it is already clear that the methyl absorption, which is a simple band at room temperature, broadens and can be resolved into two bands at approximately $-50^\circ\text{C}$. More detailed work is being planned in order to follow up these interesting observations.
VI. METHODS FOR THE CALCULATION OF BARRIERS TO ROTATION USING N.M.R. TECHNIQUES.

Application to the case of Dimethylaminophenylchloroborane.

The use of nuclear magnetic resonance as a tool in studying the phenomenon of restriction to rotation, and especially its application to the quantitative determination of the energy barrier involved, has been widely discussed in the literature. Essentially, the technique requires that some parameter characterising the N.M.R. signal (usually the absorption mode) can be related to the rate constant of the chemical exchange reaction under observation (first order kinetics being assumed).

We have reported previously upon our preliminary calculations. These were based upon observations involving four parameters viz:–

1. Ratio \( \frac{\text{Band Separation}}{\text{Band Separation at Infinitely Slow Exchange}} \) prior to coalescence

2. Ratio \( \frac{\text{Minimum Intensity}}{\text{Maximum Intensity}} \)

3. Ratio \( \frac{\text{Band Width at Half Height}}{\text{Band Separation at Infinitely Slow Exchange}} \) after coalescence

4. Ratio \( \frac{\text{Band Intensity}}{\text{Band Intensity at Infinitely Fast Exchange}} \)
Fig. 6. Plot of ratio of Land Maxims Separation to Separation at Infinitely Slow Exchange vs. Kinetic Rate Constant
Fig. 7. Ratio Band Width at Half Height to Separation at Infinitely Slow Exchange vs. Kinetic Rate Constant

Approved for Public Release
Fig. 8. Ratio Band Intensity to Band Intensity at Infinitely Fast Exchange vs. Kinetic Rate Constant
Fig. 9. Arrhenius Plot

\[ \frac{I(\text{min})}{I(\text{max})} \]

\[ \frac{T_2 \delta w_\infty}{\Delta T_2 \delta w_\infty} = 20 \]

\[ \frac{T_2 \delta w_\infty}{\Delta T_2 \delta w_\infty} = 10 \]

Chemical structure: 

\[
\begin{array}{c}
\text{Ph} \\
\text{Cl} \\
\text{B} \\
\text{N} \\
\text{Me} \\
\text{Me}
\end{array}
\]
Contrails

\[ \ln \left( \frac{K}{\delta w_\infty} \right) - \ln T \]

**TRANSITION STATE PLOT**

\[ \frac{I_{\text{min}}}{I_{\text{max}}} \]

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{Cl} & \quad \text{Me}
\end{align*}
\]

\( \frac{T_2 \delta w_\infty = 20}{\Delta T_2 \delta w_\infty = 10} \)

Fig. 10. Transition State Plot
Each of these methods has been used by individual authors in studying rate processes.

Since our earlier report\(^5\) slight modifications to our computer programme have been made, such that the relationship between the observable parameter and the natural logarithm of the rate constant (\(\ln k\)) are obtained directly, for any value of \(T_2 S\omega_0\), in addition to the simple relationship between parameter and rate constant.

Figures 5–8 show the graphs which are used to convert spectral parameters into kinetic rate constants (expressed as \(\ln k / S\omega_0\), where \(S\omega_0\) = separation of bands at infinitely slow exchange). The values of \(\ln k / \omega_0\) obtained from these graphs can then be used to obtain:

(a) activation energies (\(E_a\)) and frequency factors (\(A\)), for the process, by use of the Arrhenius Theory;
and (b) activation enthalpies (\(\Delta H^*\)) and entropies (\(\Delta S^*\)) of transition, through application of the Transition State Theory (see end of this section).

The following points are of importance in considering the value of \(E_a\) obtained for each method.

(i) Ratio of Minimum Intensity (\(I_{min} / I_{max}\), Fig. 5)

This method has been widely applied. In general it shows reasonable sensitivity over a good range of rate constants.
but is critically dependent upon the correct value of the product $T_2 \frac{\gamma}{\omega_0}$ ($T_2 =$ transverse relaxation time). Although $\frac{\gamma}{\omega_0}$ can be obtained with high precision the errors in the determination of $T_2$ can be significant.

(ii) Ratio Band Maxima Separation
Separation at Infinitely Slow Exchange

\[
\left\{ \frac{\omega}{\omega_0} \quad \text{Fig. 6} \right\}
\]

This is the original method of Gutowsky and Holm, but is only sensitive over a short range near the coalescence temperature. Since the bands are considerably broadened at this point it is difficult to measure their separation with any accuracy. In general, results by this method are considerably lower (up to 50\%) than those calculated from observations upon the other parameters. We have therefore abandoned this method in our recent calculations. It is of interest to note that similar observations were made in connection with recently reported studies on the $N$-alkyl amides.

(iii) Ratio Band Width at Half Height
Separation at Infinitely Slow Exchange

\[
\left\{ \frac{\omega}{\omega_0} \quad \text{Fig. 7} \right\}
\]

and

(iv) Ratio Band Intensity
Band Intensity at Infinitely Fast Exchange

\[
\left\{ \frac{I}{I_0} \quad \text{Fig. 8} \right\}
\]

Both these methods are applicable after coalescence of the two bands has occurred. $I_0$ (the band intensity at infinitely
fast exchange) can easily be obtained by continuing to raise the temperature until at successive temperatures, no further increase in the intensity of the band is apparent.

Both parameters are useful over a measurable range of rate constants [(iv) being better in this respect than (iii)] but can be misleading if at the higher temperatures the relaxation time ($T_2$), varies significantly from the mean value used in the analysis. In experiments where the resolution of the instrument can be controlled with success (see section VII of this report) throughout the experiment, no great variation in the value of $T_2$ is observed.

Some typical values of $\ln k/\delta \omega_\infty$ obtained from evaluation of $\text{Imin}/\text{Imax}$ following a variable temperature study of dimethylaminophenylchloroborane, $C_6H_5B(\text{Cl})\text{NMMe}_2$, are given in column 5 of Table VI. Each value of $\text{Imin}/\text{Imax}$ is the average value of the ratio calculated for 6 - 8 recordings of the doublet at each temperature. Half of the recordings at each temperature were made by sweeping to high field and half were made by sweeping through the field in the opposite direction. Values in column 5 are for a value of $T_2 \delta \omega_\infty = 20$. This would be an appropriate value in this experiment since the experimentally determined value was $T_2 \delta \omega_\infty = 22.7$.

These data can be handled as outlined above, either using the Arrhenius Theory or the Transition State Theory. If the Arrhenius Theory is used $\ln k/\delta \omega_\infty$ is plotted against $1/T$, \[31.\]
### TABLE V. EXPERIMENTAL DATA OBTAINED FROM FIGURE 5

<table>
<thead>
<tr>
<th>T°C</th>
<th>T°A</th>
<th>I/T x 10^3</th>
<th>Imin/Imax (Average)</th>
<th>lnk/δΩ_{k} T_{2}δΩ = 20</th>
<th>lnk/δΩ_{k} T_{2}δΩ = 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>295</td>
<td>3.390</td>
<td>0.033</td>
<td>-4.500</td>
<td>-</td>
</tr>
<tr>
<td>34</td>
<td>307</td>
<td>3.257</td>
<td>0.048</td>
<td>-3.940</td>
<td>-</td>
</tr>
<tr>
<td>46</td>
<td>319</td>
<td>3.131</td>
<td>0.035</td>
<td>-4.450</td>
<td>-</td>
</tr>
<tr>
<td>65.5</td>
<td>338.5</td>
<td>2.955</td>
<td>0.038</td>
<td>-4.310</td>
<td>-</td>
</tr>
<tr>
<td>86</td>
<td>359</td>
<td>2.786</td>
<td>0.101</td>
<td>-3.125</td>
<td>-4.365</td>
</tr>
<tr>
<td>91</td>
<td>364</td>
<td>2.745</td>
<td>0.135</td>
<td>-2.355</td>
<td>-3.720</td>
</tr>
<tr>
<td>100</td>
<td>373</td>
<td>2.681</td>
<td>0.259</td>
<td>-2.330</td>
<td>-2.750</td>
</tr>
<tr>
<td>110</td>
<td>383</td>
<td>2.611</td>
<td>0.577</td>
<td>-1.910</td>
<td>-1.900</td>
</tr>
<tr>
<td>116</td>
<td>389</td>
<td>2.571</td>
<td>0.849</td>
<td>-1.495</td>
<td>-1.525</td>
</tr>
</tbody>
</table>

Showing values of lnk/δΩ_{k}, corresponding to experimentally determined values Imin/Imax, obtained from Fig. 5.
in which case the slope of the graph \( E_a/R \) \( (R = \text{gas constant}) \) 
whilst the intercept = \( A/\delta \omega_o \), where \( A = \text{Arrhenius factor} \) 
(pre-exponential factor).

If the Transition State Theory is used, we plot \( \ln k/\delta \omega_o - 2.303 \log T \) against \( 1/T \). In this case the slope of the graph will be \( \Delta H^*/R \) whilst the intercept is given by

\[
2.303 \log \left( \frac{K}{\delta \omega_o} \right) + \frac{\Delta S^*}{R}
\]

\( (K = \text{Boltzmann constant}, h = \text{Planck's Constant}) \)

Hence both \( \Delta H^* \) and \( \Delta S^* \) may be obtained.

The data obtained from calculations upon the band width at half height, or on band intensity after coalescence, can be treated in an analogous way. Figures 9 and 10 show typical graphs which were obtained from our studies in this field, whilst Table VI summarises the calculated values for \( A, E_a, \Delta H^*, \) and \( \Delta S^* \) for the approximately correct value of \( T_2 \delta \omega_o (= 20) \) and for the completely incorrect value of the same product \( (T_2 \delta \omega_o = 10) \). The sensitivity of the various parameters to this product is thus illustrated.

Calculated data for the compound dimethylaminophenylbromoborane, \( C_6H_2B(\text{Br})\text{NM} \omega_2 \), are given in Table VII. Values were calculated from \( T_2 \delta \omega_o = 30 \); calculated value of \( T_2 \delta \omega_o = 29 \).
### Table VI. Calculated Kinetic Constants for C₆H₅B(Cl)NMé₂

\( T_2 \Delta \omega_0 \) calculated as 20

<table>
<thead>
<tr>
<th>METHOD</th>
<th>( T_2 \Delta \omega_0 = 20 )</th>
<th>( T_2 \Delta \omega_0 = 10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( E_a ) k. cal mole⁻¹</td>
<td>( A ) sec⁻¹</td>
</tr>
<tr>
<td>Imin/Iimax</td>
<td>14.4</td>
<td>2 \times 10^{10}</td>
</tr>
<tr>
<td>( \Delta \omega_2 / \Delta \omega_0 )</td>
<td>13.2</td>
<td>7 \times 10^{8}</td>
</tr>
<tr>
<td>( I / I_0 )</td>
<td>14.6</td>
<td>7 \times 10^{9}</td>
</tr>
</tbody>
</table>

*\( E_a \) and \( A \) derived from Arrhenius Theory; \( \Delta H^* \) and \( \Delta S^* \) derived from Transition State Theory.
<table>
<thead>
<tr>
<th>METHOD</th>
<th>$E_a$ (kcal.mole$^{-1}$)</th>
<th>$A$ (sec$^{-1}$)</th>
<th>$\Delta H^*$ (kcal.mole$^{-1}$)</th>
<th>$\Delta S^*$ (cal.mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imin/Imax</td>
<td>20.8</td>
<td>$1 \times 10^{13}$</td>
<td>20.3</td>
<td>-3.2</td>
</tr>
<tr>
<td>$\delta \omega_2 / \delta \omega_0$</td>
<td>20.3</td>
<td>$1 \times 10^{13}$</td>
<td>19.9</td>
<td>+1.8</td>
</tr>
<tr>
<td>$I / I_0$</td>
<td>21.6</td>
<td>$1 \times 10^{13}$</td>
<td>21.9</td>
<td>+5.0</td>
</tr>
</tbody>
</table>
VII. EXPERIMENTAL

The various compounds which have been prepared in connection with this work are given in tables in an appendix of this report. All have been fully characterised by elemental analysis (C, H, N, B, Hal), b.p. \( L^\text{D} \), infrared, \(^1\text{H}\), N.M.R., and in a few cases, ultraviolet spectra. Those compounds which have been described by earlier workers are indicated by an appropriate reference to the literature.

Infrared spectra were recorded on a Perkin-Elmer Model 21 (sodium chloride or calcium fluoride optics) and in a P.E. Model K14 (potassium bromide optics). Samples were studied as pure materials, or as mulls in paraffin oil.

\(^1\text{H}\) Nuclear magnetic resonance spectra were recorded on the Varian V4300B Spectrometer equipped with a variable temperature insert and operating at 40 Mc/s, on the Varian A60 spectrometer operating at 60 Mc/s, or on the A.E.I. RS2 Spectrometer operating at 60 or 25 Mc/s.

The variable temperature equipment used in the experiments described in this report was developed in these laboratories and used in conjunction with the A.E.I. spectrometer. The design of this component, which is based upon earlier ones described in the literature, is illustrated in figure 11. For high temperatures, a constant stream of gaseous nitrogen was passed over a heating element and the warm gas was then passed over the sample tube. Various temperatures, up to 220\(^\circ\)C, were
obtained by varying the output of the heating element.

Temperatures were measured by a copper/constantan thermocouple placed as close as possible to the sample site. The thermocouple was calibrated, under operating conditions, against a thermocouple placed in a spinning sample tube occupying the normal sample position. Temperatures are correct to ± 1°.

Spectra were calibrated by the superimposition of audiofrequency side-bands from tetramethyldisilane, except in the case of spectra recorded on the VA 60 spectrometer, where the use of calibrated chart paper obviates the need for other techniques.

Throughout the variable temperature experiments, slight adjustment of the electrical shim-coils was found necessary in order to maintain highest resolution, as indicated by the decay pattern in the signal from the protons of tetramethyldisilane incorporated in the sample.
Fig. 11. Dewar System for Investigation of NMR Spectra at Various Temperatures
### VIII. APPENDIX

**SUMMARY OF COMPOUNDS PREPARED IN CONNECTION WITH \( \pi \)-BONDING STUDIES**

<table>
<thead>
<tr>
<th>Compound</th>
<th>C(_{20})</th>
<th>D(_{20})</th>
<th>Method of Synthesis</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| \( \text{C}_6\text{H}_5\text{B(Cl)NMe}_2 \) | 75/2     | 1.53202 | \[ \text{C}_6\text{H}_5\text{BCl}_2 + \text{Me}_2\text{NH} \xrightarrow{\text{Et}_3\text{N}} \text{PhB(Cl)NMe}_2 + \text{Et}_3\text{N} \cdot \text{HCl} \]  
OR \[ \text{C}_6\text{H}_5\text{BCl}_2 + \text{C}_6\text{H}_5\text{B(NMe)}_2 \xrightarrow{} 2 \text{C}_6\text{H}_5\text{B(Cl)NMe}_2 \] | 10   |
| \( \text{C}_6\text{H}_5\text{B(NMe)}_2 \)  | 60/4     | 1.51684 | \[ \text{C}_6\text{H}_5\text{BCl}_2 + 4\text{Me}_2\text{NH} \xrightarrow{-78^\circ} \text{C}_6\text{H}_5\text{B(NMe)}_2 \]  
+ 2\text{Me}_2\text{NH} \cdot \text{HCl}                                                                                           | -    |
| \( \text{C}_6\text{H}_5\text{B(Br)NMe}_2 \) | 53/0.8   | 1.55539 | \[ \text{C}_6\text{H}_5\text{BBr}_2 + \text{C}_6\text{H}_5\text{B(NMe)}_2 \xrightarrow{20^\circ} 2 \text{C}_6\text{H}_5\text{B(Br)NMe}_2 \] | -    |
| \( \text{C}_6\text{H}_5\text{B(F)NMe}_2 \)  | 62/3     | 1.50581 | \[ 3\text{C}_6\text{H}_5\text{B(Cl)NMe}_2 + \text{SbF}_3 \xrightarrow{20^\circ} 3 \text{C}_6\text{H}_5\text{B(F)NMe}_2 \] | -    |
| \( \text{C}_6\text{H}_5\text{B(OMe)NMe}_2 \) | 60/6     | 1.49887 | \[ \text{C}_6\text{H}_5\text{B(Cl)NMe}_2 + \text{MeMgI} \xrightarrow{80^\circ} \text{benzene} \xrightarrow{\text{Reflux}} \text{C}_6\text{H}_5\text{B(MeNMe)}_2 \]  
+ \text{ClMgI}                                                                                                          | 10   |
| \( \text{C}_6\text{H}_5\text{B(OMe)NMe}_2 \) | 70/4.5   | 1.49661 | \[ \text{C}_6\text{H}_5\text{B(NMe)}_2 + \text{MeOH} \xrightarrow{\text{Reflux}} \text{C}_6\text{H}_5\text{B(OMe)NMe}_2 \]  
+ \text{Me}_2\text{NH}                                                                                                 | -    |
| \( \text{C}_6\text{H}_5\text{B(Cl)N(Me)Et} \)  | 82/0.2   | 1.52844 | \[ \text{C}_6\text{H}_5\text{BCl}_2 + \text{MeNHET} \xrightarrow{\text{Et}_3\text{N}} \text{C}_6\text{H}_5\text{B(Cl)N(Me)Et} \]  
+ \text{Et}_3\text{N} \cdot \text{HCl}                                                                                     | -    |
### VIII. APPENDIX Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^\circ$C</th>
<th>$^\circ$C/mm.</th>
<th>$^\nu_D$</th>
<th>Method of Synthesis</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_5B(Cl)(Me)Pr^I$</td>
<td>90/0.2</td>
<td>1.51932</td>
<td></td>
<td>$C_6H_5BCl_2 + MeNHPr^I \xrightarrow{Et_3N} C_6H_5B(Cl)(Me)Pr^I + Et_3N\cdot HCl$</td>
<td>-</td>
</tr>
<tr>
<td>$C_6H_5B(Cl)N(Me)C_6H_5$</td>
<td>102/0.2</td>
<td>1.58774</td>
<td></td>
<td>$C_6H_5BCl_2 + C_6H_5NHMe \xrightarrow{Et_3N} 2C_6H_5B(Cl)N(Me)C_6H_5 + Et_3N\cdot HCl$</td>
<td>10</td>
</tr>
<tr>
<td>$C_6H_5B(\text{Br})(Me)C_6H_5$</td>
<td>116/0.4</td>
<td>-</td>
<td></td>
<td>$C_6H_5BBBr_2 + C_6H_5(NMePh)_2 \xrightarrow{20^\circ} 2C_6H_5B(\text{Br})(Me)N(Me)Ph$</td>
<td>-</td>
</tr>
<tr>
<td>$C_6H_5B(NMePh)_2$</td>
<td>155/0.05</td>
<td>-</td>
<td></td>
<td>$C_6H_5BCl_2 + 4C_6H_5NHMe \rightarrow C_6H_5B(NMePh)_2 + 2C_6H_5NHMe\cdot HCl$</td>
<td>-</td>
</tr>
<tr>
<td>$C_6H_5B(Cl)OMe$</td>
<td>57/5</td>
<td>1.51110</td>
<td></td>
<td>$C_6H_5BCl_2 + C_6H_5B(OMe)_2 \rightarrow 2C_6H_5B(Cl)OMe$</td>
<td>20</td>
</tr>
<tr>
<td>$C_6H_5B(OMe)_2$</td>
<td>46/3</td>
<td>1.49599</td>
<td></td>
<td>$C_6H_5BCl_2 + 2MeOH \xrightarrow{-78^\circ} C_6H_5B(OMe)_2$</td>
<td>20</td>
</tr>
<tr>
<td>$C_6H_5P(\text{Cl})(NMe)_2$</td>
<td>80/0.1</td>
<td>1.57530</td>
<td></td>
<td>$C_6H_5PCl_2 + Me_2NH \xrightarrow{Et_3N} C_6H_5P(\text{Cl})(NMe)_2 + Et_3N\cdot HCl$</td>
<td>-</td>
</tr>
</tbody>
</table>
### VIII. Appendix Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^\circ$C/°E</th>
<th>$^2\text{H}$</th>
<th>Method of Synthesis</th>
</tr>
</thead>
</table>
| $\text{C}_6\text{H}_5\text{P(NMe}_2\text{)}_2$ | 58/0.1      | 1.54791     | $\text{C}_6\text{H}_5\text{POCl}_2 + 4\text{Me}_2\text{NH} \xrightarrow{-78^\circ} \text{C}_6\text{H}_5\text{P(NMe}_2\text{)}_2$
|                                  |             |             | $+ 2\text{Me}_2\text{NH.HCl}$                                                   |
| $\text{C}_6\text{H}_5\text{POCl}_{2}\text{Me}_2$ | 119/0.1     | 1.54402     | $\text{C}_6\text{H}_5\text{POCl}_2 + \text{Me}_2\text{NH} \xrightarrow{\text{Et}_3\text{N}} \text{C}_6\text{H}_5\text{POClNMe}_2$
|                                  |             |             | $+ \text{Et}_3\text{N.HCl}$                                                   |
| $\text{C}_6\text{H}_5\text{N(CH}_3\text{)}_2\text{N(CH}_3\text{)}\text{C}_6\text{H}_5$ | 138/1       | 1.61853     | $(\text{C}_6\text{H}_5\text{NH})_2 + 2\text{MeLi} \xrightarrow{\text{Me}_2\text{SO}_4} 2\text{CH}_4 + (\text{C}_6\text{H}_5\text{N(Li)}_2$
|                                  |             |             | $\xrightarrow{\text{Me}_2\text{SO}_4} (\text{C}_6\text{H}_5\text{NMe})_2$   |
| $\text{C}_6\text{H}_5\text{N(H)}\text{N(CH}_3\text{)}\text{C}_6\text{H}_5$ | m.p.63$^\circ$ | -           | $(\text{C}_6\text{H}_5\text{NH})_2 + \text{MeLi} \xrightarrow{\text{Me}_2\text{SO}_4} \text{CH}_4 + \text{C}_6\text{H}_5\text{N(H)}\text{N(Li)}\text{C}_6\text{H}_5$
|                                  |             |             | $\xrightarrow{\text{Me}_2\text{SO}_4} \text{C}_6\text{H}_5\text{N(H)}\text{N(Me)}\text{C}_6\text{H}_5$ |
IX. REFERENCES


IX. REFERENCES (CONT'D)

