Studies on the chemistry of boron subhalides

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:


Metadata Record: https://dspace.lboro.ac.uk/2134/33724

Publisher: © Margaret Susan Reason

Rights: This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at: https://creativecommons.org/licenses/by-nc-nd/4.0/

Please cite the published version.
STUDIES ON THE CHEMISTRY OF BORON SUBHALIDES

by

MARGARET SUSAN REASON, B.Sc.

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

December 1974


© by Margaret Susan Reason, 1974.
Acknowledgements

I wish to express my appreciation of all the help I have received, without which this thesis could never have been written. Primarily I wish to acknowledge the encouragement and guidance of Dr. A.G. Massey, Reader in Inorganic Chemistry, who supervised the research through all its stages of development. In addition I should also like to thank Dr. A.G. Briggs for his continual advice on aspects of spectroscopy.

I also wish to thank all the university technical staff, in particular Mr. L. Kumar, for the hundreds of mass spectra he successfully obtained, and Mr. M. Coupe, whose skill in glassblowing and ingenuity in the designing of equipment enabled this research to proceed much further than would otherwise have been possible. Thanks also to my industrial sponsors, Borax Consolidated Ltd., for their timely gift of quartz discharge cells, Mrs. Shirley Hirst for typing this thesis, and finally, but not least, Mr. L.R. Reason, for his patience during the course of the research and for all his work in drawing the diagrams and for editing the final thesis.
Publications

Some of the work in this thesis has been submitted for publication:

1. "On the Preparation of Diboron Tetrachloride";
   Journal of Inorganic and Nuclear Chemistry (in press)

2. "A Chlorine-Substituted Boro-Adamantane (BCl)₆(CH)₄";

3. "The Preparation of B₉Br₉ and Related Mixed Halides";
   submitted to Journal of Inorganic and Nuclear Chemistry

4. Paper number 83 by Margaret S. Gaunt, A.G. Briggs,
   J.D. Lee and A.G. Massey, at the Second International
   Meeting on Boron Chemistry, held at the University of

5. A brief summary of the known boron cluster systems
   was given in the article "Cage Compounds of Boron",
   by M.S. Gaunt and A.G. Massey, which appeared in
List of Diagrams

1. Some reactions of diboron tetrachloride
2. Structure of $B_8Cl_8$
3. Structure of $B_9Cl_9$
4. Structure of some boron hydrides
5. Structure of diborane
6. Energy level diagram of B-H-B bridge in diborane
7. Atomic orbital arrangements that constitute 3-centre bonds
8. The nido-carboranes formally related to $B_6H_{10}$
9. Idealised boron-cage structures found in $B_nH_{2n}^2$- ions
10. Rearrangement of $C_2B_{10}H_{12}$ carboranes
11. Schematic structure of $B_9C_2H_{11}^2$
12. Structures of $(\Pi-C_5H_5)Fe(\Pi-B_9C_2H_{11})$ and $Fe(\Pi-B_9C_2H_{11})_2$
13. Structure of $B_4Cl_4$
14. The high vacuum system
15. Typical apparatus
16. Comparison of the observed and theoretical intensities for the molecular ion in $B_9Cl_9$
17. Representation of the partial mass spectrum of $B_9Cl_9$
18. Representation of the partial mass spectrum of a mixture of boron cage subhalides
19. Apparatus used to obtain samples for laser Raman spectroscopy
20. Infra-red gas cell
21. lcm. quartz cells used to obtain electronic spectra
22. Silent electric discharge apparatus
23. Apparatus used in the preparation of dimethylamine
24. Passing of boron trichloride and boron tribromide through a microwave discharge
25. Passing of boron tribromide and carrier gas through a microwave discharge
26. Passing of boron tri-iodide vapour through a microwave discharge
27. Passing of boron tri-iodide vapour and carrier gas through a microwave discharge
28. Representation of the partial mass spectrum of the yellow boron trichloride impurity
29. Apparatus required for the preparation of diboron tetrachloride
30. Quartz discharge cell and mercury reservoir
31. Comparison of the observed and theoretical intensities for the molecular ion in $B_9Br_9$
32. Representation of the partial mass spectrum of $B_9Br_9$
33. Comparison of the infra-red spectra of $B_9Cl_9$ and $B_9Br_9$
34. Electronic spectrum of $B_9Br_9$ dissolved in boron tribromide
35. Comparison of the observed and theoretical intensities for the molecular ion $B_9Cl_7Br_2^+$
36. Representation of the partial mass spectrum of the products of the reaction between tin tetrachloride and $B_9Br_9$
37. Representation of the partial mass spectrum of a mixture of mixed boron cage subhalides
38. Some interconversion reactions of the boron subhalides

39. Comparison of the observed and theoretical intensities for the molecular ion in $(\text{BCl})_6\text{(CH)}_4$

40. The boro-adamantane structure

41. Apparatus used to obtain samples for n.m.r. analysis

42. Principle peaks in the Raman spectra of boro-adamantanes
List of Tables

1. Distances (in Å) between the atoms in diboron tetrachloride and boron trichloride 5
2. Some boron hydrides 14
3. Low temperature baths 43
4. The isomers of $\text{B}_2\text{Cl}_2^+$ 44
5. Natural abundances of the isotopes of boron and chlorine 44
6. Species detected in the partial mass spectrum of $\text{B}_9\text{Cl}_9$ 47
7. Assignment of metastable peaks 50
8. Species detected in the partial mass spectrum of a mixture of polymeric boron monochlorides 51
9. Summary of conditions used in the gas-liquid experiments 65
10. Some typical metal borides 95
11. Species detected in the partial mass spectrum of the boron trichloride impurities 100
12. Comparison between BCl band heads tabulated by Miescher and values obtained in this research 120
13. Summary of products obtained from different diboron tetrachloride decompositions 132
14. Principle structure factors of $\text{B}_9\text{Cl}_9$ 146
15. Reflections in order of increasing Ø 148
16. Observed powder lines of $\text{B}_9\text{Br}_9$ 150
17. Species detected in the partial mass spectrum of $\text{B}_9\text{Br}_9$ 152
18. Species detected in the partial mass spectrum of the products of the reaction between $\text{B}_9\text{Br}_9$ and tin tetrachloride 166

(viii)
19. Species detected in the partial mass spectrum of a mixture of mixed chloro-bromides

20. Infra-red and Raman peaks of $(\text{BCl})_6(\text{CH})_4$

21. Most intense peaks in the Raman spectra of the three boro-adamantanes
CONTENTS

Frontispiece (i)
Certificate of originality (iii)
Acknowledgements (iii)
Publications (iv)
List of diagrams (v)
List of tables (viii)
Contents (x)

1. Introduction. 1

2. Experimental 33
   2.1 Vacuum line 36
   2.2 Other handing techniques 38
   2.3 Apparatus used for reactions 39
   2.4 Low temperature baths 42
   2.5 Physical methods used for identification of samples 43
      2.5a Mass spectroscopy 43
      2.5b Raman spectroscopy 54
      2.5c Infra-red absorption spectroscopy 56
      2.5d Ultra violet and visible spectroscopy 57
      2.5e X-ray fluorescence 59
      2.5f X-ray diffraction 59
      2.5g X-ray powder photography 60
   2.6 Gas-liquid chromatography 60
   2.7 Fractional sublimation 69
2.8 Silent electric discharge
2.9 Preparation of starting materials
  2.9a Boron trichloride
  2.9b Boron tribromide
  2.9c Boron triiodide
  2.9d Boron trifluoride
  2.9e Dimethylamine
2.10 Solvents

3. Microwave discharge-induced reactions of the boron trihalides.

4. Attempts to prepare boron-cage compounds by the chlorination of boron carbide
   4.1 \(\beta\)-rhombohedral boron
   4.2 \(\alpha\)-rhombohedral boron
   4.3 Boron carbide
   4.4 \(\alpha\)-tetragonal boron
   4.5 Metal borides
   4.6 Other systems containing linked boron atoms
   4.7 Chlorination of boron carbide
   4.8 Infra-red spectroscopy
   4.9 X-ray fluorescence
   4.10 Mass spectroscopy
   4.11 Interpretation of results

5. Preparation of diboron tetrachloride and investigation into the reaction mechanism
   5.1 Electrical discharges between metal electrodes
5.2 Microwave discharges
5.3 Chemical methods
5.4 Cocondensation
5.5 Experimental procedure for the preparation of diboron tetrachloride
5.6 Identification of additional by-products
5.6a Mercurous chloride
5.6b $\text{B}_9\text{Cl}_9$ and $\text{B}_{10}\text{Cl}_{10}$
5.7 Mechanism of the reaction in the mercury discharge
5.8 Decomposition of diboron tetrachloride
5.9 Other boron subhalides
5.9a Boron subiodides
5.9b Boron subfluorides

6. Preparation and properties of $\text{B}_9\text{Br}_9$
6.1 X-ray powder diffraction
6.2 Mass spectrum
6.3 Infra-red spectrum
6.4 Ultra violet and visible spectrum
6.5 Raman spectrum
6.6 Handling properties
6.7 Solvents
6.8 Reactions of $\text{B}_9\text{Br}_9$
6.9 Chlorination reactions
6.9a Reaction between titanium tetrachloride and $\text{B}_9\text{Br}_9$
6.9b Reaction between tin tetrachloride and $\text{B}_9\text{Br}_9$
6.10 Fluorination reactions
6.10a Reaction between antimony trifluoride and \( \text{B}_9\text{Br}_9 \) 168
6.10b Reaction between titanium tetrafluoride and \( \text{B}_9\text{Br}_9 \) 169
6.11 Reaction between dimethylamine and \( \text{B}_9\text{Br}_9 \) 170
6.12 Attempts to produce hydrogen-containing neutral polyhedral boron compounds 172
6.12a Reaction between lithium aluminium hydride and \( \text{B}_9\text{Br}_9 \) 174
6.12b Reaction between tin tetramethyl and \( \text{B}_9\text{Br}_9 \) 175

7. Boron sub-bromides and related compounds 177
7.1 Fractional sublimation 182
7.2 Heat treatment 183
7.3 Partial hydrolysis 183
7.4 Thin layer chromatography 183
7.5 Gas-liquid chromatography 184
7.6 Preparation of mixed chloro-bromide cages from the mixed diboron tetrahalides 184
7.7 Preparation of chloro-bromide cages by halogen exchange reactions 188
7.7a Reaction between tin tetrachloride and the \( (\text{BBr})_n \) mixture 188
7.7b Reaction between aluminium bromide and the \( (\text{BCl})_n \) mixture 189
7.8 Stability of the \( \text{B}_9 \) cage 191
7.9 Reaction between disilicon hexabromide and diboron tetrabromide 194
7.10 Summary 197
8. A chlorine-substituted boro-adamantane 199
8.1 Preparation of 1,2-bis(dichloroboryl)-ethane 199
8.2 Decomposition of 1,2-bis(dichloroboryl)-ethane 200
8.3 Mass spectrum of the volatile solid 201
8.4 Structure of (BCl)_6(CH)_4 203
8.5 The Raman spectrum 206
8.6 The infra-red spectrum 207
8.7 The proton n.m.r. spectrum 209
8.8 Reactions of (BCl)_6(CH)_4 212
8.8a Reaction between (BCl)_6(CH)_4 and boron tribromide 212
8.8b Reaction between (BCl)_6(CH)_4 and tin tetramethyl 216
8.9 Summary 217

9. Conclusions 220
1. \textbf{INTRODUCTION}

This thesis is concerned with the chemistry of the boron subhalides. In these terms a boron subhalide is defined as a compound with a boron-to-halogen ratio of less than one to three. Clearly this definition includes the monohalides BF, BCl and BBr, and the (BX)$_n$ polymers, together with the diboron tetrahalides, in the subhalide class. The term "subhalide" is used to distinguish these compounds from the more widely known boron trihalides which exhibit the characteristic group valency of three.

A boron atom in the ground state has the electronic configuration $1s^22s^22p^1$. As expected for an element in the first short period of the periodic table, the B(I) state is unstable. Monovalent boron species such as BF, where the single p electron is involved in the bonding, are observed only at high temperatures or in electrical discharges. Under normal conditions, boron is trivalent, because the energy of formation of one bond in a BX compound is sufficiently less than the total energy released in the formation of three bonds in a BX$_3$ compound to permit the promotion of boron to a hybridised valence state of the sp$^2$ type. All monomeric, three covalent boron compounds, such as the trihalides, trialkyls or trialkoxides, have been found to be planar molecules, with B-X-B bond angles of 120°. These BX$_3$ compounds all contain an empty p orbital, which is available for further bonding. The trico-ordinate boron species therefore possess strong
electron acceptor properties, and tetraco-ordinate boron structures with approximately sp³ hybridisation are easily formed. In particular the boron trihalides all act as strong Lewis acids and form a wide variety of addition compounds. Some examples of donor-acceptor complexes formed are (CH₃)₃N BCl₃, CH₃CN BF₃ and (CH₃)₂O BF₃.

The boron-halogen bonds of the boron trihalides are susceptible to attack by compounds containing 'active' hydrogen. By using boron trichloride as the example, the following are typical reactions:

\[
3\text{H}_2\text{O} + \text{BCl}_3 \rightarrow \text{H}_3\text{BO}_3 + 3\text{HCl}
\]
\[
3\text{ROH} + \text{BCl}_3 \rightarrow \text{B(OR)}_3 + 3\text{HCl}
\]
\[
6(\text{CH}_3)_2\text{NH} + \text{BCl}_3 \rightarrow \text{B(N(CH}_3)_2}_3 + \text{N(CH}_3)_2\text{H}_2\text{Cl}.
\]

At room temperature, the mixing of any two of the boron halides- boron trifluoride, boron trichloride and boron tribromide, produces a rapid redistribution of the halogen atoms, which in turn gives rise to a mixture of the original pure halides and the mixed halides. Consequently the system may be considered to be in equilibrium, i.e.

\[
\text{BCl}_3 + \text{BBr}_3 \rightleftharpoons \text{BCl}_2\text{Br} + \text{BClBr}_2.
\]
Generally it is assumed that these redistributions take place via the transitory formation of dimers,

![Figure 1](image)

Cleavage of the dimer can take place along two paths, one of which results in the halogen exchange. So far no such dimers have been isolated, and the above equilibrium is so rapidly established that the mixed halides cannot be isolated and have only been detected spectroscopically.

Unlike boron, the halides of aluminium, gallium, indium and thallium tend to dimerise, by utilising lone pairs on the halogen atoms. The difference is thought to be due to a number of factors. One possibility is that the boron trihalides may be stabilised by \(\pi\)-bonding between filled p orbitals on the halogens and the vacant boron \(2p_z\) orbitals. With the heavier elements, d orbitals are available for bonding purposes, and it is possible that they use at least a small amount of d-character in the orbitals making up the dimers. An additional factor is the small size of the boron atom. There may be severe steric interactions which seriously hinder the formation of a four membered ring system involving two boron atoms and two halogen atoms.
Only a few compounds are known which contain simple 2-electron boron-boron bonds. They include all four diboron tetrahalides (where the boron-boron bond is extremely reactive), $B_2(NH_2)_4$, $B_2(NR)_2Cl$, and $B_2(OR)_4$.

The diboron tetrahalides are, in fact, the simplest boron derivatives that contain a direct boron-boron bond. The first compound of the series to be made was the tetrahalide, produced by Stock (1) in 1925. It was obtained by maintaining a continuous electric arc between zinc electrodes immersed in liquid boron trichloride. However, not until the work of H.L. Schlesinger (2) did the chemistry of diboron tetrachloride develop. He managed to improve the yield considerably by means of reduction in the gas phase, i.e.

$$2BCl_3 + 2Hg \xrightarrow{\text{mercury discharge}} Hg_2Cl_2 + B_2Cl_4.$$ 

Various techniques have been used to try to deduce the structure of diboron tetrachloride. One of these techniques, single crystal X-ray crystallography, has shown that in the solid state (ref. fig 2) the molecule adopts a planar structure (3)(4) whereas infra-red and Raman spectra have shown that in its liquid and gaseous states the BCl$_2$ groups are, in fact, mutually at right angles to each other (5) (ref. fig 3).
This change of configuration may be the result of a crystal lattice effect in the solid state as the barrier to rotation\(^{(5)}\) is only about 8 KJ. A similar planar shape in the solid state is also adopted by diboron tetrafluoride\(^{(6)}\), whereas in the gaseous state the molecule is again thought to be staggered\(^{(7)}\) or to undergo essentially free rotation\(^{(8)}\).

An examination of the B-Cl bonds in diboron tetrachloride shows that they are shorter than those found in tetraco-ordinate boron trichloride adducts, which suggests that a B-Cl \(\Pi\)-bonding interaction similar to the type found in the boron trihalides may occur. As for the B-B bond, this is somewhat longer than might be expected for a single bond \((1.64\text{\ Å})\).

### Table 1. Distances (in \(\text{Å}\)) between the atoms in diboron tetrachloride and boron trichloride.

<table>
<thead>
<tr>
<th></th>
<th>B(_2)Cl(_4)(^{(3)(4)})</th>
<th>BCl(_3)(^{(9)(10)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-B</td>
<td>1.75 ± 0.5</td>
<td>1.75</td>
</tr>
<tr>
<td>B-Cl</td>
<td>1.73 ± 0.2</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Extensive research into the chemistry of diboron...
tetrafluoride has shown that it has many of the expected properties of a boron chloride. Diagram 1 indicates some of the reactions of diboron tetrachloride.

Its chlorine atoms are very susceptible to hydrolysis, and on the addition of water to diboron tetrachloride at low temperatures, sub-boric acid is formed:\(^{(12)}\):

\[
B_2\text{Cl}_4 + \text{H}_2\text{O} \xrightarrow{0^\circ\text{C}} B_2(\text{OH})_4 + 4\text{HCl}.
\]

At higher temperatures, or with the addition of a solution of sodium hydroxide, the reaction proceeds further with the rupture of the boron-boron bond and the subsequent formation of hydrogen:\(^{(12)}\). Reactions with methyl and ethyl alcohol (almost quantitative at \(-78,5^\circ\)) produce the corresponding tetra-alkoxides:\(^{(13)}\):

\[
B_2\text{Cl}_4 + \text{CH}_3\text{OH} \xrightarrow{-78,5^\circ} B_2(\text{OCH}_3)_4 + 4\text{HCl}.
\]

Diboron tetrachloride can also be used to prepare the tetrafluoride and the tetrabromide. The action of antimony trifluoride on diboron tetrachloride causes complete fluoridation:\(^{(14)}\), which results in the formation of diboron tetrafluoride:

\[
4\text{SbF}_3 + 3B_2\text{Cl}_4 \rightarrow 3B_2\text{F}_4 + 4\text{SbCl}_3.
\]
1. SOME REACTIONS OF DIBORON TETRACHLORIDE

\[ \text{B}_2\text{H}_6 + \text{BCl}_3 \rightarrow \text{B}_4\text{Cl}_4 \]

\[ \Delta \text{MeOH} \rightarrow \text{B}_2\text{(OMe)}_4 \]

\[ \Delta \rightarrow \text{B}_2\text{(OH)}_4 \]

\[ \text{Na}_3\text{BO}_3 \rightarrow \text{NaOH} \]

\[ \text{C}_2\text{H}_4 \rightarrow \text{B}_2\text{Cl}_4 \]

\[ \text{H}_2 \rightarrow \text{B}_2\text{H}_6 \]

\[ \text{H}_2 \text{O} \rightarrow \text{B}_2\text{Cl}_4 \]

\[ \text{H}_2 \text{O}^0 \rightarrow \text{B}_2\text{(OH)}_4 \]

\[ \text{B}_{2n}(\text{CH}_3)_2 \rightarrow \text{B}_2\text{Cl}_4 \]

\[ \text{B}_{2(\text{OH})_4} \rightarrow \text{B}_2\text{(OH)}_4 \]

\[ \text{BO} \rightarrow \text{B}_2\text{(OH)}_4 \]

\[ \text{B}_2\text{Cl}_4 \rightarrow \text{B}_{2(\text{OH})_4} \]

\[ \text{B}_2\text{Cl}_4 \rightarrow \text{B}_2\text{(OMe)}_4 \]
Bromination can be carried out by the action of boron tribromide on diboron tetrachloride for about 30 minutes at room temperature (13):

\[ 3 \text{B}_2\text{Cl}_4 + 4 \text{BBr}_3 \rightarrow 3 \text{B}_2\text{Br}_4 + 4 \text{BCl}_3. \]

An interesting reaction of diboron tetrachloride is the formation of 1:1 adducts with unsaturated hydrocarbons. With ethylene(15), for example, where the reaction is quantitative at -78.5°C overnight, the product was shown no longer to contain the direct boron-boron bond, the two boron atoms now being bridged by the \(-\text{CH}_2-\text{CH}_2-\) group from the ethylene molecule in the manner

\[
\begin{array}{c}
\text{Cl} \\
\text{B} - \text{CH}_2 - \text{CH}_2 - \text{B} \\
\text{Cl}
\end{array}
\]

Figure 4

X-ray diffraction studies on single crystals have shown the B-C-C-B backbone to be bent(16), with the B-C-C angles giving a planar, trans, configuration.

As far back as 1925, Stock(1) had noted the thermal instability of diboron tetrachloride, but he had erroneously suggested that the products were simply boron trichloride and boron:

\[ 3 \text{B}_2\text{Cl}_4 \rightarrow 4 \text{BCl}_3 + 2 \text{B}. \]
However, after being studied over the last two decades in several laboratories, it is now known that the decomposition is much more complex than this. Firstly, Schesinger\(^{13}\) discovered that at temperatures above 0\(^0\), diboron tetrachloride decomposes to produce boron trichloride, an additional slightly volatile highly coloured material (containing yellow, purple and red components), and a non-volatile white solid. Maximum yields of this dark purple material can be obtained when diboron tetrachloride is allowed to decompose over a period of three days at temperatures around 80\(^0\); whereas lower temperatures give a larger proportion of the red glassy material.

This volatile solid material has been found to consist of polymeric boron subchlorides, all of which have the empirical formula \((BCl)_n\). The major component is a dark red solid, which sublimes at 110\(^0\) in vacuo. Urry and Schram\(^{17}\) have described conventional analyses and molecular weight determinations on this glassy red solid and suggest that it has the formula \(B_{12}Cl_{11}\), but later work has since shown the material to be a mixture of \(B_nCl_n\) derivatives \((n = 10-12)\). A sample of the solid \("B_{12}Cl_{11}\"\) produced by Urry was sent to Lipscomb for X-ray examination. After recrystallisation from boron trichloride, a crystal was selected, which on examination was found\(^{18}\) to be \(B_8Cl_8\). This molecule has a closed cage (or cluster) of boron atoms, containing...
the eight boron atoms in the shape of a dodecahedron, with a single terminal chlorine atom attached to each boron atom (See diagram 2).

It is now known (19)(20) that the slightly volatile yellow and purple material described by Urpy(21) consists of a mixture of $B_8Cl_8$ and $B_9Cl_9$. The $B_9Cl_9$ has also been shown (22) to have the typical boron cage structure (in this case a tricapped trigonal prism; see diagram 3).

Perhaps the most unusual property of all these monochlorides is their colour - for almost all other boron compounds are colourless. This suggested to other researches in the field the possibility of the chlorides being paramagnetic. Indeed $B_8Cl_8$, for example, has had its e.s.r. spectrum recorded and published (21); although at that time the research workers did not know its identity. Since $B_8Cl_8$ is now known (19) to be diamagnetic, only exhibiting an e.s.r. spectrum when traces of water are added to a solution of $B_8Cl_8$, it demonstrates how extremely sensitive these compounds are to water.

This tendency to form structures containing clusters of boron atoms is also exhibited in elemental boron and boron carbide as well as in many metal borides and boron hydrides. Apart from carbon, boron forms
2. STRUCTURE OF $\text{BgCl}_3$

3. STRUCTURE OF $\text{BgCl}_9$
more known, volatile hydrides than any other element, and most of them can be considered as fragments of an icosahedron. The bonding in these molecules, while being common in boron chemistry, is uncommon elsewhere, and as such leads to unusual nomenclature problems. Consequently in this thesis, although many of the compounds can be regarded as derivatives of the boranes, formulae or trivial names will often be used in preference to the more bulky systematic nomenclature, since the structures are usually clear from the context.

The accepted rules for naming boron compounds are those proposed by the Nomenclature Committee of the Division of Inorganic Chemistry of the American Chemical Society\(^{(23)}\); the following points summarise the procedure used in naming boron compounds:

(i) the number of boron atoms in the molecule is indicated by an appropriate numerical suffix;

(ii) the number of hydrogen atoms is shown in brackets following the name;

(iii) for molecules where ambiguities would otherwise arise, a uniform system for numbering atoms of the boron hydride structures has been devised;

(iv) closed-cage and open-cage systems are designated by the prefixes \textit{cose} and \textit{nido} respectively;
(vi)ions are given the ending -borate and the charge is enclosed in brackets;

(vi)compounds containing substituent atoms either attached to the boron atoms or replacing the skeletal boron atoms are named as for the parent unsubstituted borane.

Examples are given below:

\[
\begin{align*}
B_2H_6 & \quad \text{diborane(6)} \\
B_2(OCH_3)_4 & \quad \text{tetramethoxydiborane(4)} \\
Cl_2BCH_3 & \quad \text{dichloromethylborane} \\
B_{10}H_{14} & \quad \text{nido - decaborane(14)} \\
B_4Cl_4 & \quad \text{tetrachloro-closo-tetraborane(4)} \\
B_9Cl_9 & \quad \text{nonachloro-closo-nonaborane(9)} \\
B_5C_2H_7 & \quad \text{dicarba-closo-heptaborane(7)} \\
Na_2[B_{10}H_{10}] & \quad \text{sodium decahydro-closo-decaborate(2-)}
\end{align*}
\]

This nomenclature system permits the continued use of commonly-used trivial names for binary compounds such as BCl\textsubscript{3} (boron trichloride) and the diboron tetrahalides [B\textsubscript{2}Cl\textsubscript{4} is properly named tetrachlorodiborane(4)].

Unlike the boron halides, there is no simple boron trihydride, and the borane unit is only stabilised by a suitable donor as in (CH\textsubscript{3})\textsubscript{3}PBH\textsubscript{3}; the directly hydrogenated counterpart of diboron tetrachloride is also unknown except as an adduct with triphenylboron phosphine.
Attempts to hydrogenate diboron tetrachloride with lithium borohydride, for example, led to the formation of tetraborane(10) and diborane(6):

$$4 \text{LiBH}_4 + \text{B}_{2}\text{Cl}_4 \rightarrow 4 \text{LiCl} + \text{B}_2\text{H}_6 + \text{B}_4\text{H}_{10}.$$ 

Diborane(6) is the simplest member of the complex array of boron hydrides. The pioneering work in this field was undertaken by Alfred Stock and his collaborators. They were attempting to prepare boron hydrides similar to the carbon-hydrogen homologous series. After Stock finished working on the boron hydrides in 1932, no more were discovered until 1957 when nonaborane(15) was isolated. Some of the boron hydrides are shown in Table 2.

**Table 2. Some Boron Hydrides**

<table>
<thead>
<tr>
<th>Boron hydrides identified by Stock</th>
<th>Modern discoveries</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{B}_2\text{H}_6)</td>
<td>(\text{B}<em>6\text{H}</em>{12})</td>
</tr>
<tr>
<td>(\text{B}<em>4\text{H}</em>{10})</td>
<td>(\text{B}<em>8\text{H}</em>{12})</td>
</tr>
<tr>
<td>(\text{B}_5\text{H}_9)</td>
<td>(\text{B}<em>8\text{H}</em>{18})</td>
</tr>
<tr>
<td>(\text{B}<em>5\text{H}</em>{11})</td>
<td>(\text{B}<em>9\text{H}</em>{15})</td>
</tr>
<tr>
<td>(\text{B}<em>6\text{H}</em>{10})</td>
<td>iso-(\text{B}<em>9\text{H}</em>{15})</td>
</tr>
<tr>
<td>(\text{B}<em>{10}\text{H}</em>{14})</td>
<td>(\text{B}<em>{10}\text{H}</em>{16})</td>
</tr>
<tr>
<td></td>
<td>(\text{B}<em>{18}\text{H}</em>{22})</td>
</tr>
<tr>
<td></td>
<td>iso-(\text{B}<em>{18}\text{H}</em>{22})</td>
</tr>
<tr>
<td></td>
<td>(\text{B}<em>{20}\text{H}</em>{16})</td>
</tr>
</tbody>
</table>
The structures of some of these compounds are shown in diagram 4.

Many innovations in the design of laboratory equipment were needed by Stock to handle and separate the boranes, since many of them burst spontaneously into flame in the air, as well as attacking tap grease. Most of the boranes are volatile at room temperature, so that Stock was able to overcome many of his problems by developing a design of glass vacuum apparatus, in which conventional greased glass stop-cocks were replaced by mercury float valves.

Diborane(6) has been shown to have the bridged structure (see diagram 5). There are only twelve valency electrons in diborane (three per boron and one per hydrogen), so that the bonding in the molecule cannot be described in terms of simple electron pair bonds, which would require sixteen electrons for the type shown (ref. diagram 5). Such molecules, with insufficient electrons to form 2-centre electron pair bonds between all the atoms, are termed "electron deficient".

From the evidence of bond lengths and bond angles, the terminal boron-hydrogen bonds in diborane seem to be normal single bonds. This leaves the bridging hydrogen atoms and four electrons to be fitted into the picture. The solution to the problem was first put
5. Diborane

\[ \text{Diborane} \]

\[ \text{D}(s^3) \] \[ \text{H}(1s) \]

\[ \text{Antibonding} \]

\[ \text{Nonbonding} \]

\[ \text{Pair of Three-Centre Bonds} \]

6. Energy Level Diagram of D-H-D Bridge in Diborane

Central 3-Centre

Open 3-Centre

B-H-B Bridge

7. Atomic Orbital Arrangements That Constitute Three-Centre Bonds
forward by Longuet-Higgins in 1949 (25). This is the 3-centre 2-electron bond. If the boron atoms form sp\(^3\) hybrid orbitals, the remaining orbitals may overlap with the 1s orbitals of the bridging hydrogen atoms. These three atomic orbitals produce three molecular orbitals - one bonding, one non-bonding and one antibonding. The two electrons available in each boron-hydrogen-boron bridge fill up the bonding orbital, leaving the other two molecular orbitals empty. The energy level diagram for the pair of three-centre bonds in diborane is shown in diagram 6.

As with diborane, it is impossible to describe the higher boranes in terms of two-centre electron pair bonds. Lipscomb (26) developed a theory of the "three-centre bond" applying to the larger molecules, thus postulating three idealised types to predict the distribution of charge (ref. diagram 7). These are the B-H-B bridge (as described for diborane) and two types of B-B-B three centre bonds termed "closed" (or "central") and "open". The boron atoms involved are normally considered sp\(^2\) or sp\(^3\) hybridised as the geometry of the system demands. This theory only gives unique solutions to fairly simple molecules such as tetraborane(10); larger molecules have to be described in terms of resonance structures. Lipscomb has used three-centre resonance structures to give some indications of the likely existence of other as yet unknown boranes.
In the past few years it has proved possible to substitute some of the boron atoms in the boron hydrides by carbon to give a new class of compound, the nido-carboranes ("Nido" is Latin for "nest"). These compounds form open, nest-like structures; the nomenclature distinguishes them from the closo-carboranes, in which boron and carbon atoms cluster together in the form of closed cages. Diagram 8 shows some nido-carboranes based on the hexaborane(10) structure. It will be noticed that no carbon atom participates in hydrogen bridging.

The majority of the known boron hydrides resemble fragments of a regular icosahedron, which is an apolyhedron with twelve vertices and twenty triangular faces; thus decaborane(14), disregarding the hydrogen atoms, may be considered as a slightly distorted icosahedron with two apices missing, and similarly the boron atoms in hexaborane(10) form the base of an icosahedron. Other "icosahedral fragments" among the neutral boranes include $B_{5}H_{11}$, $B_{6}H_{12}$, $B_{8}H_{12}$, and $B_{9}H_{15}$ ($B_{5}H_{9}$ with square pyramidal geometry, is an exception). The icosahedron also occurs as a structural unit in all allotropes of elemental boron, in boron carbide ($B_{12}C_{3}$), and in several metal borides.

The icosahedron of boron atoms seems to be exceptionally stable. Each boron atom has five nearest neighbours in the icosahedron, quite apart from the
THE NIDO CARBORANES FORMALY RELATED TO $B_6H_{10}$

$B_6H_{10}$

$CB_5H_9$

$C_2B_4H_8$

$C_3B_3H_7$

$C_4B_2H_6$

- Boron Atom
- Carbon Atom
- Bridging Hydrogen Atom
- Terminal Hydrogen Atom
external atom to which it is usually bonded, so that it is impossible to interpret the structure in terms of the ordinary rules of covalency. In 1935, Roberts and Longuet-Higgins (27) suggested from group theoretical arguments that only thirteen molecular orbitals could be considered responsible for holding an icosahedral \( B_{12} \) cage together. There are sufficient electrons available in elemental boron and borides to allow these bonding orbitals to be filled, whereas a discrete molecule such as \( B_{12}H_{12} \) lacks two electrons to fill the thirteenth orbital. Because of this, Roberts and Longuet-Higgins considered that \( B_{12}H_{12} \) would probably be unstable, whereas, they pointed out, the ion \( B_{12}H_{12}^{2-} \) would have all the cage bonding orbitals full, and hence be capable of synthesis.

Their first prediction seems to be correct, since decaborane(14) and diborane(6), when heated together at \( 100^\circ \), lose about four moles of hydrogen and produce an unstable, yellow solid, \((BH)_{12}\):

\[
\text{B}_{10}\text{H}_{14} + \text{B}_{2}\text{H}_{6} \rightarrow 4\text{H}_{2} + (\text{BH})_{12}.
\]

On the other hand, if diborane is added to decaborane(14) in the form of its trimethylamine-borane complex \( \text{Et}_{3}\text{N BH}_{3} \), a different reaction occurs to produce an ionic solid (28):

\[
\text{B}_{10}\text{H}_{14} + 2 \text{Et}_{3}\text{N BH}_{3} \rightarrow [\text{Et}_{3}\text{NH}^+]_{2} \text{B}_{12}^{2-}\text{H}_{12}.
\]
The $^{11}$ nuclear magnetic resonance spectrum of the product consisted of a simple doublet, showing that all the boron atoms were (probably) equivalent, and that each carried a single terminal hydrogen, which caused the doublet splitting of the boron resonance. This suggested that the $\text{B}_{12}^{12-}$ ion contained an icosahedron of boron atoms, a fact later verified by X-ray crystallography\(^{(29)}\). In agreement with the proposal made by Roberts and Longuet-Higgins, this ion is exceptionally stable both thermally and towards a wide variety of chemical reagents.

It is now known that the icosahedral cage is not the only type of boron cluster capable of existence; all the cage ions in the series $\text{B}_n \text{H}_{2n}^{2-}$ ($n = 6-12$), have been prepared and shown to possess high thermal stability (ref. diagram 9).

Although the cage $\text{B}_n \text{H}_{2n}^{2-}$ ions are relatively inert (for example, towards strong bases), the hydrogens may be substituted\(^{(50)}\) by treatment with the free halogens in either aqueous or alcoholic solutions;

\[
\text{e.g. } \text{B}_{10} \text{H}_{14} + 2 \text{N(C}_2\text{H}_5\text{)}_3 \rightarrow [\text{N(C}_2\text{H}_5\text{)}_3\text{H}^+]_2 \text{B}_{10} \text{H}_{2-} \text{Cl}_2 \rightarrow \text{B}_{10} \text{Cl}_{10}^{2-}
\]

Ion exchange experiments produce the free acids such as $(\text{H}_3\text{O})_2 \text{B}_{10} \text{H}_{10}$ and $(\text{H}_3\text{O})_2 \text{B}_{12} \text{H}_{12}$, which are almost as strong as sulphuric acid. A wide variety of metal salts have been made either by neutralising these acids or by
9. Idealised Boron-Cage Structures Found in $B_nH_{n-2}$ Ions

1. Tetrahedron
2. Trigonal Bipyramid
3. Octahedron
4. Pentagonal Bipyramid
5. Dodecahedron
6. Symmetrically Tricapped Square Antiprism
7. Hexadecahedron
8. Icosahedron
precipitation reactions:

\[ \text{e.g. } B_{10}^{2-} + CuCl_2 \longrightarrow Cu^2_2 B_{10}^{2-} \]

In all these cage compounds, it appears that there is one more cage bonding orbital than the number of boron atoms constituting the cage, hence the two negative charges required by the ions for stability. A carbon atom possess one electron more than boron, hence if two carbon atoms could be inserted into the cages, the extra two electrons required to fill the \((n + 1)^{th}\) bonding orbital would be available to give the entity a "closed shell" electronic configuration. Decaborane(14) lacks just two atoms required to complete an icosahedral cage; an obvious method by which to add two carbon atoms is to treat it with acetylene:

\[ B_{10}^{2-} + C_2H_2 \longrightarrow B_{10}^{2-} C_2H_2 \]

The product, a discrete, uncharged molecule, is called a "carborane" for the simple reason that it contains both carbon and boron atoms in the cage. The other \(B_{10}^{2-}\) ions besides \(B_{12}^{2-}\) have their isoelectronic carborane analogues, and the series \(B_{10}^{2-}C_{2n+2}\) now extends \((31)\) from \(n = 3\) (i.e. a five-membered cage) up to \(n = 10\).

In these carboranes the possibility of isomers arises due to the relative positions taken up by the
carbon atoms in the cages. It has been deduced from a study of such isomers that, for a given cage size, the carborane isomer having the highest stability is that in which the two carbons have the least number of neighbouring atoms, and are as far away from each other as possible. This can be illustrated by reference to the dicarba-closo-dodecaboranes (commonly known as the carboranes, see diagram 10). The isomer arising directly from the reaction of decaborane(14) with acetylene has the carbon atoms next to each other in the 1,2 positions. Heating the 1,2-carborane ("orthocarborane") to about 500°C causes it to change to the 1,7-isomer ("metacarborane") in very high yield; the most stable isomer, 1,12-B_{10}C_{2}H_{12} ("paracarborane") results when 1,7-B_{10}C_{2}H_{12} is held at 700°C, and has the carbons as far apart as possible.

Now that the principle of substituting some of the boron atoms in the clusters has been demonstrated, the question naturally arises as to whether carbon is unique in this respect. In fact, an enormous number of polyhedral boranes containing atoms other than boron and carbon in the cage have been synthesised. The first discoveries in this field involved only transition metals, but recently it has been extended to include several non-transition metals as well.

Investigations into the possibility of including
10. REARRANGEMENT OF C₂B₁₀H₁₂ CARBORANES

Ortho- or 1,2 - Carborane  Meta- or 1,7 - Carborane  Para- or 1,12 - Carborane (Most Stable Isomer)

11. SCHEMATIC STRUCTURE OF B₉C₂H₁₁⁻²

12. STRUCTURES OF (π-C₅H₅)Fe(π-B₉C₂H₁₁) & Fe(π-B₉C₂H₁₁)⁻¹
transition metals in polyhedral boranes were stimulated by the discovery of the "dicarbolide" ion $B_9C_2H_{11}^{2-}$ (ref. diagram 11). This ion is made by nucleophilic attack on orthocarborane by methoxide ions:

$$B_{10}C_2H_{12} + OCH_3^- \rightarrow B_9C_2H_{12}^- + B(OCH_3)_3,$$

followed by reaction with sodium hydride (32):

$$Na^+B_9C_2H_{12}^- + NaH \rightarrow Na_2B_9C_2H_{11} + H_2.$$ 

The dicarbolide ion contains an open pentagonal face, which is isoelectronic with the cyclopentadienide ion. Recognising this, Hawthorne and his co-workers examined (32)(33) the intriguing possibility that the dicarbolide ion might co-ordinate to transition metals containing partly filled d-shells, to form sandwich compounds analogous to ferrocene and other metallocenes. In a remarkable discovery which has enormously broadened the scope of boron chemistry, these workers prepared the ferrocene analogues

$$[\Pi-(3)-1,2-C_2B_9H_{11}]_2Fe^- \text{ and } (\Pi-(3)-1,2-C_2B_9H_{11})Fe(\Pi-C_5H_5),$$

followed by a wide variety of similar complexes involving many transition metals (ref. diagram 12). This type of compound is known as a "metallocarborane".

Similarly some non-metals have been incorporated into icosahedral molecules (34). For example, the phosphorus derivative $B_{10}CPH_{11}$ (isoelectronic with $B_{10}C_2H_{12}$)
has been prepared by heating phosphorus trichloride with the dicarboalloide anion $B_{10}C\,H_{11}^{2-}$:

$$Na_2B_{10}C\,H_{11} + PCl_3 \rightarrow B_{10}C\,H_{11}P$$ also for As and Sb.

The possibility of exchanging atoms of a carborane for members of Group IV other than carbon has been examined, and derivatives such as $B_{10}C\,H_{11}(GeCH_3)$, $B_9C_2H_{11}Sn$ and $B_9C_2H_{11}Pb$ have been isolated in the "icosahedral series".

Hawthorne (33) has developed another method of inserting metal atoms into polyhedral boranes which he terms "polyhedral expansion". He investigated the reactions which the polyhedral carboranes $B_6C_2H_8$, $B_8C_2H_{10}$ and $B_{10}C_2H_{12}$ undergo with transition metal derivatives following the initial addition of electrons to the neutral carboranes. Polyhedral metallocarborane derivatives were discovered amongst the products of this type of reaction, with the overall geometry of the next highest homologue of the polyhedral series.

The overall sequence is as follows:

$$B_nC_2H_{n+2} + 2e^- \rightarrow B_nC_2H_{n+2}^{2-}$$

$$B_nC_2H_{n+2}^{2-} + Co^{2+} + C_5H_5^- \rightarrow (B_nC_2H_{n+2})Co(C_5H_5)^-$$

oxidise

$$(B_nC_2H_{n+2})Co(C_5H_5).$$

28.
As molecules containing as many as two and three metal atoms\(^{(35)}\) have been isolated from the products of this reaction, it seems as if this sequence can be repeated starting with the product of the above reaction. The most notable success of the polyhedral expansion reaction has been the preparation of the previously unknown thirteen\(^{(36)}\)- and fourteen\(^{(37)}\)-vertex metallocarboranes from icosahedral carborane.

The polyhedral \(B_nH_n^{2-}\) ions and the \(C_2B_nH_{n+2}\) carboranes clearly contain two electrons per molecule more than the corresponding neutral polymeric boron monohalides \((BCl)_n\). Neutral \((BH)_n\) compounds are not stable, but the boron-chlorine cages withstand the addition of electrons since the \([B_{10}Cl_{10}]^{2-}\) ion can readily be obtained by treating the polyhedral \([B_{10}H_{10}]^{2-}\) ion with chlorine\(^{(30)}\). However on pyrolysis of \([H_2O]_2 [B_{10}Cl_{10}]\), one of the products was found\(^{(38)}\) to be \(B_9Cl_8H\), a neutral cage compound. One of the intermediates produced on hydrolysis of this volatile orange-red crystalline compound was claimed to be the dianion \([B_9Cl_8H]^{2-}\), which was isolated from the hydrolysis reaction by precipitation with a large cation. There have been no other reports of interconversion reactions between the borohydride ions and the neutral polyhedral boron subhalides.

Most of the polyhedral boron halides are highly
coloured, and, despite being thermally stable, the boron cages readily break down when exposed to moist air. Their appearance contrasts with the colourless polyhedral boron hydride ions and carboranes. Some of the latter are very stable units, being resistant to both boiling acid and boiling alkali.

It therefore appears that the loss of two bonding electrons from the electron configuration of the polyhedral frameworks of the borohydride ions and 2-carbon carboranes renders the corresponding boron halides comparatively unstable. The degree to which the halogen atoms participate in any detail except for the case of $\text{B}_4\text{Cl}_4$. This molecule was one of the first molecular polyhedra to be isolated, and no four-membered polyhedral borohydride ions or carboranes have yet been synthesised. The bonding of $\text{B}_4\text{Cl}_4$ was discussed by Longuet-Higgins (39), who showed that the molecule could not exist without electron donation from the chlorine atoms to the boron cage. He considered the six edges of the $\text{B}_4$ tetrahedron (see diagram 13) as being electron pair bonds, yet each boron atom can produce only two electrons to enter this bonding system. However, there are combinations of the 3p lone pair electrons on the chlorine atoms with the same symmetry as the unfilled molecular orbitals on the boron cage. The "back co-ordination" from the chlorine atoms into the $\text{B}_4$ tetrahedron is allowed. Evidence for B-Cl TI-bonding has also been deduced from the
13 STRUCTURE OF $\text{B}_4\text{Cl}_4$
photoelectron spectrum of $\text{B}_4\text{Cl}_4$. No such interaction could occur with hydrogen substituents, and all attempts to prepare $\text{B}_4\text{H}_4^{2-}$ and $\text{B}_2\text{C}_2\text{H}_4$ have failed. Other research workers\(^{(41)}\) have also discussed the electronic structure of $\text{B}_4\text{Cl}_4$, and suggest that both $\text{B}_4\text{F}_4$ and $\text{B}_4\text{O}_4^{4-}$ might be unstable.

Although the series of polyhedral boron halides is extensive, there is no similar series of compounds among the boron halides to the many open-cage boron hydrides. This may be due to the inability of the halogen atoms to bridge two boron atoms. A similar explanation was put forward earlier in this introduction to account for the non-existence of boron halide dimers.
2. EXPERIMENTAL
2. EXPERIMENTAL

As the boron halides are air-sensitive, they must be handled in anaerobic conditions. The manipulation of the volatile reagents and products was carried out using either a high vacuum line or a dry box, and the majority of the reactions were undertaken using individually-produced glass breakseal vessels similar to the type shown in diagram 15. Because of the reactivity and sensitivity to traces of water of the boron halides, it was decided to use no quantitative techniques to measure either the reagents or the reaction products. The normal method adopted for the analysis of the boron subchlorides was that of mass spectrometry. These compounds are stable in the mass spectrometer and are reluctant to transform into other boron-chlorine species even at high temperatures. An added advantage of this technique is that it enables the positive identification of the various molecular ions to be made, since both boron and chlorine possess two isotopes. The mass spectrum of a particular boron-chlorine species therefore gives a characteristic pattern which can be compared with calculated values to give the desired identification.

Analyses have also been performed using spectral methods (infra-red, ultra-violet and Raman spectrometry). An advantage of these techniques is that samples are often recoverable. Liquids and condensible gases were
occasionally identified by comparing the data obtained from the infra-red absorption spectrum of their vapour, or from their vapour pressure at a given temperature with tabulated values. Involatile solid products were never separated and rarely analysed; however two X-ray techniques (X-ray powder diffraction and X-ray fluorescence) were used to identify certain solids.

The technique of X-ray powder diffraction is used in the analysis of polycrystalline materials since the diffraction pattern given by each substance is unique, being determined by the spacing between the layers of atoms in the crystal. If the positions and intensities of the Bragg reflections can be determined, then this information can be checked against the data on about 5,000 compounds given in the A.S.T.M. index (American Society on Testing Materials), and an identification effected.

The X-ray fluorescent effect is produced when atoms irradiated with short wavelength X-rays emit their own characteristic radiation. As the wavelength of the fluorescent radiation is characteristic of the sample, this enables the identification of constituent elements to be made. Fluorescence is most marked in elements in the middle of the periodic table; the lighter elements do not produce this effect.

Chemical analytical methods and isopiestic
molecular weight measurements were not used because other research workers have found them to give results now known to be misleading. The major problem has been the sensitivity of the subchlorides to traces of water; any slight hydrolysis occurring during preliminary handling would lead to the loss of hydrogen chloride and a consequent error in the amount of chlorine determined. Results obtained following such conventional analyses led Urry to conclude (13) that the volatile subhalides produced during the thermal decomposition of diboron tetrachloride could be represented by the formula \((\text{BCl}_4\cdot 0.9)_x\). Partial hydrolysis of the boron subchlorides would also lead to errors in the isopiestic determination of molecular weights since the consequent formation of insoluble hydrolysed species would have the effect of increasing the apparent molecular weight. In fact Urry claimed (22) that a dark purple crystalline substance isolated from the diboron tetrachloride thermal decomposition products, which from its description is now thought to have consisted of \(\text{B}_8\text{Cl}_8\) (molecular weight = 370) had a molecular weight in the range from 650 to 750.

The ability of the boron-boron bonds in the boron subhalides to withstand total degradation during hydrolysis reactions presents additional problems in attempts to perform accurate analyses. Even diboron tetrachloride has to be heated at 160° in the presence of water before all boron-boron bonds are broken. It
should also be noted that determinations of boron are complicated by the possibility of leaching from borosilicate glass containers. Corrections to allow for this tend to be rather inaccurate.

2.1 Vacuum Line

During the course of this research, the design of the vacuum line was frequently altered, although for most of the time it consisted of the system shown in diagram 14. This comprised three sections:

(i) The system used for the preparation of diboron tetrachloride (see Chapter 5),

(ii) Various insertion points for introducing or removing material from the line without it losing vacuum or allowing the materials to come into contact with the air,

(iii) A fractionating train of three U-traps.

Evacuation was achieved by means of a triple stage mercury diffusion pump backed by a rotary oil pump. A Tesla coil was used to estimate the vacuum and to test for leaks. This instrumentation showed that the system achieved a vacuum better than approximately $10^{-4}$ mm mercury (the pressure at which the discharge induced by the Tesla coil begins to fade, giving "black" vacuum).

One of the most important requirements of a high vacuum line is the ability to separate mixtures with
14. THE HIGH VACUUM SYSTEM

- Air Inlet
- Mercury Diffusion Pump
- Cold Trap
- Emergency Glass Bulb
- Oil Pump
- Manometer
- U Traps (see insert)
- Insertion Point
- Insertion Points
- Mercury Diffusion Pump
- Silica Cell (refdiag 30)
components which are volatile at room temperature. The fractionating train of three U-traps connected in series, each in turn being capable of isolation from the others, was used to carry out this function. Separation was achieved by fractionally condensing the mixture through the series of U-traps each cooled to a successively lower temperature. Judicious selection of the temperatures (maintained by cold baths) determines the efficiency of the separation. Further explanation of the choice of cold baths used is given later on in this chapter.

The very reactive boron halides used in this work readily attack the grease normally used for lubricating taps, consequently the fractionating train was fitted with greaseless taps (supplied by Fischer-Porter). Each of these taps consists of a glass barrel with a threaded P.T.F.E. plunger.

The various insertion points consisted of B1/4 sockets attached to a greased high vacuum tap (hmm). Two of these systems were joined closely to the main vacuum line, and a third to a height of more than one metre from the bench surface in order to allow the introduction of large reaction vessels.

2.2 Other Handling Techniques

A dry-box and a polythene glove bag were
occasionally used to handle the boron subhalides. However, sufficiently dry conditions could not be produced to handle boron halides for any length of time without their complete hydrolysis (despite circulating the "dry-box gases" through columns containing molecular sieves and phosphorus pentoxide, and the thorough flushing of the polythene glove bag with "white spot" nitrogen).

2.3 Apparatus Used for Reactions

As the boron subhalides tend to be air and moisture sensitive, and react with tap grease, any reactions can best be carried out in all glass, or glass and P.T.F.E. systems.

For convenience the reactions studied in this research can be divided into two main groups:

(i) Reactions in which all reagents and products were volatile at room temperature,

(ii) Reactions in which either a reagent and/or a product was a volatile solid.

The first group of reactions was carried out in one of the U-traps on the vacuum line; whereas the second required the use of glass breakseal systems.

Diagram 15a illustrates the type of vessel used
15. TYPICAL APPARATUS

(a) [Diagram showing B and A]

(b) [Diagram showing X and A]

(c) [Diagram showing B and A]

(d) [Diagram showing Copper Tube, Glass, Thermometer, and Aluminium Block]

(e) [Diagram showing G, E, F, and B]

(f) [Diagram showing Glass U tube, Dewar, Coolant, Detector, and Chromatograph]
for reactions of the second type, in which the reagents were either volatile at room temperature or where a solid reagent was air stable. The tube has two limbs - A and B. A contains a Bl4 cone (to match the Bl4 socket on the vacuum line) and a constriction. This latter was positioned in the area where the tube was to be sealed off to help prevent the production of leakages during the sealing off process. B contains a completely airtight breakseal, yet could be broken to allow access into the vessel. Using this design another glass system could be added above the breakseal so permitting the removal of any volatile products and the transfer of volatile solids into the new system, without the latter coming into contact with the atmosphere or the tap grease (ref. diagram 15b).

If one of the reagents in the experiment was an air sensitive solid, this could be inserted into the reaction vessel either manually in the dry-box, or, if the reagent was the product of a previous reaction, the second reaction could be performed using equipment similar to that shown in diagram 15e. Equipment such as this allowed the reaction to be carried out in solution and would also permit material to be added and removed during the course of a reaction. During the course of a typical reaction, the air-sensitive solid reagent is contained in the breakseal tube A. The bottom of this tube is weak as a result of it having been sealed off
under vacuum. Because of A's proneness to fracture, the reactions are carried out in the larger diameter tube B.

After evacuating the system through cone C, tube A is opened through the breakseal and the solvent allowed to condense into tube B. Cone C is then sealed off. The solid reactant is washed into tube B, and the original breakseal tube A sealed off. Volatile reagents can now be added through system D, which is then removed. On completion of the reaction, the solvent and any volatile products are removed through E and any volatile solid products sublimed into the breakseal tube F. Limb G permits the addition of a solvent if the solid reaction products are not volatile.

2.4 Low Temperature Baths

The two main baths to be used for the necessary low temperature requirements were liquid nitrogen (-196°) and a mixture of solid carbon dioxide and alcohol or acetone, which gave a temperature of -78.5°. Other coolants used consisted of "slush" baths, which were produced by mixing a low melting point liquid with liquid nitrogen. Such a slush bath can be prepared by slowly pouring liquid nitrogen into a Dewar Flask containing the solvent, continuously stirring the mixture until the desired consistency is obtained. When properly mixed, the consistency of the crystallised solvent is that of
a fluid slush, which will maintain at constant temperature as long as the bath is kept slushy (done by occasionally blending in more liquid nitrogen). Some cold baths used are shown in Table 3.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Coolant</th>
</tr>
</thead>
<tbody>
<tr>
<td>-25°C</td>
<td>carbon tetrachloride</td>
</tr>
<tr>
<td>-45°C</td>
<td>chlorobenzene</td>
</tr>
<tr>
<td>-65°C</td>
<td>chloroform</td>
</tr>
<tr>
<td>-116°C</td>
<td>ethanol</td>
</tr>
</tbody>
</table>

Ethanol, like other alcohols, forms a heavy syrup rather than a slush.

2.5 Physical Methods used for Identification of Samples

a. Mass spectrometry

Since it is difficult and troublesome to analyse the boron subchlorides using conventional "wet" techniques, the best method of analysis of these cluster derivatives appears to be mass spectrometry. The compounds seem, in fact, to be ideally suitable for analysis in this way since their volatility and stability are such that they pass through the mass spectrometer without a great deal of degradation or any apparent transformation into other boron-chlorine species. However, even quite simple species produce very complex
mass spectra, since both boron and chlorine possess two isotopes, all four being present in relatively high abundance. For example, as shown in table 4, even the apparently simple ion $B_2Cl_2^+$ produces nine ions of seven different masses in the mass spectrometer.

<table>
<thead>
<tr>
<th>Isotopic combination</th>
<th>Approximate mass</th>
<th>Accurate mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}<em>{B}^{10}</em>{B}^{35}<em>{Cl}^{35}</em>{Cl}$</td>
<td>90</td>
<td>89.965586</td>
</tr>
<tr>
<td>$^{10}<em>{B}^{11}</em>{B}^{35}<em>{Cl}^{35}</em>{Cl}$</td>
<td>91</td>
<td>90.959953</td>
</tr>
<tr>
<td>$^{11}<em>{B}^{11}</em>{B}^{35}<em>{Cl}^{35}</em>{Cl}$</td>
<td>92</td>
<td>91.956310</td>
</tr>
<tr>
<td>$^{10}<em>{B}^{10}</em>{B}^{35}<em>{Cl}^{37}</em>{Cl}$</td>
<td>92</td>
<td>91.960637</td>
</tr>
<tr>
<td>$^{10}<em>{B}^{11}</em>{B}^{35}<em>{Cl}^{37}</em>{Cl}$</td>
<td>93</td>
<td>92.957004</td>
</tr>
<tr>
<td>$^{11}<em>{B}^{11}</em>{B}^{35}<em>{Cl}^{37}</em>{Cl}$</td>
<td>94</td>
<td>93.953371</td>
</tr>
<tr>
<td>$^{10}<em>{B}^{10}</em>{B}^{37}<em>{Cl}^{37}</em>{Cl}$</td>
<td>94</td>
<td>93.957687</td>
</tr>
<tr>
<td>$^{10}<em>{B}^{11}</em>{B}^{37}<em>{Cl}^{37}</em>{Cl}$</td>
<td>95</td>
<td>94.954054</td>
</tr>
<tr>
<td>$^{11}<em>{B}^{11}</em>{B}^{37}<em>{Cl}^{37}</em>{Cl}$</td>
<td>96</td>
<td>95.950421</td>
</tr>
</tbody>
</table>

The relative intensity of the peaks in the mass spectrum corresponding to the mass to charge (m/e) values of these ions is a measure of the natural abundance ratio of the element. The natural abundancies of the isotopes of boron and chlorine are shown in table 5.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{10}_{B}$</td>
<td>18.83</td>
</tr>
<tr>
<td>$^{11}_{B}$</td>
<td>81.17</td>
</tr>
<tr>
<td>$^{35}_{Cl}$</td>
<td>75.53</td>
</tr>
<tr>
<td>$^{37}_{Cl}$</td>
<td>24.47</td>
</tr>
</tbody>
</table>

44.
As the distribution of peaks for each boron-chlorine species always appears constant, knowledge of the expected patterns will enable positive identification of any ion to be made. It is possible to calculate the relative abundancies produced in the mass spectrum of a given boron-chlorine species. For large molecules it becomes extremely complicated to determine manually the number and intensity of peaks expected in their mass spectrum and the use of a computer program\(^{(42)}\) simplifies the calculation of the mass numbers and ion clusters in the mass spectra of compounds containing elements with more than one isotope. The process of comparing the observed (solid line) and theoretical (broken line) intensities for the example of \(\text{B}_9\text{Cl}_9\) is illustrated in diagram 16.

On preliminary investigations, the mass spectrum of a pure boron subhalide seems extremely complex. Yet it can be seen from diagram 17 (a representation of the partial mass spectrum of \(\text{B}_9\text{Cl}_9\)) that overlap between different species is rare, and that certain patterns of degradation repeatedly occur to assist the assignment of groups of peaks. For example, the base peak in diagram 17 is not the molecular ion \(\text{B}_9\text{Cl}_9^+\), but \(\text{B}_8\text{Cl}_6^+\), the ion formed by loss of "BCl\(_3\)" from the parent. Evidence that this loss of "BCl\(_3\)" occurs in one step as a neutral boron trichloride molecule is given by a broad metastable peak at approximately m/e 215 which corresponds
16. COMPARISON OF THE OBSERVED & THEORETICAL INTENSITIES FOR THE MOLECULAR ION IN DgClg
Table 6.

Species detected in the partial mass spectrum of $\text{B}_9\text{Cl}_9$ (see diagram 17; the m/e values listed are those of the most intense peak observed in any group).

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/e Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_9\text{Cl}_9^+$</td>
<td>416</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_7^+$</td>
<td>334</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_6^+$</td>
<td>299</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_5^+$</td>
<td>264</td>
</tr>
<tr>
<td>$\text{B}_7\text{Cl}_5^+$</td>
<td>253</td>
</tr>
<tr>
<td>$\text{B}_6\text{Cl}_5^+$</td>
<td>242</td>
</tr>
<tr>
<td>$\text{B}_7\text{Cl}_4^+$</td>
<td>217</td>
</tr>
<tr>
<td>$\text{B}_6\text{Cl}_4^+$</td>
<td>206</td>
</tr>
<tr>
<td>$\text{B}_7\text{Cl}_3^+$</td>
<td>181</td>
</tr>
<tr>
<td>$\text{B}_6\text{Cl}_3^+$</td>
<td>171</td>
</tr>
<tr>
<td>$\text{B}_5\text{Cl}_3^+$</td>
<td>160</td>
</tr>
<tr>
<td>$\text{B}_4\text{Cl}_3^+$</td>
<td>149</td>
</tr>
<tr>
<td>$\text{B}_5\text{Cl}_2^+$</td>
<td>138</td>
</tr>
<tr>
<td>$\text{B}_2\text{Cl}_3^+$</td>
<td>127</td>
</tr>
<tr>
<td>$\text{B}_4\text{Cl}_2^+$</td>
<td>114</td>
</tr>
<tr>
<td>$\text{B}_3\text{Cl}_2^+$</td>
<td>103</td>
</tr>
<tr>
<td>$\text{B}_2\text{Cl}_2^+$</td>
<td>92</td>
</tr>
<tr>
<td>$\text{BCl}_2^+$</td>
<td>81</td>
</tr>
</tbody>
</table>
17. REPRESENTATION OF THE PARTIAL MASS SPECTRUM OF $^{89}$C
17. REPRESENTATION OF THE PARTIAL MASS SPECTRUM OF BgClg
to the reaction

\[
B_9Cl_9^+ \rightarrow BCl_3 + B_8Cl_6^+.
\]

A metastable peak at approximately m/e 111 shows that the base peak ion also readily loses "BCl_3"

\[
B_8Cl_6^+ \rightarrow BCl_3 + B_7Cl_3^+.
\]

Presumably these two metastable transitions reflect the high stability of boron trichloride because it is known that there are no labile BCl_2 groups within the molecule. All the boron monohalides currently under investigation exhibit the metastable loss of BX_3 from the parent ion, suggesting that all the molecules possess the same type of structure. Table 7 summarises the metastable peaks noted and assigned in this work.

Mixtures of the polymeric boron monohalides can also be readily identified using the mass spectrometer. Diagram 18 is a representation of the partial mass spectrum obtained from a mixture of the boron monochlorides. The species which have been assigned to each m/e value are given in table 8.
Table 7. Assignment of Metastable Peaks

<table>
<thead>
<tr>
<th>First ion</th>
<th>New ion</th>
<th>Entity lost</th>
<th>Approximate position of Metastable Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₈Cl₈⁺</td>
<td>B₇Cl₅⁺</td>
<td>BCl₃</td>
<td>173</td>
</tr>
<tr>
<td>B₉Cl₉⁺</td>
<td>B₈Cl₆⁺</td>
<td>BCl₃</td>
<td>215</td>
</tr>
<tr>
<td>B₁₀Cl₁₀⁺</td>
<td>B₉Cl₇⁺</td>
<td>BCl₃</td>
<td>258</td>
</tr>
<tr>
<td>B₁₁Cl₁₁⁺</td>
<td>B₁₀Cl₈⁺</td>
<td>BCl₃</td>
<td>302</td>
</tr>
<tr>
<td>B₇Br₇⁺</td>
<td>B₆Br₄⁺</td>
<td>BBr₃</td>
<td>233</td>
</tr>
<tr>
<td>B₉Br₉⁺</td>
<td>B₈Br₆⁺</td>
<td>BBr₃</td>
<td>392</td>
</tr>
<tr>
<td>B₉Cl₅Br₄⁺</td>
<td>B₈Cl₃Br₃⁺</td>
<td>BCl₂Br</td>
<td>315</td>
</tr>
<tr>
<td>B₉Cl₆Br₃⁺</td>
<td>B₈Cl₄Br₂⁺</td>
<td>BCl₂Br</td>
<td>274</td>
</tr>
<tr>
<td>B₉Cl₇Br₂⁺</td>
<td>B₈Cl₅Br⁺</td>
<td>BCl₂Br</td>
<td>234</td>
</tr>
<tr>
<td>B₉Cl₈H⁺</td>
<td>B₈Cl₆⁺</td>
<td>BCl₂H</td>
<td>234</td>
</tr>
<tr>
<td>B₉Cl₇H₂⁺</td>
<td>B₈Cl₅H⁺</td>
<td>BCl₂H</td>
<td>202</td>
</tr>
</tbody>
</table>

This mixture contains B₈Cl₈, B₉Cl₉, B₁₀Cl₁₀ and B₁₁Cl₁₁, and it can be seen that the largest peaks at the high m/e end of the spectrum are caused by the species formed by loss of "BCl₃" from the molecular ions. Again overlap between different species is rare, so permitting the unique identification of any group of peaks.

In addition to using computed data to interpret mass spectra, positive identification of a species can be made using accurate mass determination if high resolving power is available. Apart from carbon-12, all isotopes have non-integral masses, which have been
Table S.
Species detected in the partial mass spectrum of a mixture of polymeric boron monochlorides
(See diagram 18; the m/e values listed are those of the most intense peak in any group).

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/e Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{11}Cl_{11}^+$</td>
<td>509</td>
</tr>
<tr>
<td>$B_{10}Cl_{10}^+$</td>
<td>462</td>
</tr>
<tr>
<td>$B_{11}Cl_{9}^+$</td>
<td>438</td>
</tr>
<tr>
<td>$B_{9}Cl_{9}^+$</td>
<td>416</td>
</tr>
<tr>
<td>$B_{10}Cl_{8}^+$</td>
<td>391</td>
</tr>
<tr>
<td>$B_{8}Cl_{8}^+$</td>
<td>370</td>
</tr>
<tr>
<td>$B_{9}Cl_{7}^+$</td>
<td>345</td>
</tr>
<tr>
<td>$B_{9}Cl_{6}^+$</td>
<td>310</td>
</tr>
<tr>
<td>$B_{8}Cl_{6}^+$</td>
<td>299</td>
</tr>
<tr>
<td>$B_{9}Cl_{5}^+$</td>
<td>274</td>
</tr>
<tr>
<td>$B_{8}Cl_{5}^+$</td>
<td>263</td>
</tr>
<tr>
<td>$B_{7}Cl_{5}^+$</td>
<td>253</td>
</tr>
<tr>
<td>$B_{9}Cl_{4}^+$</td>
<td>239</td>
</tr>
<tr>
<td>$B_{7}Cl_{4}^+$</td>
<td>217</td>
</tr>
<tr>
<td>$B_{6}Cl_{4}^+$</td>
<td>206</td>
</tr>
<tr>
<td>$B_{8}Cl_{3}^+$</td>
<td>192</td>
</tr>
<tr>
<td>$B_{7}Cl_{3}^+$</td>
<td>182</td>
</tr>
<tr>
<td>$B_{6}Cl_{3}^+$</td>
<td>172</td>
</tr>
</tbody>
</table>
accurately determined to six decimal places. If the mass of an ion (usually the molecular ion) can be accurately measured, then it is logical that the atomic combination of the ion in question can be determined. For example, an accurate mass determination on the peak at m/e 415 of B\textsubscript{9}Cl\textsubscript{9}\textsuperscript{+}, which was calculated to consist 99.9 per cent of the isotopomer 11\textsubscript{B} 10\textsubscript{B} \textsuperscript{35}Cl\textsubscript{8} \textsuperscript{37}Cl\textsuperscript{+}, yielded\textsuperscript{(20)} a value of 414.80385; this was in excellent agreement with the theoretical value of 414.804111.

The mass spectra of the polymeric boron monochalides were obtained by means of an AEI MS12 using a direct insertion probe. As the boron subhalides decomposed when exposed to the atmosphere, samples were inserted into the mass spectrometer via a nitrogen-filled polythene glove bag, which was attached to the inlet part of it. To give an element of stability to the glove bag, a small, specially constructed table was fixed near to this inlet. A sealed tube containing the sample was opened in the glove bag and the material introduced to the mass spectrometer through the direct insertion probe in the usual way.

The equipment used to obtain a sample for mass spectral analysis is similar to the arrangement shown in diagram 15c. The mass spectral sampling tube itself is about 6-in. long. A similar tube can be incorporated into any of the breakseal apparatus of the type previously described if the mass spectrum of an intermediate or a
product is required.

b. Raman Spectroscopy

Raman spectra were obtained with the assistance of Dr. A.G. Briggs (Lecturer in Physical Chemistry at Loughborough University of Technology), using a Cary 83 Laser Raman Spectrophotometer. This instrument has an argon-ion laser source. Two different methods were used to prepare samples for examination:

(i) Liquids (including solutions) and solids volatile at room temperature were analysed in pyrex capillary tubes, each of which was 1mm. internal diameter and approximately 25mm. long. These air-sensitive samples were introduced into the capillary tubes (which were ground flat at the end to minimise laser beam distortions) using equipment similar to that shown in diagram 19. This equipment permits the introduction of solvents via the vacuum line. It was possible to pour solutions into the sampling capillary, whereas it was necessary to condense liquids and volatile gases into the capillary by cooling the latter. This was then sealed off,

(ii) Solids which were involatile at room temperature were examined in narrow tubes similar to those used for obtaining samples for mass spectral
19. APPARATUS USED TO OBTAIN SAMPLES FOR LASER RAMAN SPECTROSCOPY

20. INFRARED GAS CELL
analysis, although this time a thinner walled tubing was used (i.d. 4mm; o.d. 6mm). The solids were simply sublimed into the narrow tube using apparatus similar to that used in obtaining samples for mass spectral analysis (ref. diagram 15c).

c. **Infra-red Absorption Spectroscopy**

Infra-red spectra were obtained by using a Perkin-Elmer 457 Infra-red Spectrophotometer. Three different methods were used to obtain these spectra:

(1) For gas samples, and samples of liquids and solids having appreciable vapour pressures at room temperature, a gas cell was used (see diagram 20). This was fitted with a B1/4 cone and a P.T.F.E. tap (supplied by Fischer-Porter). Windows were held in place by means of plastic screw caps and sealed with rubber "O" rings.

(11) For some liquids, the samples were simply held between infra-red transparent windows. By using this method, it was found that it successfully prevented air from penetrating to that part of the sample in the beam of radiation, thus enabling air-sensitive materials to be handled in this way.

(iii) For solids, satisfactory results were obtained using pressed potassium bromide discs, made up in a glove bag. The potassium bromide powder
(200mg.) was dried at 200° in an oven before use; it was then ground up with the sample and pressed to produce a disc. Sandwich discs were also made, where the sample (together with 100mg. of potassium bromide) was shielded from the atmosphere by two outer layers of potassium bromide (each 100mg.); however this produced no improvement in preventing the hydrolysis of air-sensitive materials.

d. Ultra Violet and Visible Spectroscopy

Ultra violet and visible spectra were recorded on a Pye-Unicam SP 8000 Recording Spectrophotometer using modified 1cm. quartz cells (see diagram 21). The cells were fitted with greaseless high vacuum taps (supplied by Young's) and Bl4 cones so that they could be filled with air-sensitive solvents using the vacuum line; cell (a) was the solution cell and cell (b), the reference cell. Solutions were made up in cell (a) as follows: the solvent was condensed into the side tube, and, after breaking the breakseal, the solvent was used to wash the sample into the cell. The breakseal limb was subsequently sealed off. However when these cells were in position in the spectrophotometer, it was found that they protruded, and that it was impossible to close the lid. Consequently, a light shield had to be constructed in order to exclude all the extraneous light from the instrument. The shield consisted of opaque black polythene, to prevent light
21. 1\text{cm.} QUARTZ CELLS USED TO OBTAIN ELECTRONIC SPECTRA
entering the instrument; the polythene was itself faced with a dense dark-coloured woollen material in order to prevent any internal reflections.

c. **X-ray Fluorescence**

X-ray fluorescence analyses were obtained and interpreted by Mr S.J. Anderson (a research student in Inorganic Chemistry at Loughborough University of Technology). Samples were mixed with potassium chloride and pressed into discs using 30 tons pressure for a period of about 10 minutes. The analyses were carried out using a Phillips PW1540 vacuum spectrograph attachment with a wide range goniometer PW1050. A LiF(100) crystal was used with a NaI(Tl) scintillation counter. The pulses from the detector were fed via a pulse height analyser into a ratemeter/scalar unit, which was simply read off.

f. **X-ray Diffraction**

X-ray powder diffraction analyses were carried out and interpreted by Mr R.E. Humphreys (Demonstrator in Inorganic Chemistry at Loughborough University of Technology). Specimens were prepared for analysis by pressing a powdered sample onto a greased glass plate. These were then analysed using a Phillips PW1010 generator and a PW1050/25 goniometer, with a nickel filter and a copper target, running at 1000W. The detector unit itself was a Phillips PW1051 X-ray diffractometer.
g. X-ray Powder Photographs

The Debye-Scherrer photographs were taken by Dr. D. S. Brown (Lecturer in Chemistry at Loughborough University of Technology), using a Unicam Weissenberg camera with copper Kα radiation. The camera diameter was 5.73 cm. The air-sensitive solid samples were sealed in fine Lindemann glass capillaries, which were 0.5 and 1.0 mm i.d. (supplied by Pantak Ltd).

2.6 Gas-Liquid Chromatography

The original purpose of this research studentship was to attempt the separation and isolation of $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$ and $\text{B}_{12}\text{Cl}_{12}$. These compounds are the major product of the thermal decomposition of diboron tetrachloride at room temperature, and constitute the red glassy material described as $\text{B}_{12}\text{Cl}_{11}$ by Urry$^{(17)}$. Mass spectral evidence has substantiated the hypothesis that this glassy material is a mixture of boron subchlorides rather than it just being one compound. No quantity of the proposed molecular ion $\text{B}_{12}\text{Cl}_{11}^+$ has ever been found in mass spectra of all the samples analysed in this research. If this proposed compound was unstable in the mass spectrometer, then it could be expected always to produce the same break-down pattern. Various samples of this red material (obtained from different diboron tetrachloride decompositions) have been analysed, and the resulting mass spectra show that the proportions of $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$ and $\text{B}_{12}\text{Cl}_{12}$ vary from sample to sample.
A study of metastable transitions has also been made, and peaks have been observed for the loss of "BCl_2" from B_10O_10 and B_11O_11. This is similar to the behaviour of B_8Cl_8 and B_9Cl_9, which suggests that all the molecules may have cage-like structures.

To prove that this red material is a mixture of boron-chlorine cages, one of these compounds must be isolated. Many attempts were made to do this, but to no avail. The method of separation which was thought to have the greatest chance of success was gas-liquid chromatography (g.l.c.). It was chosen as a result of the heavier polymeric boron monochlorides being relatively volatile and able to withstand high temperatures when contained in an evacuated sealed tube. In g.l.c., a solution of the mixture to be separated is injected into a moving stream of gas which carries it through a column containing a support material coated with a stationary (or liquid) phase. The column is itself kept in a thermostatted oven. After passing through the column, the solution and stream of gas flows into a detector, which in turn sends a signal to a pen recorder.

The boron monochlorides were dissolved in dichloromethane, and the solutions kept in a small flask sealed with a Viton septum (supplied by Beldam Asbestos Co. Ltd., Hounslow).
A Pye Series 104 Chromatograph was used for the majority of the attempts to separate the compounds. This instrument contains two columns, only one of which is normally used for the purpose of injections. Consequently, the recorded signal is the difference between the values given by the two detectors. The sample itself is not destroyed as it passes through a katharometer detector, which operates by detecting changes of thermal conductivity in the carrier gas due to eluted material. This allows the vapour which elutes from the instrument to be passed through a cold trap so allowing the separated sample to be collected. A system was developed (ref. diagram 15f) to collect the boron subchlorides in this way. A metal tube, attached to the katharometer exit by a short piece of rubber tubing, conveyed the vapours into a long glass U-tube, which was cooled at -23° by a carbon tetrachloride slush bath contained in a Dewar flask. A heating tape was wrapped around the metal tubing and the top of the glass U-tube, so that crystals of the boron subchlorides could collect in the U-tube below it.

Two other g.l.c. instruments have been used, both of which possessed flame ionisation detectors, which destroy any combustible material passing through. Thus, if any of the injected material is to be collected, some form of sample splitter must be incorporated between the column and the detector. This splitter sends only a portion of the gases passing through the column.
into the detector. The remainder leaves the instrument in an undecomposed form which is then collected.

Attempts were made to collect large amounts of separated samples by injecting solutions of the subhalide mixture into the Aerograph Autoprep 705 Preparative Chromatograph. A chromatograph with a flame ionisation detector was used in an effort to obtain mass spectral analyses of material eluting from the instrument. In this case, a Pye Series 104 Chromatograph with a single flame ionisation detector was linked to the mass spectrometer AEI MS12. With the preparative instrument, only a small fraction of the eluent passed into the detector, thus enabling the majority of the injected samples to be collected; whereas with the g.l.c.-mass spectrometer, approximately equal amounts were passed into the detector and the mass spectrometer.

Helium, hydrogen and nitrogen have all been used as carrier gases. On analytical machines, because of its low viscosity and high molecular diffusion, hydrogen produces the best results for small injections (less than 10 μl). This emphasis changes for larger injections (up to 2ml.) on preparative instruments, where nitrogen is preferred both on grounds of cost and safety.

There appears to be no reason why the boron subchlorides should not be separated in the gas-liquid
chromatograph and emerge from the instrument for
collection and analysis, if an inert column material and
an inert and dry carrier gas could be found. Extensive
research has been undertaken to find favourable conditions
for the g.l.c. separation of the five cage boron
subchlorides (i.e. $B_8Cl_8$, $B_9Cl_9$, $B_{10}Cl_{10}$, $B_{11}Cl_{11}$ and
$B_{12}Cl_{12}$). These conditions are summarised in Table 9.

The first stage was to find a liquid which
would prove inert to the boron subchlorides. Poly
(chlorotrifluoro) ethylene grease (supplied by Indermann
and Co., Ltd; manufactured by E. Merck Laboratory Chemicals)
was tried first, but it was found to thermally decompose
above a temperature of about $100^\circ$. No transfer of the
boron subchlorides would be expected to occur at
temperatures as low as this.

So that higher temperatures could be used, a
silicone gum rubber (SE70, obtained from J.J's
(Chromatography) Ltd) with a maximum operating temperature
of $250^\circ$ was the next to be tried. Although reproducible
tracer peaks were recorded using different kinds of
chromatograph, nothing could be collected. Use of the
g.l.c.-mass spectrometer link showed that the appearance
of the peaks coincided with the appearance of an
indeterminate, probably polymeric material from the column.
It was found that these peaks, observed on the g.l.c.
traces, did not correspond to any boron subchlorides,
### Table 9.

Summary of Conditions Used in the Gas-Liquid Chromatography Experiments

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Column dimensions</th>
<th>Liquid phase</th>
<th>Solid phase</th>
<th>Carrier gas</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pye 104 (Katharometer)</td>
<td>5ft X 1/8in.</td>
<td>15% poly (chlorotrifluoro) ethylene</td>
<td>60-80 brickdust</td>
<td>hydrogen</td>
<td>150, 200, 250, 300.</td>
</tr>
<tr>
<td>Aerograph 705</td>
<td>5ft X 3/8in.</td>
<td>15% SE30</td>
<td>60-80 Celite 545</td>
<td>nitrogen</td>
<td>150</td>
</tr>
<tr>
<td>Pye 104 (Katharometer)</td>
<td>5ft X 1/8in.</td>
<td>15% SE30</td>
<td>60-80 Celite 545</td>
<td>hydrogen</td>
<td>150</td>
</tr>
<tr>
<td>Pye 104 (f.i.d.)</td>
<td>5ft X 1/8in.</td>
<td>15% SE30</td>
<td>60-80 Celite 545</td>
<td>helium</td>
<td>150</td>
</tr>
<tr>
<td>Pye 104 (Katharometer)</td>
<td>5ft X 1/8in.</td>
<td>10% Voltalef 90</td>
<td>Chromosorb W60-80</td>
<td>hydrogen</td>
<td>200</td>
</tr>
<tr>
<td>Pye 104 (Katharometer)</td>
<td>5ft X 1/8in.</td>
<td>10% Voltalef 90</td>
<td>Chromosorb W60-80</td>
<td>helium</td>
<td>200</td>
</tr>
<tr>
<td>Pye 104 (Katharometer)</td>
<td>5ft X 1/8in.</td>
<td>10% Voltalef 90</td>
<td>Voltalef 300</td>
<td>helium</td>
<td>200</td>
</tr>
<tr>
<td>Pye 104 (Katharometer)</td>
<td>5ft X 1/8in.</td>
<td>Glass beads</td>
<td></td>
<td>helium</td>
<td>100, 150, 200, 250, 300.</td>
</tr>
</tbody>
</table>
but were probably the products of reactions between the SE50 on the column and the injected subchlorides.

It thus became clear that the liquid phase must combine thermal stability with non-reactivity towards the polymeric boron monochlorides. Voltalef 90 (obtained from B.D.H. Chemicals Ltd), an inert halogenated carbon polymer stable up to 200° was selected. It took several injections onto the column before white fumes were seen to be emanating from it. By use of the equipment shown in diagram 15f, yellow crystals were collected, and to prevent their decomposition, they were sealed off in the glass tubing. Examination of the mass spectral evidence indicated the presence of \( \text{B}_9\text{Cl}_9 \) and a trace of \( \text{B}_{10}\text{Cl}_{10} \) in the yellow crystals, however no separation proved possible and no peaks were obtained on the pen recorder.

Various alterations were made to the conditions of the experiments in an attempt to explain both the apparent disappearance of the boron subchlorides and to try to obtain separations. The first hypothesis to be tested was that the hydrogen carrier gas was reducing the majority of the injected material, for it was known that this material contained only a small proportion of \( \text{B}_9\text{Cl}_9 \). To test whether this was the case, the carrier gas was changed, first to nitrogen, and then to helium.

With nitrogen, very high cylinder pressures were
required in order to obtain a sufficiently rapid flow rate of the gas. Even so, the material injected onto the column appeared to elute only very slowly. Short columns (3 ft. in length) were made up, but again only a yellow material was collected.

With helium, an improvement in performance was achieved. Air-sensitive black material eluting from the column was collected and shown by mass spectral analysis to contain both $B_8Cl_8$ and $B_9Cl_9$. However, no trace was found of the heavier monochlorides, and again no peaks were obtained on the pen recorder.

The second hypothesis put forward was that the support phase in the g.l.c. columns might be reacting with the injected material. The support phases previously used were diatomaceous earths. In an attempt to produce a still more inert system, a different support material was chosen, namely Voltalef 300 (obtained from J.J's (Chromatography)Ltd.). This is chemically similar to the stationary phase Voltalef 90, but has a higher molecular weight. Unfortunately, the results obtained with a column consisting of 10% Voltalef 90 on Voltalef 300 were no better than any of the previous systems.

It seems that there can only be two possible reasons for the non-appearance of the heavier boron
subchlorides; either they never reach the column, or they decompose on the column itself. Credence was given to the first theory by the knowledge that the instrument used for the bulk of the g.l.c. work did not possess an injection heater. This resulted in the first part of the column into which injections were made being much cooler than the thermostatically controlled oven (i.e. 100° when the oven was set at 200°). A result of this temperature difference could be seen in that a plug of the injected material always collected in this region. Accordingly, an injection heater was fitted to the instrument, and by using this improvement, reproducible peaks were obtained. Following an injection, two very broad peaks were recorded corresponding to the emergence of two materials. The first was a black material (containing no B9Cl9), and the second, a yellow material (containing no B8Cl8). Despite these improvements, there was still no evidence of significant quantities of B10Cl10, or any B11Cl11 or B12Cl12, in the material eluting from the column. Increasing the oven temperature (using columns filled with uncoated glass beads since both Voltalef materials are unstable above 200°) produced no improvement; in fact nothing at all was eluted at temperatures above 250°.

It seems that the heavier monochlorides must decompose before they can pass through the column. 

B10Cl10, B11Cl11 and B12Cl12 are thermally more stable
than \( B_8\text{Cl}_8 \), the former being stable for short periods (up to one hour) at temperatures as high as \( 450^\circ \) in a sealed tube. This apparent difference in stabilities may be due to the non-equilibrium in the g.l.c. case, where any volatile products (such as boron trichloride) will be swept away through the column. When the subchlorides are contained in a sealed tube, a build-up in pressure may prevent their decomposition.

2.7 Fractional Sublimation

This technique was used in attempts to separate mixtures of the boron monohalides. The subchlorides to be separated were forced into the long glass sublimation tube (outer diameter 6mm., 90cm. long) by means of the apparatus shown in diagram 15c. After evacuation, the breakseal was broken and the system sealed off at the constriction. Heat was used to force the polymeric monochlorides into the long tube, and it also allowed the tube to be sealed off ready for insertion into the sublimation equipment (ref. diagram 15d). In this system, the long, scaled sublimation tube was encased in a length of tightly fitting copper tubing (internal diameter 6mm.) which in turn was placed in an aluminium block. The copper tubing was partially insulated from air currents and temperature fluctuations by using a jacket of a glass tube covered with aluminium foil.

To heat the aluminium block, various sources
were tried - microhunsen burner, an oil bath and an electric oven. Easily the most satisfactory separations were obtained by heating the block in the top of an electric oven for long periods (1-2 weeks), with the tubing protruding from it.

2.8 Silent Electric Discharge

The apparatus used for silent electric discharge reactions consisted of the discharge cell connected via a Young's greaseless high vacuum tap to a U-trap. Diagram 22 shows the construction of the equipment used. Reactants were admitted into the apparatus via another tap and a B1/4 cone, which allowed the system to be connected up to the high vacuum line.

As can be seen in diagram 22, the discharge cell consisted of an outer, large diameter glass tube and a narrower, inner glass tube; the latter was sealed to the larger tubing at the top. In this way, a narrow space was formed between the inner and the outer walls of the cell, in addition to the open central gap. The central gap allowed an electrode to be inserted into the cell, and another electrode (copper mesh) was then wrapped outside it. With this design it was possible to increase the potential difference between the electrodes sufficiently to produce a discharge in the vapour, which itself was contained in the narrow space between the electrodes. The discharge was operated in a fume
22. SILENT ELECTRIC DISCHARGE APPARATUS

Diagram showing the silent electric discharge apparatus with labeled parts:
- Copper Foil Electrodes
- 16 mm Dewar Seal
- 30 cm
- 28 mm
- 12 kV
cupboard because it was found to generate large quantities of highly poisonous ozone.

In a typical reaction, the apparatus was attached to the vacuum line and, with both taps open, the reagents were condensed into the U-trap. Tap A was closed, the apparatus was removed to the fume cupboard, and the electrodes were fitted. Transfer of the reagents was started by holding the lower end of the discharge cell in a low temperature cold bath (usually at -78.5°), with the U-trap at room temperature. The discharge was induced by "winding up" the autotransformer (input 230V, output 0-260V at 5A (max.)). Best yields were produced with the transformer (input 240V, output 12KV) running at about 11KV, whilst discharging the reactants between the discharge cell and the U-trap.

On finishing a reaction and removing the electrodes, the solid products produced in the discharge cell were washed into the breakseal tube C using liquid products and any remaining reactant material, the apparatus itself being inverted to accomplish this transfer. The system was attached to the vacuum line (in the inverted configuration, using an extension to make contact with the insertion point on the vacuum line), and the volatile material was removed. The solid products were then sealed off in the breakseal tube C.
2.9 Preparation of Starting Materials

a. Boron trichloride

This was initially obtained from Borax Consolidated Ltd. in 500ml glass flasks closed with "Rotaflo" taps. Of the four flasks received, one contained pure boron trichloride, but the three others contained yellow-orange impurities which were subsequently analysed (see Chapter 4). Further quantities of boron trichloride were obtained from B.D.H. Chemicals Ltd. The volatile impurities were removed by fractionating the boron trichloride through cold baths held at -78.5° and -116°, the pure starting material remaining in the -116° bath. To check for purity, the vapour pressure of the boron trichloride at 0° was compared with the accepted value of 470mm.

b. Boron tribromide

Boron tribromide was obtained from B.D.H. Chemicals Ltd. in 25ml. ampoules, and any bromine present was removed from the boron tribromide by shaking with mercury. Mass spectral evidence proved that one of the ampoules contained significant quantities of phosphorus pentabromide. This impurity was present because of inadequate purification by the manufacturers, since the boron tribromide was prepared by the halogen exchange reaction between boron trichloride and phosphorus pentabromide.

To check for purity, the vapour pressure of
boron tribromide at 0° and 20° was compared with the accepted values (45) of 17.5mm and 50mm.

e. Boron Tri-iodide

This was obtained from Koch-Light Laboratories in sealed, black painted test tubes. Samples of the boron tri-iodide were found to be contaminated not only with iodine, which was very difficult to remove, and appeared to form due to the action of light on the boron tri-iodide, but also with significantly large amounts of the mixed halides chlorodi-iodoborane and bromodi-iodoborane. Small amounts of tin tetraiodide were also detected in the boron tri-iodide.

d. Boron Trifluoride

This was supplied in a "lecture bottle" by Cambrian Chemicals Ltd. The gas was purified in the vacuum line apparatus by passing it through a cold trap held at -116°, into a trap which was cooled by means of liquid nitrogen.

e. Dimethylamine

Dimethylamine was obtained as a 60% solution in water from J.C.I. Heavy Organic Chemicals Division. On heating this solution with sodium hydroxide pellets in the apparatus shown in diagram 23, the dimethylamine condensed in the form of a liquid at -78.5°. The U-trap
23. APPARATUS USED IN THE PREPARATION OF DIMETHYLAMINE
system was attached to the vacuum line and the
dimethylamine distilled from the -78.5° bath onto freshly
potassium and left for two days. No blue solution was
formed and no hydrogen was evolved. The amine was
warmed to 0° and the most volatile fraction removed
until the vapour pressure of the remaining amine, obtained
at -78.5° and 0°, showed it to be pure.

accepted value of vapour pressure at -78.5° 2.8mm.
accepted value of vapour pressure at 0° 565mm.

2.10 Solvents

When purifying the solvents, the most important
criterion was taken to be the removal of water. With
this aim in view, the preliminary purification procedure
was normally followed by the addition to the solvent of
boron trichloride via the vacuum line, to react with any
traces of water remaining in the solvent.

Carbon tetrachloride was refluxed over phosphorus
pentoxide and then redistilled, collecting the fraction
coming over between 76° and 77°. Similar drying
procedures were also used for chloroform and dichloromethane;
in these particular cases the fractions collected were those
which came over at 60.5° to 61.5° (for chloroform) and
39.5° to 40.5° (for dichloromethane).

Diethyl ether was taken off from a still where
the ether was kept refluxing over sodium

Benzene, n-hexane and methyl cyclohexane were
dried by refluxing over sodium wire and then redistilled.
3. MICROWAVE DISCHARGE-INDUCED REACTION OF THE BORON TRIHALIDES
3. MICROWAVE DISCHARGE-INDUCED REACTIONS OF THE BORON TRIHALIDES

Although Stock\(^{(1)}\) succeeded in preparing and identifying diboron tetrachloride in 1925, no other binary halides with boron-boron bonds were reported until 1949, when Schumb, Gamble and Banus\(^{(4/4)}\) reported the preparation and characterisation of diboron tetraiodide. They had assumed from the known thermal instability of diboron tetrachloride that it would be unlikely that synthetic methods would yield such compounds as diboron tetrabromide and diboron tetraiodide unless their decomposition could be held in check. This, they thought, could be done by choosing a preparative method whereby the temperature of the products was not raised above room temperature. Various alternatives were tried without success until a radiofrequency electrodeless discharge was used to supply the energy to bring about the reduction of the boron triiodide:

\[
2\text{BI}_3 \rightarrow \text{B}_2\text{I}_4 + \text{I}_2.
\]

In addition to the diboron tetraiodide, a black, non-volatile solid identified as \((\text{BI})_n\) and a boron iodide of variable composition, \(\text{B}_x\text{I}_y\) (where the atomic ratio of boron to iodine varied between one and three), were also produced.
Diboron tetraiodide was isolated in the form of a pale yellow crystalline substance, which at room temperature showed signs of slow decomposition, which increased rapidly with rising temperature and exposure to sunlight:

\[ xB_2I_4 \rightarrow yBI_3 + (BI)_{2x-y} + (x-y)I_2 \]

At room temperature only a trace of iodine was formed, so the decomposition at this temperature was essentially a disproportionation. The only other chemistry of diboron tetraiodide or \((BI)_n\) described by these research workers was their hydrolysis reactions. Thus part of this research has been concerned with using similar methods of preparation to theirs in order to investigate these compounds more fully.

Diboron tetrachloride has also been prepared\(^{(45)}\) by the action of an electrodeless discharge on the boron trihalide, although in this case the resonance cavity was operated in the microwave region. The emission spectrum of this discharge was subsequently examined\(^{(46)}\) and all the observed bonds were identified as \(BCl\), suggesting that \(BCl\), not \(BCl_2\), was an intermediate in the preparation of diboron tetrachloride.

The electrodeless discharge therefore seems to be a potentially useful method for the preparation of the
diboron tetrahalides directly from the corresponding trihalides. No other direct method for the synthesis of diboron tetraiodide has been reported (diboron tetrabromide is normally prepared by exchange of halogens with the tetrachloride). A clear advantage of this type of discharge is that it is externally induced, consequently there are fewer possible sources of contamination than with the electrical discharges which are used to prepare diboron tetrachloride, where the electrodes are in contact with the reactive species.

Attempts were therefore made to synthesise diboron tetrachloride, diboron tetrabromide and diboron tetraiodide by the action of a microwave discharge on the trihalides. The emission spectra of these microwave discharges were examined in the ultraviolet and visible regions in an attempt to discover the nature of any reactive intermediates or impurities.

The instrument used to generate the microwave discharge was the Microtron 200 Microwave Generator Mark 2 (Electromedical supplies, Greenham, Ltd), which generates power at 2.54 GHz. This microwave generator is coupled to the discharge tube by a resonance cavity. The discharge tube was constructed from a quartz tube, which was sealed to the remainder of the pyrex system via graded seals, and the emission spectrum of the discharges were investigated using a Hilger and Watts Medium Quartz
Spectrograph (Type E498). In attempts to vary the experimental conditions, the glass apparatus used to pass the boron trihalides through the microwave discharge was frequently altered. For example, whereas boron trichloride was circulated by simple trap-to-trap distillation, boron tribromide and boron triiodide (after initial experimentation with trap-to-trap distillation) were drawn through the discharge tube using a carrier gas.

The equipment used to pass boron trichloride, and boron tribromide vapour through the discharge is shown in diagram 24. It consisted of a circuit containing two U-traps either side of the quartz discharge tube. Boron trichloride or boron tribromide vapour could be circulated in either direction by holding the traps at suitable temperatures.

Large amounts of the halogens were always produced in the discharges through the boron trihalides. The free halogen had to be removed if any of the diboron tetrahalide was to be collected since the reaction

$$2BX_3 \longrightarrow B_2X_4 + X_2$$

is reversible. The chlorine produced in the discharge through boron trichloride was readily removed by fractionating the reaction products through a cold bath.
To Vacuum Line

Microwave Cavity

Gas Storage Bulb

Cold Finger

Tube Filled With Copper Wool

Boron Tribromide

-Manometer

Mercury

24. PASSING OF DCl₃ & DBr₃ VAPOUR THROUGH A MICRO-WAVE DISCHARGE

25. PASSING OF D DCl₃ & CARRIER GAS THROUGH A MICRO-WAVE DISCHARGE
held at -116° (chlorine being volatile at this temperature), but the volatilities of boron tribromide and bromine are too similar for this type of separation. However, bromine was successfully removed from the mixture formed in the discharge through boron tribromide by passing it through a tube packed with copper wool.

Diagram 25 shows the apparatus which allowed a carrier gas to draw the boron tribromide through the discharge tube. The gas was admitted to the large bulb (volume 5 litres) from a gas cylinder coupled up to the vacuum line. When operating the discharge, the gas (argon or helium) bubbled through the boron tribromide, carrying the mixture into the discharge tube. The mixture and any volatile products were then passed through the tube packed with copper wool to a cold U-trap. Continual pumping removed the carrier gas from the U-trap.

The equipment used to pass boron tri-iodide vapour through the discharge is shown in diagram 26. Vapour was drawn through the discharge by cooling the U-trap at -196°. Unfortunately this system was found to be unsatisfactory since the discharge tubing quickly became coated with a thick deposit, making it impossible to photograph the spectrum of the discharge.

Another system was accordingly constructed
26. PASSING OF B I_{3} VAPOUR THROUGH A MICRO- WAVE DISCHARGE

27. PASSING OF B I_{3} VAPOUR & CARRIER GAS THROUGH A MICROWAVE DISCHARGE
(ref. diagram 27), where the problem of the coating of the discharge tube was overcome by positioning the resonance cavity and the tube at the same height as the slit of the spectrograph, and cementing a silica window to an extension of the discharge tube. In this way, the discharge could be photographed without interference from the surface deposits on the tube. This system also allowed a carrier gas to be used.

Yields were very disappointing. Although large quantities of the halogens were invariably produced, showing that the boron trihalides were reacting, no diboron tetrabromide or diboron tetraiodide and only traces of diboron tetrachloride could be detected in the material collected from the discharge. Large quantities of involatile dark coloured solids invariably built up on the tubing where the discharge occurred. This suggests that if the boron trihalides participate in the type of reaction postulated by Frazer and Holzmann(45) for the microwave decomposition of boron trichloride,

$$2\text{BCl}_3 \rightarrow \text{B}_2\text{Cl}_4 + \text{Cl}_2,$$

further decomposition must then occur, leading to the production of more halogen, and yielding an involatile and probably boron-rich subhalide.

The spectra of discharges through boron trichloride
and boron tribromide vapour are known\(^{(47)}\) to contain lines due to the monohalides BCl and BBr. The spectra of these two species, and that of BF, are well known, and have been studied by a number of research workers, but the spectrum of the fourth monohalide, BI, has never been reliably reported. An ultraviolet band system between 265 and 280nm, formed in the flash photolysis of boron tri-iodide has been measured and has been assigned to the BI species\(^{(48)}\). However, the known electronic spectrum of BCl occurs exactly in this region, and since the (0,1) band of BBr was also detected in the emission spectrum of the "BI", it is a reasonable hypothesis that the band system observed between 265 and 280 nm in these flash photolysis experiments was indeed produced by BCl, caused by chlorine impurity in the boron tri-iodide. These research workers also observed two narrow, red degraded diffuse bands with heads at 349.07 and 349.29nm., and they suggested that these arose from the presence of "BI" in an excited electronic state. If the first band sequence between 265 and 280 nm, may indeed be assigned to BCl, there is a possibility that the two bands at lower frequency were caused by BI.

Analysis of the photographs taken of the emission spectra of the microwave discharges through boron trichloride and boron tribromide showed that both of the monohalides BCl and BBr were present in each
discharge, and it was considered that the emission spectrum of the microwave discharge through boron tri-iodide might similarly contain BI. In fact, the emission spectrum of the boron tri-iodide microwave discharge was unlike those obtained with boron trichloride and boron tribromide in that it contained a continuous spectrum associated with a series of diffuse bands (instead of clearly-resolved lines and band system). This bore a close resemblance to the emission spectrum of iodine. To discover whether the halogen was present in this spectrum, iodine was passed through the discharge. The resulting spectrum was found to be substantially similar to that produced by boron tri-iodide.

Attempts were therefore made to produce different results by changing the experimental conditions. The glass discharge apparatus was altered as described above (ref. diagram 27) so that a gas could be used to carry the boron tri-iodide vapour through the discharge. Photographs were then taken of the emission spectrum of the discharge using different flow rates of the argon carrier gas. The boron tri-iodide emission spectra were no different until a very fast flow rate of argon was used, so fast that the discharge was almost extinguished. Only under these conditions were the continua of the iodine emission spectrum absent. Instead, a very complex spectrum was produced, which contained a complicated system of lines and bands. It
was difficult to analyse this spectrum and assign bands accurately owing to the large number of lines and bands. Having photographed the emission spectrum of the discharge through the argon alone, it was discovered that many of the lines were produced by the carrier gas. Another problem was that the resolution produced by the spectrograph (Hilger and Watts, Medium Quartz Spectrograph) was insufficient to separate many of the lines and bands. More accurate results may have been obtained with the larger dispersion of the Large Glass-Quartz Spectrograph.

Despite these difficulties, by comparing the spectra produced by argon alone and by the boron tri-iodide carried through the discharge by argon, it was possible to identify three band sequences which were only present in the boron tri-iodide spectrum. One of these, from 266 to 279 nm., was the hypothesised "BI" system, but on investigation this was found to be identical to the emission spectrum of BCl. The second, which was between 294.5 and 310 nm., was identified as being part of the emission spectrum of BBr, and the third, which appeared to be a similar type of band system to the other two, was located between 349.8 and 353.7 nm. The following values were obtained for the third band sequence (calibrated using emission lines from a zinc-cadmium-mercury lamp):

<table>
<thead>
<tr>
<th>Band</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>349.83</td>
</tr>
<tr>
<td>2</td>
<td>350.75</td>
</tr>
<tr>
<td>3</td>
<td>351.23</td>
</tr>
<tr>
<td>4</td>
<td>352.48</td>
</tr>
</tbody>
</table>
The bands degraded to the red (longer wavelengths).

In order to provide an indication where the emission spectrum of the BI species could be expected to occur, an extrapolation was produced from the positions of greatest emission of BCl and BBr, using the progressions of various infra-red vibrations of the boron trihalides to establish the trend. The third above band system lay near not only this calculated position, but also near the positions found by Briggs and Piercy (48) in their experiments for the bands produced in the flash photolysis of boron tri-iodide. The bands of both systems degrade towards the red. Since the third band system only occurs when the systems identified as the emission spectra of BCl and BBr are produced, it has been postulated that they may, in fact, be part of the BI emission spectrum.

Following the identification of the emission spectra of BCl and BBr in the spectrum of the microwave discharge through boron tri-iodide vapour, a sample of the unreacted material was subjected to mass spectral analysis. This showed that the boron tri-iodide used in these experiments contained up to one third of the mixed halides chlorodi-iodoborane and bromodi-iodoborane. The amount by weight of chlorine and bromine impurity that this represents is about 11%. Significant amounts of tin tetraiodide were also detected. Further
microwave decomposition and flash photolysis reactions must therefore be carried out on a purer sample of boron tri-iodide to discover whether, in fact, this new band system may definitely be assigned to BI.
4. ATTEMPTS TO PREPARE BORON-CAGE COMPOUNDS BY THE CHLORINATION OF BORON CARBIDE
4. ATTEMPTS TO PREPARE BORON-CAGE COMPOUNDS BY THE CHLORINATION OF BORON CARBIDE

The neutral cage boron subhalides have been investigated much less comprehensively than the polyhedral boron hydride ions. This apparent lack of interest may be due to handling difficulties and the greater instability of the monohalides (although less stable compounds than these have certainly been extensively examined). However, the major reason why the chemistry of the polyhedral boron hydrides has been developed so much more seems to be that methods are available to synthesise large quantities of the pure compounds. For example, the $B_{10}H_{10}^{2-}$ cage is easily prepared by reacting decaborane(14) with triethylamine:

$$B_{10}H_{14} + 2N(C_2H_5)_3 \rightarrow [HN(C_2H_5)_3]^+ \cdot [B_{10}H_{10}H_{10}]^{2-}$$

However no such preparative reactions have been found for the boron cage subhalides, and they continue to be synthesised via the diboron tetrahalides, which normally require complicated discharge apparatus for their production. An additional disadvantage of these indirect syntheses is that the decomposition of the diboron tetrahalide usually produces a mixture of cage compounds rather than one pure product, leading to problems of separation.
An obvious way of overcoming these problems would be to devise a method to partially chlorinate the clusters of boron atoms which exist in the allotropes of crystalline boron, in boron carbide (and other non-metal borides) and in boron-rich metal borides. This type of disruption of the boron lattice may occur in the acid hydrolysis of some metal borides, where compounds like tetraborane(10) and diboronic acid, which contain boron-boron bonds, can be produced.

The main structural unit of the allotropes of boron, boron carbide, and several metal borides is an icosahedral grouping of twelve boron atoms. The preferred way of linking icosahedra is for each boron atom to project one external bond. Considering one icosahedron, it is apparent that each boron atom is six-coordinate, with a pentagonal pyramid as the coordination polyhedron. If no other structural entity or element is utilised in a framework, these directional bonding characteristics specified for the $\text{B}_{12}$ icosahedron cannot be fully satisfied, and consequently every boron polymorph is in some degree the result of a structural or stereochemical compromise. Extraordinarily complex frameworks, in which rigid three-dimensional networks are interspersed with holes large enough to incorporate large impurity atoms, are required to approach the preferred stereochemistry. The three best known allotropes of boron (the $\alpha$- and $\beta$-rhombohedral and the $\gamma$-tetragonal forms) and boron carbide, all have
this type of structure, and have been investigated more closely than any other materials in this class.

4.1 $\beta$-Rhombohedral Boron

Of the three most widely known allotropes of boron, only the $\beta$-rhombohedral modification is thought to be thermodynamically stable. It has the most complex structure, and the boron atoms are close to their preferred geometry. The structure can be described as consisting of units containing 156 atoms, each unit being an icosahedral array of $B_{12}$ icosahedra around a central icosahedron. Purification presents difficulties since the structure contains large cavities which can be occupied by impurity atoms. The formula corresponding to saturation of these cavities is $MB_{55}$; and true borides are known to exist where some of these cavities are occupied by metal atoms.

4.2 $\alpha$-Rhombohedral Boron

The second rhombohedral form of boron is also constructed from icosahedra of boron atoms alone, although in this case only half of the boron atoms in the icosahedra have their preferred pentagonal pyramid arrangement. The others are involved in rather weak three-centre two-electron inter-icosahedral bonds. This allotrope of boron is less stable than the $\beta$-rhombohedral form, and reverts to the $\beta$ form when heated above 1500°.
4.3 Boron Carbide

Boron carbide, which is formulated most commonly as $\text{B}_4\text{C}$ or $\text{B}_{12}\text{C}_7$, has a structure derived from $\alpha$-rhombohedral boron. The carbon atoms are in linear chains of three atoms, and bond with the $\text{B}_{12}$ icosahedra in such a way that the boron atoms which were involved in the rather weak multi-centre bonding link with orbitals on the carbon chain. This gives the boron atoms the nearest approximation to ideal stereochemistry of any of these icosahedral systems.

Although the empirical formula of boron carbide is normally given as $\text{B}_4\text{C}$, implying that the material consists of $\text{B}_{12}$ icosahedra and $\text{C}_3$ chains, the compound formulated as $\text{B}_{15}\text{C}_2$ in which the linear $\text{C}_3$ group is replaced by a linear $\text{C}-\text{B}-\text{C}$ group, is thought to be more stable. Another intermediate has been identified as $\text{B}_{11}\text{C}_3\text{CBC}$, where the carbon atoms on the $\text{B}_{11}\text{C}$ icosahedra are randomly distributed amongst the twelve positions. Many other non-metals (such as silicon, oxygen, phosphorus and sulphur) can also be incorporated into the type of structure formed by carbon in boron carbide.

4.4 $\gamma$-Tetragonal Boron

The third form of crystalline boron is different from the two rhombohedral forms in that the structure contains single boron atoms outside the $\text{B}_{12}$ icosahedra.
There are layers of $\text{B}_{12}$ icosahedra interleaved with single atoms which tie the layers of icosahedra together, the unit cell containing 50 atoms: 48 in four icosahedra and two present as individual atoms. The structure is known to contain several large holes, the two largest of which are thought to contain the nickel atoms in the boride $\text{Ni}_{2}\text{B}_{50}$.

4.5 Metal Borides

The tendency for the boron atoms to join together is also shown in the majority of the metal borides. These contain chains, sheets or clusters of boron atoms. Table 10 lists some typical formulae and some structures. It should be noted that whereas $\text{BeB}_{12}$ and $\text{AlB}_{12}$ may have a related (rhombohedral) structure formed from icosahedral $\text{B}_{12}$ units like those found in elemental boron, the boron network in the majority of the $\text{MB}_{12}$ species consists of linked cubo-octahedra. These polyhedra are not found in any other boron-containing compounds, although it has been suggested that the cubo-octahedral structure may be involved as an intermediate in the isomerism of the $\text{C}_{2}\text{B}_{10}\text{H}_{12}$ carboranes.

4.6 Other Systems Containing Linked Boron Atoms

Many of the arrangements of boron atoms in metal borides also occur in discrete molecules or ions, as in
Table 10. Some Typical Metal Borides

<table>
<thead>
<tr>
<th>Formula</th>
<th>Boron atom structure</th>
<th>Boride examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_2B$</td>
<td>Single atoms</td>
<td>Be, Cr, Fe, Ni, Co, Mo, Ta, W, Mn.</td>
</tr>
<tr>
<td>$M_B$</td>
<td>Pairs</td>
<td>V, Nb, Ta.</td>
</tr>
<tr>
<td>$M_B$</td>
<td>Single chains</td>
<td>V, Cr, Mn, Fe, Co, Ni, Nb, Ta, Mo, W.</td>
</tr>
<tr>
<td>$M_B^4$</td>
<td>Double chains</td>
<td>V, Cr, Mn, Ni, Nb, Ta.</td>
</tr>
<tr>
<td>$M_B^2$</td>
<td>Sheets</td>
<td>Be, Mg, Al, Sc, Ti, V, Cr, Mn, Y, Lu, U, Pu, Zr, Hf, Nb, Ta, Tc, Ru, Ds, Ag, Au.</td>
</tr>
<tr>
<td>$M_B^4$</td>
<td>Sheets linking $B_6$ octahedra</td>
<td>Mg, Ca, Mn, Y, Ln, Th, U, Pu, Mo, W.</td>
</tr>
<tr>
<td>$M_B^6$</td>
<td>$B_6$ octahedra (which occupy Cl$^-$ positions in a CsCl structure with the metals)</td>
<td>Na, K?, Be, Mg, Ca, Sr, Ba, Sc, Y, La, Th, Pu.</td>
</tr>
<tr>
<td>$M_B^{12}$</td>
<td>Three-dimensional lattice which can be considered as consisting of linked $B_{24}$ clusters with metal atoms in the middle of each cluster.</td>
<td>Be, Mg, Al, Sc, Y, Ln from Tb to Lu, U, Zr.</td>
</tr>
</tbody>
</table>
the boron hydrides and related systems. For example, boron chains have been stabilised by attaching $R_2N$ sidegroups, and so far compounds in the series $B_n(R_2N)_{n+2}$ with $n$ up to 8 have been isolated\(^{(50)}\). Clusters of boron atoms also occur in $B_6H_6^{2-}$ (octahedral) and $B_{12}H_{12}^{2-}$ (icosahedral) and their derivatives. Unfortunately it has never been possible to isolate partially any of these boron lattices. Any reactions attempting to do this have always occurred with complete disruption of the boron lattice\(^{(49)}\). The only apparent exception to this is the formation of boron hydrides and diboronic acid in hydrolysis reactions with aqueous acids. It seems most likely that the products are in fact formed from the polymerisation and hydrolysis of 'nascent' borane ($BH_3$).

4.7 Chlorination of Boron Carbidte

One possible direct route to the preparation of the subchloride $B_{12}Cl_{12}$ could be the partial chlorination of one of the materials containing $B_{12}$ icosahedra. This type of method is used to manufacture boron trichloride on a large scale. The preparation involves passing a stream of chlorine through a heated iron column containing boron carbide (the most easily accessible of the high boron content materials). It was consequently held to be of great interest that during this preparation, red-orange impurities are formed, which are normally removed.
by passing the impure product over heated boron. The colour of these impurities is very similar to that of a mixture of the boron monochlorides $B_{10}^1 Cl_{10}$, $B_{11}^1 Cl_{11}$ and $B_{12}^1 Cl_{12}$, and it was suggested that these impurities might prove to be one or more of the boron cage subchlorides. If so, cage compounds containing carbon atoms from the known substituted $B_{11}^4 C$ icosahedra might also be expected to be present. This process could thus not only provide a relatively easy way of producing large quantities of the uncharged boron cage subchlorides, so enlarging this aspect of boron chemistry, but also prove an invaluable way of giving further insight into the complicated boron carbide structure.

To test whether this hypothesis was in fact the case, the following experiment was carried out. The impure boron trichloride was supplied by Borax Consolidated Ltd in 500ml flasks fitted with 'rotaflo' taps. In order to remove the bulk of the boron trichloride, one of the flasks was connected to an insertion point on the vacuum line using a short piece of heavy walled rubber tubing attached to a Bl4 cone. The rubber was sealed to the glass tubing using piece-in wax, and after evacuating this connection system, the 'rotaflo' tap was opened and the boron trichloride condensed into another vessel. Contrary to expectations, the boron trichloride abstracted from the storage vessel was not pure as it froze in the cold vessel as a yellow
solid. Later investigations showed that in fact it contained large amounts of silicon tetrachloride. The bulk of the impurities remaining in the storage vessel after the removal of the boron trichloride was found to be considerably more volatile than would be expected for B_{12}Cl_{12}, for it was possible to sublime a yellow-orange substance from the original vessel at room temperature. Only much smaller boron cages than in B_{12}Cl_{12} could possess such high volatility. Furthermore the yellow crystals could be melted by heat from the hand (approximately 350), a much lower melting point than any cage boron subchloride yet isolated. To check for the presence of any smaller boron cages, samples were taken for analysis by subliming material from the storage vessels into small tubes, which were then sealed off from the vacuum line. The following three analytical methods were used: infra-red spectroscopy, X-ray fluorescence and mass spectroscopy.

4.8 Infra-red Spectroscopy

The infra-red spectrum of the yellow material (taken with caesium iodide windows) contained no peaks near 1000cm\(^{-1}\), which is the characteristic absorption region for boron cage compounds. Only at 380 and 475cm\(^{-1}\) were peaks produced. Absorptions in this region are produced by metal-halogen compounds rather than boron compounds.

98.
4.9 X-Ray Fluorescence

The sample investigated using X-ray fluorimetry was allowed to hydrolyse (in an agate mortar) before it was incorporated into a disc. Tin and bromine were identified in the trace produced by this disc.

4.10 Mass Spectroscopy

Diagram 26 is a representation of the partial mass spectrum of the yellow material. This diagram shows the vast majority of the yellow material to consist of titanium tetrabromide (with only a small proportion of the chlorine-substituted TiClBr$_2$). Most of the tin present is similarly fully brominated.

4.11 Interpretation of Results

No boron compounds were found in the material isolated from the impure boron trichloride. It can be seen from diagram 26 that the vast majority of the coloured impurities in fact consisted of titanium tetrabromide; the other analytical results are consistent with this (X-ray fluorescence in the conditions used detected only the heavier elements). The properties of titanium tetrabromide (an amber-yellow crystalline material, melting point 39$^\circ$) are in agreement with the observed nature of the material isolated from the impure boron trichloride. It should be noted that very few other metal bromides possess the volatility of titanium.
Table II

Species detected in the partial mass spectrum of the boron trichloride impurities

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/e value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnBr$_4^+$</td>
<td>458</td>
</tr>
<tr>
<td>TiBr$_4^+$</td>
<td>368</td>
</tr>
<tr>
<td>SnBr$_3^+$</td>
<td>359</td>
</tr>
<tr>
<td>TiClBr$_3^+$</td>
<td>325</td>
</tr>
<tr>
<td>TiBr$_3^+$</td>
<td>228</td>
</tr>
<tr>
<td>SnBr$_2^+$</td>
<td>279</td>
</tr>
<tr>
<td>TiClBr$_2^+$</td>
<td>242</td>
</tr>
</tbody>
</table>

(See diagram 28; the m/e values listed are those of the most peak observed in any group).
28. REPRESENTATION OF THE MASS SPECTRUM OF YELLOW BCl₃ IMPURITY
tetra-bromide and tin tetrabromide, suggesting that if any other metals were present, their bromides would not be isolated.

The presence of bromine must be due to the use of impure chlorine in the manufacturing process. It seems remarkable that despite the large excess of boron trichloride, the isolated titanium and tin compounds were found to be almost completely brominated. Any attempt to remove these metal impurities should therefore be treated with caution, as there seems to be a possibility that they act as accidental purification agents. Were they not present, the product could be contaminated with significantly large quantities of "bromine", probably largely present as BCl₂Br and hence difficult to remove from the boron trichloride by distillation.
5. PREPARATION OF DIBORON TETRACHLORIDE &

INVESTIGATION INTO THE REACTION MECHANISM
5. PREPARATION OF DIBORON TETRACHLORIDE
AND INVESTIGATIONS INTO THE REACTION MECHANISM

Several methods have been devised to prepare diboron tetrachloride, usually by means of reducing boron trichloride. The majority of these methods of reducing boron trichloride have involved the use of an electrical discharge between metal electrodes, however it is claimed that alternative methods can produce better results. Some of the more widely known preparative methods are listed below.

5.1 Electrical Discharges Between Metal Electrodes

Diboron tetrachloride was first prepared in the laboratory of Stock\(^{(1)}\). The method he used was to strike an electrical discharge between a zinc anode and an aluminium cathode immersed in liquid boron trichloride. Yet the success of this attempt was so limited as to only isolate one drop of diboron tetrachloride, and even that contained about 12% of silicon tetrachloride impurity.

It took a further twenty years before a more satisfactory method was devised to prepare larger quantities of the subchloride. This time the work was carried out by Schlesinger\(^{(2)}\). Again an electrical discharge was used to achieve a successful synthesis. However, on this occasion the reduction involved passing the boron trichloride in the gaseous phase between
mercury electrodes:

$$2\text{BCl}_3 + 2\text{Hg} \xrightarrow{\text{mercury discharge}} \text{B}_2\text{Cl}_4 + \text{Hg}_2\text{Cl}_2.$$ 

In the first preparations\(^{(2)}\), the circulation of boron trichloride through the discharge was brought about by trap-to-trap distillations. Subsequently the system was changed\(^{(13)}\) to involve the use of a modified Töpler pump to pass the boron trichloride through the discharge.

Massey, Urch and Holliday have since described\(^{(51)}\) a more reliable and continuous method for the preparation of gramme-quantities of diboron tetrachloride using the mercury discharge; and it is their technique which has been used in the course of this research. Their method made two major modifications to the system used and described by Schlesinger\(^{(13)}\). The first of these was to increase the electrical current in the discharge and the second involved the improvement to the circulation of the boron trichloride by means of a mercury diffusion pump (rather than the somewhat cumbersome and inefficient Töpler pump used by Schlesinger\(^{(13)}\)). With these two improvements it was possible to improve the rate of production of diboron tetrachloride to about 100-200mg. per hour.

This mercury discharge system also produces many other materials in addition to the diboron
tetrachloride. One of these is $B_4Cl_4$ (tetrachloro-
close-tetraborane(4)), another subchloride(52). It
is a pale yellow crystalline solid which is slightly
volatile at room temperature. By using this method it
is feasible to produce $B_4Cl_4$ at the rate of 1-2 mg. per
day(51).

Several silicon compounds have also been isolated
from the other reaction products(51). The glass discharge
tube is thought to be the source of the silicon, for the
tube is etched away when the discharge touches the walls.
Of the silicon compounds present, silicon tetrachloride
has been identified, as well as $Si_2Cl_6$ and $Si_3Cl_8$, where
the silicon-silicon coupling is apparently brought about
by the adventitious passage of the silicon tetrachloride
through the discharge. The presence of hexachloro-
disiloxane, $Cl_3SiOSiCl_3$, may indicate a partial, instead
of total, chlorination of the silicon dioxide molecules.
By far the most interesting silicon compound to be
detected was trichlorosilylboron dichloride, $Cl_3SiBCl_2$,
which possibly arose by a boron-silicon coupling reaction
in the discharge, although other reactions

$$ e.g. \ B_2Cl_4 + SiCl_4 \rightarrow BCl_3 + Cl_3SiBCl_2, $$

involving the insertion of a $BCl$ radical into a silicon-
chlorine bond of silicon tetrachloride, cannot be ruled
out.
Another successful electrical discharge procedure has involved the use of copper\(^{(53)}\) rather than mercury electrodes. In this case, the reaction involves the attack of metallic copper by gaseous boron trichloride, according to the equation

\[
2\text{BCl}_3 + 2\text{Cu} \rightarrow \text{B}_2\text{Cl}_4 + 2\text{CuCl}.
\]

Rates of diboron tetrachloride production have been claimed to be as high as 1g. per hour with a new reactor tube, dropping to 2 to 5g. per hour with a tube having a relatively long service. With this format no other boron subchlorides are produced.

5.2 Microwave Discharge

The microwave discharge preparation\(^{(45)}\) of diboron tetrachloride, which proceeds according to the equation

\[
2\text{BCl}_3 \rightarrow \text{B}_2\text{Cl}_4 + \text{Cl}_2,
\]

is described in chapter 3. This method is claimed to be capable of a production rate equal to those of the electrical discharges.

5.3 Chemical Methods

It is possible to make diboron tetrachloride without resorting to the use of electrical discharges.
When boron trichloride is passed over heated boron monoxide, a 13% yield of diboron tetrachloride is obtained:

\[
\frac{6}{x}(BO)_x + 4BCl_3 \xrightarrow{200^\circ C} 3B_2Cl_4 + B_2O_3.
\]

The boron monoxide (which has a structure involving boron-boron bonds) can be made by first hydrolysing tetrakis-(dimethylamino) diborane(4) carefully at low temperature and then dehydrating the diboric acid so formed at 250\(^\circ\)C under reduced pressure:

\[
\text{Hydrolysis: } \text{(CH}_3\text{)}_2\text{N}_2\text{B-B(N(CH}_3\text{)}_2)_2 \xrightarrow{\text{HCl solution}} \text{B}_2\text{(OH)}_4 \xrightarrow{250^\circ C \text{ reduced (BO)}_x \text{ pressure}} \text{BO}_2
\]

Tetrakis (dimethylamino) diborane(4) is one of the more readily available diboron compounds as it can be prepared on a large scale by treating bis (dimethylamino) boron chloride with highly dispersed sodium:

\[
2(\text{CH}_3\text{)}_2\text{N}_2\text{BCl} + 2\text{Na} \rightarrow 2\text{NaCl} + \text{B}_2\text{(N(CH}_3\text{)}_2)_4}.
\]

5.4 Cocondensation

Copper vapour has been shown to react with boron trichloride at low temperatures (-196\(^\circ\)) to give good yields of diboron tetrachloride(55). This method has been developed into a laboratory preparation of diboron tetrachloride on a 10g. scale:

\[
2\text{Cu}(g) + 2\text{BCl}(g) \rightarrow \text{B}_2\text{Cl}_4(1) + 2\text{CuCl}(s).
\]
5.5 Experimental Procedure for the Preparation of Diboron Tetrachloride

Diboron tetrachloride was prepared using the method described by Massey, Urch and Holliday (51). Diagram 29 shows schematically the apparatus required for the reduction of the boron trichloride. Liquid boron trichloride is held in the U-traps A and B (which are so designed that they both fit in the same Dewar vessel) at -78°. This is the temperature at which its vapour pressure is about 4 mm. The vapour is circulated through the discharge by means of an electrically heated mercury diffusion pump. Any diboron tetrachloride formed in the discharge is carried through to the U-traps where it condenses, because it is almost involatile at -78.5°. The majority of the newly-formed diboron tetrachloride is then trapped in A; whilst trap B will hold any diboron tetrachloride escaping from A. The unreacted boron trichloride is recirculated to complete the system.

The design of the discharge cell is shown in diagram 30. The cell is made of quartz in order to withstand the high temperatures generated; and it is connected to the pyrex system by means of B19 joints sealed with piccin wax (which unlike normal tap grease is unaffected by the boron-chlorine compounds present in the system). Various cells with different path lengths (120 mm., 100 mm., 90 mm.) have been used. There was, however, no apparent difference in their performances except for the voltages required to maintain the discharge (1500 V., 1200 V. and
29. DISCHARGE APPARATUS FOR PREPARATION OF DIDORON TETRACHLORIDE

Flow of \( \text{BCl}_3 \)

Mercury Discharge

A

B

Mercury Diffusion Pump

QUARTZ DISCHARGE & MERCURY RESERVOIR

B \( \text{Cl}_3 \)

Glass Sheathed Tungsten Wire

Mercury

Mercury

Mercury
1000V., respectively). The cell has a limited life as the silicon dioxide is attacked when the mercury in either limb evaporates sufficiently to allow the discharge to impinge on the silica surface. There is a periodic need for mercury to be added to the cell from the reservoir. Any excess mercury falls into bulb B, and does not cause a short circuit. The cell is cooled by means of a water bath, the temperature of which is kept reasonably constant by adding cooling water from the diffusion pump to the bottom of the bath and taking off any excess water by means of an overflow.

The potential across the cell is maintained by a high voltage transformer (potential 240V, secondary 3000V and 500mA) connected to the mains supply via a "Variac" autotransformer (output 0-240V at 10A). The current in the cell circuit is smoothed by a choke (which in this case is actually the secondary coil in a transformer, rated as 1000V at 1A) in series with the discharge and transformer.

The discharge apparatus (diagram 29) is pumped down through tap T (greaseless P.T.F.E. manufactured by Fischer-Porter) and flamed out to remove any trace of adsorbed water. Pumping is stopped and boron trichloride allowed to melt with partial vapourisation at -78.5°. To permit the boron trichloride to attack any traces of moisture remaining in the system, the apparatus is left overnight. Any hydrogen chloride produced during this
procedure is removed by pumping away a small proportion (2-3%) of the boron trichloride.

The system is now ready to be used. With the diffusion pump in operation, the arc is struck by turning up the "Variac" until the striking voltage across the cell is reached (about 2500V). The "Variac" is then turned down until the lowest potential at which the discharge will operate without extinguishing (less than 1000V). If the discharge is functioning correctly, within 10-30 minutes of switching on, a yellow film will appear in trap A just above the level of the coolant. The non-appearance of this colouration normally indicates the presence of hydrogen chloride in the system and it should be pumped away. No diboron tetrachloride will form when any trace of hydrogen chloride is present.

As the preparation proceeds, the whole tube connecting the discharge cell to trap A becomes coated with mercury and a yellow film of boron monochloride polymer $(\text{BCl}_x)$. If the reaction is allowed to proceed until most of the boron trichloride is converted into the subchlorides (normally after about 20 hours) the vapour pressure of the system, recorded on the manometer, drops below the initial value of about 4mm. The volatile boron chlorides can then be distilled out of the discharge system for fractionation. Any excess boron trichloride is removed by holding the mixture at a
temperature of \(-78.5^\circ\) overnight and condensing out the volatile material by means of liquid nitrogen. \(B_4\text{Cl}_4\) can be separated by distilling the partially purified product through a U-trap held at a temperature of \(-25^\circ\).

During the course of the discharge, grey-black solids build up in the discharge cell. These must be removed after about 20 hours to allow the circulation of boron trichloride to continue. This removal is done when the boron halides have been removed from the discharge system. It is carried out by removing the cooling bath; the quartz cell is then heated to dislodge these grey-black solids, which fall into the bulb B (ref. diagram 50). The system can now be re-used, using the same procedure as before, until the bulb B is filled with excess mercury and solid debris, when it is necessary for the cell to be removed and cleaned.

5.6 Identification of Additional By-products

a. Mercurous chloride

- It has generally been assumed that mercurous chloride is formed in the discharge, yet there is a lack of positive evidence to substantiate this. To try to clarify this assumption, samples of the copious quantities of brownish-grey deposits produced in the discharge cell were subjected to X-ray powder photography. It resulted in positive identification of mercurous chloride (\(Hg_2\text{Cl}_2\)), whilst no sign of
mercuric chloride was found.

b. \( \text{B}_9\text{Cl}_9 \) and \( \text{B}_{10}\text{Cl}_{10} \)

During the mercury discharge preparation of diboron tetrachloride, the exit tube of the discharge cell becomes covered with a bright yellow film. Despite it being a very conspicuous product of the discharge, there are no known attempts to identify it. To attempt this identification, a section of the yellow coated tubing was carefully sealed off from the rest of the apparatus and opened in a dry box. The yellow material was found to be freely soluble in dry carbon tetrachloride, so it could be decanted into a vessel of the type shown in diagram 15a, the solvent removed and the solid introduced into a mass spectrometer. The mass spectrum showed that the yellow film was mainly \( \text{B}_9\text{Cl}_9 \) with a small percentage (less than 5%) of \( \text{B}_{10}\text{Cl}_{10} \). No difference was found between material sublimed from the bulk and the unpurified solid.

5.7 Mechanism of the Reaction in the Mercury Discharge

Schlesinger postulated a simple mechanism for the formation of diboron tetrachloride. He claimed that at first, mercury atoms excited by the discharge would strip off a chlorine atom from the boron trichloride:

\[
2\text{Hg} + 2\text{BCl}_3 \rightarrow 2\text{BCl}_2 + \text{Hg}_2\text{Cl}_2.
\]
Secondly, the BCl₂ radicals dimerised, to give diboron tetrachloride:

\[ 2\text{BCl}_2 \rightarrow \text{B}_2\text{Cl}_4. \]

Another possible intermediate is the monohalide radical BCl. The band system of BCl was detected in the emission spectrum of the diboron tetrachloride—preparing microwave discharge through boron trichloride, and it is thought that BCl is an intermediate in this case.

The emission spectrum of BCl and BCl₂ have both been described in the literature. In 1924 the \( \Pi - \Sigma^+ \) band system of BCl was discovered to be in the region 2600–2900 Å. Subsequently the vibrational structure was analysed by Miescher, who described a total of 134 bands consisting of well-developed sequences, some of which degraded to the violet (shorter wavelengths) and some to the red (the longer wavelength end of the spectrum). The emission spectrum of BCl₂ lies in the region 2920–3600 Å, thus the species emit radiation at different wavelengths.

In attempting to investigate the mechanism more thoroughly, the emission spectrum of the electrical discharge was studied using both a small quartz and a large glass–quartz spectrograph. The small quartz spectrograph (Hilger and Watts, type E484), was used to
ascertain whether the emission spectrum of the mercury discharge through boron trichloride vapour contained any lines or bands in the regions of interest. The spectrograph records values from approximately 2000Å to 6500Å on photographic plates (measuring 5\(\frac{1}{2}\)in. by 4\(\frac{1}{2}\)in.).

So as to enable light emerging from the discharge cell to pass into the spectrograph, a 2cm. silica window was cemented into the bath containing the cell's cooling water, and the spectrograph raised on its optical bench to the same height as the silica cell and window.

Initially the photographic plates were exposed for just a few seconds. The developed plate revealed several lines, and as a wavelength scale had been printed onto the plate, it was perfectly easy and straightforward to determine the position of these lines. On their investigation they were found to be part of the emission spectrum of mercury. To find out if any other species were present in the discharge spectrum, longer exposures (10-20 min.) were attempted. The resulting photographic plates were found to contain band systems around 2700Å, which is the position where the most intense part of the spectrum of the BCl species is known to occur. However, neither examination of the spectrum with a travelling microscope nor photographic
enlargement could sufficiently clarify the bands for proper analysis.

As the spectrum appeared to contain band systems, a large glass-quartz spectrograph (Hilger and Watts, type E742) was substituted for the small quartz one. The discharge apparatus had to be altered in order to bring the cell exactly in line with the entry slit of the large spectrograph. The dispersion produced by this spectrograph is approximately nine times larger than that given by the smaller one; larger photographic plates were used and only one third of the spectrum range (2000 to 6500Å) was exposed at a time.

Exposures were made within the range 2300Å to 3100Å. Optimum conditions for the production of spectra of sufficient intensity and clarity were found to be an exposure time of 60 minutes and an entry slit of 0.03mm. A calibration scale (consisting of equally-spaced units numbered 0-23) was superimposed on the emission spectrum to help in the measurement of band and line positions.

The lines in the spectrum were all assigned to the known emission spectra of either mercury, silicon or boron. Since they were well distributed throughout they also served as useful internal calibrants to
determine the positions of the very large number of observed bands. The spectrum was calibrated by plotting observed positions against the known wavelength of the mercury, boron and silicon lines. The resulting calibration graphs were used to determine the positions of the observed band heads; accuracy was estimated to be within ±0.04 mm of literature values. Nearly all the observed bands corresponded to the values of BCl described by Miescher (47) in position, intensity and direction of degrading. However, in some regions, the resolution was insufficient to enable closely-spaced bands to be adequately distinguished. This is demonstrated in photographs I and II, which show sections of the recorded spectrum. A list of the observed BCl band heads and a comparison with values obtained by Miescher is given in table 12.

As can be seen from the photographs, the main features of the spectrum of BCl are progressions of band sequences. In a band sequence, transitions are 1-0, 2-1, 3-2 etc., the numbers referring to \( v_1 \), being the vibrational quantum number of the excited state and \( v_{11} \), being the vibrational quantum number of the ground state. The positions of the following band sequences are indicated on the photographs: \( \Delta v = 1, \Delta v = -1, \Delta v = -2 \) and \( \Delta v = -3 \). No further band sequences were observed or assigned either by Miescher (47) or by Herzberg and Hushley (58), who carried out the rotational analysis of the BCl species.
\( \Delta v = -1 \)

\( \Delta v = 0 \)

\( \Delta v = +1 \)
Values calculated for the series $\Delta v = -4$

$\Delta v = -3$

$\Delta v = -2$
Table 12

Comparison between BCl band heads tabulated by Miescher* and values obtained in this research

\(I = \text{intensity, } d = \text{direction of degrading}\).

<table>
<thead>
<tr>
<th>Position (Å)</th>
<th>I</th>
<th>d</th>
<th>Position (Å)</th>
<th>I</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2598.2</td>
<td>0</td>
<td>r</td>
<td>2598.3</td>
<td>vw</td>
<td>r</td>
</tr>
<tr>
<td>2600.75</td>
<td>0</td>
<td>r</td>
<td>2600.7</td>
<td>vw</td>
<td>r</td>
</tr>
<tr>
<td>2604.15</td>
<td>1</td>
<td>r</td>
<td>2604</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2604.65</td>
<td>0</td>
<td>r</td>
<td>2604.7</td>
<td>vw</td>
<td>r</td>
</tr>
<tr>
<td>2607.70</td>
<td>0</td>
<td>r</td>
<td>2608</td>
<td>vw</td>
<td>r</td>
</tr>
<tr>
<td>2610.65</td>
<td>2</td>
<td>r</td>
<td>2610.7</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2611.25</td>
<td>0</td>
<td>r</td>
<td>2611.4</td>
<td>vw</td>
<td>r</td>
</tr>
<tr>
<td>2615.55</td>
<td>1</td>
<td>r</td>
<td>2615.5</td>
<td>vw</td>
<td>r</td>
</tr>
<tr>
<td>2618.07</td>
<td>3</td>
<td>r</td>
<td>2618</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2618.52</td>
<td>2</td>
<td>r</td>
<td>2618.5</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2619.85</td>
<td>1</td>
<td>r</td>
<td>2620</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2625.00</td>
<td>1</td>
<td>r</td>
<td>2625</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2626.85</td>
<td>4</td>
<td>r</td>
<td>2627.7</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2627.95</td>
<td>2</td>
<td>r</td>
<td>2628</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2637.58</td>
<td>3</td>
<td>r</td>
<td>2637.7</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2638.38</td>
<td>2</td>
<td>r</td>
<td>2638.2</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2640.95</td>
<td>6</td>
<td>r</td>
<td>2641</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2653.96</td>
<td>6</td>
<td>r</td>
<td>2654</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2659.76</td>
<td>8</td>
<td>r</td>
<td>2660</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>2660.19</td>
<td>8</td>
<td>v</td>
<td>2660.4</td>
<td>ms</td>
<td>v</td>
</tr>
<tr>
<td>2662.18</td>
<td>7</td>
<td>v</td>
<td>2662.2</td>
<td>s</td>
<td>v</td>
</tr>
<tr>
<td>Position (Å)</td>
<td>I</td>
<td>d</td>
<td>Position (Å)</td>
<td>I</td>
<td>d</td>
</tr>
<tr>
<td>-------------</td>
<td>---</td>
<td>---</td>
<td>-------------</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2662.49</td>
<td>5</td>
<td>v</td>
<td>2663.5</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2663.50</td>
<td>7</td>
<td>r</td>
<td>2664.95</td>
<td>9</td>
<td>r</td>
</tr>
<tr>
<td>2665.32</td>
<td>9</td>
<td>v</td>
<td>2665.59</td>
<td>5</td>
<td>v</td>
</tr>
<tr>
<td>2668.46</td>
<td>3</td>
<td>r</td>
<td>2668.5</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2669.71</td>
<td>8</td>
<td>r</td>
<td>2669.8</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2672.67</td>
<td>1</td>
<td>r</td>
<td>2673.14</td>
<td>5</td>
<td>r</td>
</tr>
<tr>
<td>2673.15</td>
<td>1</td>
<td>r</td>
<td>2675.69</td>
<td>5</td>
<td>r</td>
</tr>
<tr>
<td>2681.99</td>
<td>4</td>
<td>r</td>
<td>2682</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2683.52</td>
<td>2</td>
<td>r</td>
<td>2684.27</td>
<td>5</td>
<td>r</td>
</tr>
<tr>
<td>2684.49</td>
<td>6</td>
<td>r</td>
<td>2685.1</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2694.49</td>
<td>6</td>
<td>r</td>
<td>2694.5</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2697.45</td>
<td>6</td>
<td>r</td>
<td>2697.5</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2703.60</td>
<td>7</td>
<td>r</td>
<td>2703.5</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2706.28</td>
<td>7</td>
<td>r</td>
<td>2706</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2714.16</td>
<td>8</td>
<td>r</td>
<td>2714.3</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2720.04</td>
<td>10</td>
<td>v</td>
<td>2720</td>
<td>vs</td>
<td>v</td>
</tr>
<tr>
<td>2720.23</td>
<td>7</td>
<td>v</td>
<td>2721.82</td>
<td>6</td>
<td>v</td>
</tr>
<tr>
<td>2721.68</td>
<td>10</td>
<td>v</td>
<td>2722.2</td>
<td>m</td>
<td>v</td>
</tr>
<tr>
<td>2722.18</td>
<td>10</td>
<td>v</td>
<td>2722.35</td>
<td>7</td>
<td>v</td>
</tr>
<tr>
<td>Values obtained by Miescher</td>
<td>Values obtained in this research</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Position (Å)</strong></td>
<td><strong>I</strong></td>
<td><strong>d</strong></td>
<td><strong>Position (Å)</strong></td>
<td><strong>I</strong></td>
<td><strong>d</strong></td>
</tr>
<tr>
<td>2723.60</td>
<td>8</td>
<td>v</td>
<td>2723.5</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2723.98</td>
<td>10</td>
<td>v</td>
<td>2724.1</td>
<td>vs</td>
<td>v</td>
</tr>
<tr>
<td>2724.48</td>
<td>7</td>
<td>v</td>
<td>2724.5</td>
<td>s</td>
<td>v</td>
</tr>
<tr>
<td>2727.21</td>
<td>8</td>
<td>r</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2727.59</td>
<td>10</td>
<td>r</td>
<td>2727.5</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td>2727.85</td>
<td>9</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2729.11</td>
<td>3</td>
<td>r</td>
<td>2729.2</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2729.37</td>
<td>6</td>
<td>r</td>
<td>2730.94</td>
<td>3</td>
<td>r</td>
</tr>
<tr>
<td>2730.94</td>
<td>3</td>
<td>r</td>
<td>2735.12</td>
<td>7</td>
<td>r</td>
</tr>
<tr>
<td>2735.55</td>
<td>9</td>
<td>r</td>
<td>2735.1</td>
<td>s</td>
<td>r</td>
</tr>
<tr>
<td>2734.70</td>
<td>4</td>
<td>r</td>
<td>2734.7</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2738.03</td>
<td>3</td>
<td>r</td>
<td>2738.7</td>
<td>ms</td>
<td>r</td>
</tr>
<tr>
<td>2738.58</td>
<td>7</td>
<td>r</td>
<td>2740.6</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2740.80</td>
<td>6</td>
<td>r</td>
<td>2740.6</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2748.60</td>
<td>2</td>
<td>r</td>
<td>2749.1</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2750.60</td>
<td>2</td>
<td>r</td>
<td>2750.9</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2752.58</td>
<td>2</td>
<td>r</td>
<td>2761.6</td>
<td>w</td>
<td>r</td>
</tr>
<tr>
<td>2761.70</td>
<td>2</td>
<td>r</td>
<td>2762.4</td>
<td>m</td>
<td>r</td>
</tr>
<tr>
<td>2762.55</td>
<td>5</td>
<td>r</td>
<td>2763</td>
<td>vv</td>
<td>r</td>
</tr>
<tr>
<td>2763.1</td>
<td>0</td>
<td>r</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

122.
### Table 12. (continued)

<table>
<thead>
<tr>
<th>Position (Å)</th>
<th>I</th>
<th>d</th>
<th>Values obtained by Miescher</th>
<th>Position (Å)</th>
<th>I</th>
<th>d</th>
<th>Values obtained in this research</th>
</tr>
</thead>
<tbody>
<tr>
<td>2782.22</td>
<td>7</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2782.74</td>
<td>7</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2783.27</td>
<td>6</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2783.69</td>
<td>9</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2784.13</td>
<td>8</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2784.44</td>
<td>8</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2785.08</td>
<td>3</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2785.63</td>
<td>2</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2786.18</td>
<td>7</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2786.44</td>
<td>8</td>
<td>r</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2786.71</td>
<td>8</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2786.99</td>
<td>2</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2787.77</td>
<td>6</td>
<td>v</td>
<td></td>
<td>2787.6</td>
<td>vs</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>2789.09</td>
<td>1</td>
<td>v</td>
<td></td>
<td>2789.2</td>
<td>w</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>2789.59</td>
<td>6</td>
<td>v</td>
<td>2789.3</td>
<td>mw</td>
<td>v</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>2790.68</td>
<td>2</td>
<td>v</td>
<td>2790.4</td>
<td>w</td>
<td>v</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>2791.77</td>
<td>6</td>
<td>r</td>
<td></td>
<td>2792</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2792.11</td>
<td>5</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2792.40</td>
<td>9</td>
<td>r</td>
<td></td>
<td>2792.8</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2792.75</td>
<td>8</td>
<td>v</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2795.47</td>
<td>5</td>
<td>r</td>
<td>2795.7</td>
<td>w</td>
<td>r</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2796.08</td>
<td>8</td>
<td>r</td>
<td>2796.5</td>
<td>w</td>
<td>r</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2798.96</td>
<td>2</td>
<td>r</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2799.69</td>
<td>6</td>
<td>r</td>
<td>2800.1</td>
<td>m</td>
<td>r</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2833.19</td>
<td>0</td>
<td>r</td>
<td>2833.4</td>
<td>w</td>
<td>r</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 12. (continued)

<table>
<thead>
<tr>
<th>Values obtained by Miescher</th>
<th>Values obtained in this research</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Position (Å)</strong></td>
<td><strong>I</strong></td>
</tr>
<tr>
<td>28.3688</td>
<td>2</td>
</tr>
<tr>
<td>28.4194</td>
<td>3</td>
</tr>
<tr>
<td>28.4288</td>
<td>3</td>
</tr>
<tr>
<td>28.4730</td>
<td>7</td>
</tr>
<tr>
<td>28.4747</td>
<td>7</td>
</tr>
<tr>
<td>28.4859</td>
<td>6</td>
</tr>
<tr>
<td>28.4884</td>
<td>3</td>
</tr>
<tr>
<td>28.4956</td>
<td>1</td>
</tr>
<tr>
<td>28.5078</td>
<td>2</td>
</tr>
<tr>
<td>28.5085</td>
<td>2</td>
</tr>
<tr>
<td>28.5139</td>
<td>7</td>
</tr>
<tr>
<td>28.5171</td>
<td>7</td>
</tr>
<tr>
<td>28.5196</td>
<td>7</td>
</tr>
<tr>
<td>28.5294</td>
<td>2</td>
</tr>
<tr>
<td>28.5392</td>
<td>6</td>
</tr>
<tr>
<td>28.5424</td>
<td>1</td>
</tr>
<tr>
<td>28.5548</td>
<td>6</td>
</tr>
<tr>
<td>28.5728</td>
<td>7</td>
</tr>
<tr>
<td>28.5817</td>
<td>6</td>
</tr>
<tr>
<td>28.5924</td>
<td>8</td>
</tr>
<tr>
<td>28.6039</td>
<td>10</td>
</tr>
<tr>
<td>28.6245</td>
<td>2</td>
</tr>
<tr>
<td>28.6581</td>
<td>6</td>
</tr>
<tr>
<td>28.6696</td>
<td>6</td>
</tr>
<tr>
<td>28.6715</td>
<td>7</td>
</tr>
<tr>
<td>Position (Å)</td>
<td>I</td>
</tr>
<tr>
<td>-------------</td>
<td>----</td>
</tr>
<tr>
<td>2869.55</td>
<td>5</td>
</tr>
<tr>
<td>2874.95</td>
<td>1</td>
</tr>
<tr>
<td>2877.20</td>
<td>1</td>
</tr>
<tr>
<td>2879.07</td>
<td>2</td>
</tr>
<tr>
<td>2880.65</td>
<td>6</td>
</tr>
<tr>
<td>2911.45</td>
<td>8</td>
</tr>
<tr>
<td>2912.36</td>
<td>3</td>
</tr>
<tr>
<td>2912.74</td>
<td>3</td>
</tr>
<tr>
<td>2913.53</td>
<td>3</td>
</tr>
<tr>
<td>2914.91</td>
<td>3</td>
</tr>
<tr>
<td>2919.80</td>
<td>3</td>
</tr>
<tr>
<td>2922.15</td>
<td>4</td>
</tr>
</tbody>
</table>
The sequences $\Delta v=1$ and $\Delta v=0$ are shown in detail in photograph I. From this it can be seen that for one transition from an excited state vibrational level to a ground state vibrational level there is very often more than one band. This is because there are three main complicating factors affecting the complexity of the observed spectrum:

1. Four isotopic species of BCl exist ($^{10}$B$^{35}$Cl, $^{11}$B$^{35}$Cl, $^{10}$B$^{37}$Cl and $^{11}$B$^{37}$Cl), whose spectra overlap;

2. In general, each band has two heads;

3. The bands are not all shaded in the same direction.

In all, over eighty band heads were measured, and these calculated positions agreed with the literature values within experimental error (± 0.04nm.); the intensities and direction of degrading of these bands were in accordance with expectation. Very few lines or bands remained unassigned, although some lay in the region from 2920-3600Å where the emission spectrum of the triatomic BCl$_2$ radical is known to occur (57). However, as photograph II shows, these lines (which lie between the mercury lines at 296.73 and 302.15nm.) are very weak, and their positions do not correspond to values given for BCl$_2$. Calculations were therefore made to discover if these lines could be assigned to a previously unobserved BCl system. Using the formula devised by Herzberg and Hushloy (58) for calculating the
positions of Q heads for the $^{10}\text{B}^{35}\text{Cl}$ and $^{11}\text{B}^{35}\text{Cl}$ molecules:

$$
\nu^{(10,\text{B}^{35}\text{Cl})} = 36750.92 + 880.58(\nu^1 + 1/2) - 12.25(\nu^1 + 1/2)^2 \\
-0.01116(\nu^1 + 1/2)^3 - 0.0313(\nu^1 + 1/2)^4 \\
- 870.29(\nu^{11} + 1/2)^2 - 5.50(\nu^{11} + 1/2)^2
$$

and

$$
\nu^{(11,\text{B}^{35}\text{Cl})} = 36750.92 + 849.04(\nu^1 + 1/2) - 11.37(\nu^1 + 1/2)^2 \\
-0.100(\nu^1 + 1/2)^3 - 0.027(\nu^1 + 1/2)^4 \\
- 837.12(\nu^{11} + 1/2)^2 - 5.11(\nu^{11} + 1/2)^2
$$

and incorporating the difference factor between the observed band head and the calculated zero line:

$$
\nu_{\text{vertex}} - \nu_0 = -\frac{(B_{\nu}^1 + B_{\nu}^{11})^2}{4(B_{\nu}^1 + B_{\nu}^{11})}
$$

(using Herzberg and Hushley's $B_{\nu}$ values), it was found that the sequence $\Delta \nu = -4$ gave bands in the region of interest.

It is perhaps not surprising that this new band sequence may have been observed in this research, for the mercury discharge generates very high energy conditions during the preparation of diboron tetrachloride. In contrast with these energetic
conditions, the research workers interested solely in vibrational and rotational analysis of the emission spectrum of BCl used much less powerful methods to produce and excite the radicals. For example, Herzberg and Hushley (58) used an electrodeless discharge through helium with a small amount of boron trichloride added, and they only observed the sequences \( \Delta v = +1, \Delta v = 0, \Delta v = -1 \) and \( \Delta v = -2 \).

Consequently, there are two possible precursors for the production of diboron tetrachloride: either boron atoms or the diatomic molecule BCl. Holzmann and Morris (46) detected only bands identified as BCl and lines due to atomic boron and atomic chlorine in the emission spectrum of the diboron tetrachloride preparing microwave discharge. They postulated that BCl was, in fact, the intermediate in the production of diboron tetrachloride:

\[
\text{BCl}_3 + \text{BCl} \rightarrow \text{B}_2\text{Cl}_4.
\]

As a result of this research, it seems probable that BCl is similarly the intermediate in the mercury discharge synthesis. If the boron atom in BCl has its orbitals sp hybridised, then the molecule will have a lone pair of electrons in one of the two sp hybrids:
As such, the molecule can act as a Lewis base to the boron trichloride (which has a vacant p orbital at right angles to the plane of the three chlorine atoms):

If the above Lewis acid-base complex is considered as the reaction intermediate, a chlorine migration from one boron to the other, will generate a molecule of diboron tetrachloride:
Assuming that the above mechanism for the diboron tetrachloride synthesis is correct, then each molecule of B$_9$Cl$_9$ produced on the exit tubes of the discharge cell must be formed at the expense of nine molecules of diboron tetrachloride. This suggests that the yield of diboron tetrachloride should increase if the pressure of boron trichloride passing through the discharge were increased (so as to trap all the BCl molecules with boron trichloride). Perhaps this is partly the reason for the higher yields quoted by Wartik\textsuperscript{(53)} for his copper discharge preparation of diboron tetrachloride; the pressures of boron trichloride which he used were approximately five times greater than those used in the course of this work (although the temperatures generated may be substantially less than in the mercury discharge, so lowering the tendency for the diboron tetrachloride, once formed, to undergo irreversible thermal decomposition).

Relatively large quantities of the yellow deposit of B$_9$Cl$_9$ and B$_{10}$Cl$_{10}$ (and B$_4$Cl$_4$) are produced when diboron tetrachloride is passed through the mercury discharge, presumably because there is virtually no boron trichloride present which can trap the BCl molecules; the latter then polymerise to the B$_n$Cl$_n$ derivatives.

5.8 Decomposition of Diboron Tetrachloride

The thermal decomposition of diboron tetrachloride is also thought to involve the BCl species
since several BCl polymers are formed:

\[
\text{B}_2\text{Cl}_4 \longrightarrow \text{BCl}_3 + \text{BCl} \longrightarrow (\text{BCl})_n \quad n=8-12.
\]

Strong evidence in support of this comes from adiabatic flash photolysis reactions\(^{(60)}\) which were carried out on diboron tetrachloride. Since this equation is the exact opposite to that postulated for the formation of the diboron tetrachloride, it would appear that the reaction is reversible under certain conditions,

\[
\text{B}_2\text{Cl}_4 \longrightarrow \text{BCl}_3 + \text{BCl},
\]

and that during the decomposition the equilibrium is shifted to the right by the formation of BCl polymers.

The mechanism of the thermal decomposition of diboron tetrachloride is not understood, although the reaction products are known to be temperature dependent. At room temperature, the decomposition produces a majority of the larger boron-chlorine cage compounds (\(\text{B}_{10}\text{Cl}_{10}, \text{B}_{11}\text{Cl}_{11}\) and \(\text{B}_{12}\text{Cl}_{12}\)), whereas at higher temperatures (\(80^\circ\)), the smaller cages (particularly \(\text{B}_6\text{Cl}_8\)) predominate. The fact that, contrary to earlier reports\(^{(13)}\), no \(\text{B}_4\text{Cl}_4\) is formed in the thermal decomposition of diboron tetrachloride has led to consideration of the possibility that the larger cages are built up from insertion of BCl into the smaller cages.
However, the addition of $\text{B}_4\text{Cl}_4$ to the decomposing diboron tetrachloride showed that the $\text{B}_4\text{Cl}_4$ could be recovered after the reaction was completed. This indicates in fact that the $\text{B}_4\text{Cl}_4$ cage is not involved in the formation of larger cages. The only reasonable mechanism for the production of the cage compounds must involve nido-species (ie. open frameworks) of boron subchlorides, which can either grow larger by the addition of BCl or close up to form a completed cage. So far, no such intermediates have been detected.

The action of a silent electric discharge accelerates the decomposition of the diboron tetrachloride, leading to the production of $\text{B}_4\text{Cl}_4$ (which decomposes in the discharge if it is not removed) together with a mixture of the $(\text{BCl})_n$ cage compounds. Table 13 lists the products of the three different methods which have been used to decompose diboron tetrachloride. Since different combinations of products are obtained, it would appear that the three methods must either involve different reaction mechanisms, or, if BCl is the intermediate in all cases, then the conditions prevailing in each decomposition method must cause the postulated nido-cages to close at different stages.
Table 13. Summary of products obtained from different diboron tetrachloride decompositions

<table>
<thead>
<tr>
<th>Decomposition Method</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal decomposition</td>
<td>B₈Cl₈, B₉Cl₉, B₁₀Cl₁₀, B₁₁Cl₁₁, B₁₂Cl₁₂</td>
</tr>
<tr>
<td>Mercury discharge</td>
<td>B₄Cl₄, B₉Cl₉, B₁₀Cl₁₀</td>
</tr>
<tr>
<td>Silent electric discharge</td>
<td>B₄Cl₄, B₈Cl₈, B₉Cl₉, B₁₀Cl₁₀, B₁₁Cl₁₁, B₁₂Cl₁₂</td>
</tr>
</tbody>
</table>

5.9 Other Boron Subhalides

Diboron tetrachloride can be used to prepare the other diboron tetrahalides. Diboron tetrabromide and diboron tetraiodide can be made by treating diboron tetrachloride with the suitable boron trihalide, diboron tetrafluoride being formed when antimony trifluoride reacts with the tetrachloride. The thermal decomposition reactions of both diboron tetrabromide and diboron tetraiodide are known to produce \((BX)\) polymers. The composition of the boron monoiiodide \((BI)_x\) is unknown as it was found to be involatile, but the boron subbromides \(B_7Br_7\), \(B_8Br_8\) and \(B_9Br_9\) have been isolated from the diboron tetrabromide and again have been identified by means of mass spectrometry. Part of this research has been involved with investigations into the boron subbromides; and these are described in a later section.
a. Boron Subiodides

In order to discover the nature of iodine-containing boron monohalide compounds, a small amount of boron tri-iodide was added to decomposing diboron tetrachloride. It was hoped to substitute both chlorine and iodine atoms onto a boron cage, which might prove volatile and so could be identified mass spectrosopically. At first, bright yellow crystals of diboron tetraiodide were formed, but these decomposed when the mixture was heated at 90°. After three days, the reaction vessel was removed from the oven and the volatile solid products were removed in the usual way for mass spectral analysis. This was found to be complicated by the overlap between fully chlorinated cages, and compounds each containing both chlorine and iodine substituents. For example, the largest peak given by $\text{B}_{11}\text{Cl}_{11}^+$ is at m/e 509, whereas the largest peak of $\text{B}_9\text{Cl}_8\text{I}^+$ is at m/e 510. Nevertheless it has proved possible to assign observed peaks in the mass spectrum to $\text{B}_{11}\text{Cl}_{10}\text{I}$, $\text{B}_{10}\text{Cl}_8\text{I}_2$ (or $\text{B}_{12}\text{Cl}_{11}\text{I}$), and $\text{B}_{11}\text{Cl}_9\text{I}_2$.

b. Boron Subfluorides

Diboron tetrafluoride was first prepared by a halogen exchange reaction (61):

$$3\text{B}_2\text{Cl}_4 + 4\text{SbF}_3 \rightarrow 3\text{B}_2\text{F}_4 + 4\text{SbCl}_3.$$
A more recent synthesis\(^{(64)}\) has involved the monofluoride BF, which is prepared by passing boron trifluoride over boron at \(2000^\circ\) and 0.1 to 1.0 mm pressure. Under these conditions, the equilibrium

\[
2\text{B}(s) + \text{BF}_3(g) \rightleftharpoons 3\text{BF}(g)
\]

is appreciably shifted to the right and the resultant greenish-white polymeric deposit, on warming to room temperature, gives off three major fractions besides boron trifluoride; these are diboron tetrafluoride, \(\text{B}_2\text{F}_5\) and colourless, slightly volatile boron fluorides containing up to fourteen boron atoms. At least some of the diboron tetrafluoride is thought to be formed from the direct combination of BF and boron trifluoride. The higher boron fluorides have also been prepared by the reaction between BF and diboron tetrafluoride. The main product is \(\text{B}_3\text{F}_5\), which is formed as an unstable solid and quickly disproportionates to diboron tetrafluoride and the yellow liquid \(\text{B}_8\text{F}_{12}\).

The structures of these polymeric boron fluorides do not involve the boron cages commonly found in the boron subchlorides. \(\text{B}_3\text{F}_5\) has been formulated as \(\text{F}_2\text{B.BF.BF}_2\), and it is probably the first compound to be isolated with a simple \(\text{B}_5\) chain (although dimethylamino derivatives with up to five
members in the boron chain are now known \(^{(49)}\). Evidence from its \(^{19}\text{F}n.m.r.\) spectrum suggests that \(B_8F_{12}\) may be formulated as \(B_2(BF_2)_6\), and it behaves chemically like diborane, reacting with many Lewis bases to give stable complexes \(^{(65)}\) (ie. \((BP_2)_3BL\), analogous to \(H_3BL\)).

No boron cages containing fluorine substituents have yet been characterised. Attempts were made during this research to substitute fluorine atoms onto boron-chlorine cages by allowing diboron tetrachloride to decompose in the presence of boron trifluoride (at a room-temperature pressure of approximately 2 atmospheres). However the volatile solid products of this reaction were found to contain no fluorine. It should also be noted that following investigations into the electronic structure of \(B_4Cl_4\) (the only boron cage subhalide yet examined in this way), it was suggested that \(B_4F_4\) might be unstable \(^{(41)}\).
6. PREPARATION & PROPERTIES OF $\text{B}_9\text{Br}_9$
6. PREPARATION AND PROPERTIES OF B₉Br₉

For many years, it seemed that chlorine was the only halogen capable of forming neutral polyhedral boron monohalides. This contrasted with the \( B_nX_n^{2-} \) series, where the boron cages can be substituted with a variety of substituent groups \( X \), including all the halogens. Because of this, it was interesting to note that some years ago Diener and Pflugmacher (66) obtained a red-brown boron monobromide from the action of a silent electric discharge on boron tribromide. They demonstrated the volatility of the compound in a vacuum, yet identified it only as \( (BBr)_X \). Although Rosenberg (67) failed to repeat this work, the silent electric discharge equipment was set up in this research in an attempt to reproduce the original results and to characterise the products more fully.

In the initial experiments, a liquid sample of boron tribromide was kept at room temperature in a vessel similar to that shown in diagram 22, and the vapour above it was passed through a silent electric discharge. Under these conditions, the liquid rapidly assumed a red colour, but on disconnection of the discharge, the colour slowly disappeared. This red colour was due to free bromine, which appeared to attack any of the sub-bromide formed; which in turn
reconstituted boron tribromide. To remove the bromine produced during the operation of the discharge, the apparatus was reconstructed, with clean, dry copper wool inserted into the discharge cavity. Using this system, no free bromine was observed, however the discharge had a noticeable effect on the copper wool. On switching off the discharge and removing the electrodes, the copper wool was found to be black in colour. This black surface layer slowly changed to a white material, which was shown by X-ray powder diffraction to consist of \( \gamma \)-copper(I) bromide. It is thought that a surface layer of cupric bromide (black) forms whilst the discharge is in operation, with the bromine atoms continually diffusing into the copper. When the production of bromine ceases, the surface layer reverts to cuprous bromide (white), which is the more stable compound of the two under these conditions.

A colourless, spontaneously inflammable compound was the initial product of this reaction. It has been assumed that this is diboron tetrabromide, since the two compounds have similar properties. Using trap-to-trap distillation, the further action of the discharge on the diboron tetrabromide produced a dark red compound which was found to be soluble in the excess boron tribromide to give a ruby-red solution. (Separate experiments have shown that pure diboron tetrabromide produces only \( \text{B}_9\text{Br}_9 \) when passed through the copper-free
discharge. This differs from diboron tetrachloride which gives a mixture of polymeric boron monochlorides. Evaporation of the boron tribromide, followed by vacuum sublimation of the red material, showed it to be a single compound, identified by mass spectrometry as $B_9Br_9$ (ref. diagram 31).

The copper wool in the discharge effectively removed all the bromine produced, so preventing the reversal of the proposed first step in the preparation of $B_9Br_9$:

$$2BBr_3 \rightleftharpoons B_2Br_4 + BBBr_2$$
$$9B_2Br_4 \rightarrow (BBBr)_9 + 9BBBr_3.$$

Free bromine and boron tribromide cannot be separated easily by simple fractionation since the volatilities of the two materials are very similar.

The reason for Rosenberg's lack of success may have been that he made no attempt to remove the free halogen, rather than, as he suggested, the use of conditions insufficiently vigorous to bring about the decomposition of the boron tribromide. As Diener and Pflugmacher did not state whether or not they made use of a "bromine getter", it is possible that in their experiments the $B_9Br_9$ was quickly formed in a static situation, without any circulation of the reactants.
31. COMPARISON OF THE OBSERVED & THEORETICAL INTELSITIES FOR THE MOLECULAR ION IN $B^g_9D^g_9$
$B_9Br_9$ readily forms large, dark red crystals either when it is sublimed under vacuum conditions or when allowed to crystallise from boron tribromide. Similar to the corresponding chloride $^{(20)}$, it was found impossible to record the melting point of $B_9Br_9$ due to its rapid sublimation (to a bright yellow vapour).

As with the polymeric boron monochlorides, $B_9Br_9$ has insufficient substituent nuclei to accommodate an open structure such as that of nonaborane $^{(15)}$ (ref. diagram 4), and can therefore be proposed to possess a cage structure from its formula alone. Comparison of X-ray diffraction data has shown that $B_9Br_9$ and $B_9Cl_9$ have the same molecular shape and crystallise in the same form, and comparisons of the mass spectra, infra-red spectra and ultraviolet spectra of the two compounds also provide evidence leading to the same conclusion.

5.1 X-Ray Powder Diffraction

The X-ray crystallographic determination of a single crystal is often the only method capable of unambiguously determining the structure of a solid. If, however, the structure of one compound has been determined in this way, then a second compound can sometimes be shown to possess the same crystal structure as the first by the comparison of the X-ray diffraction patterns of polycrystalline samples of the two compounds.
It was hoped to use this procedure to prove that \( B_9\text{Br}_9 \) possesses the same structure as \( B_9\text{Cl}_9 \), which has been shown by the X-ray crystallographic determination of a single crystal to have a monoclinic boron cage structure with a terminal chlorine atom on each boron \(^{22}\). The cage has the shape of a tricapped trigonal prism with three boron atoms and their associated chlorines sitting on the crystallographic plane. If the two compounds were indeed isostructural, then \( B_9\text{Br}_9 \) would be expected to have a larger unit cell than \( B_9\text{Cl}_9 \). The X-ray powder diffraction photograph should therefore contain lines at slightly lower angles than those of \( B_9\text{Cl}_9 \) (this follows from the Bragg equation:

\[
\sin \theta = \frac{n \lambda}{2d},
\]

where \( d \) is the distance between parallel planes in the crystal). The intensity distributions might also be expected to be similar, particularly at lower angles.

An X-ray powder diffraction photograph was accordingly taken of a powdered sample of \( B_9\text{Br}_9 \), using the Debye-Scherrer method (as described on page 60). Several sharply defined rings were produced, as can be seen in the photograph shown on page 143. Unfortunately no suitable samples of \( B_9\text{Cl}_9 \) could be prepared. Not only were insufficient amounts available (it was prepared by heating a mixture of \( B_8\text{Cl}_8 \) and \( B_9\text{Cl}_9 \) at 450° for
30 minutes; under these conditions all the $B_9Cl_8$ decomposes, but the original mixture normally only contains a small proportion of $B_9Cl_9$, but also the compound was found to be much more air-sensitive than $B_9Br_9$. The methods used to insert the sample into the Lindemann tubes (which involved handling the sample on the open bench) were inadequate to prevent the partial hydrolysis of the inserted sample.

The published data\(^{(68)}\) from the X-ray crystallographic determination of the structure of $B_9Cl_9$ was therefore used to obtain a prediction of the powder diffraction picture which would be produced with the same equipment that was used to obtain the powder diffraction photograph of $B_9Br_9$. This procedure first of all involved the abstraction from the data of the reflections, those which were likely to have the highest intensities. The criteria used to select the reflections were:

i. All reflections in the range $\sin \theta / \lambda = 0 \rightarrow 0.13$ were taken (since $Lp$ is large in this region).

ii. If these were inappropriate then reflections with $F \geq 100$ were taken.

The intensities of the selected reflections were determined using the equation
\[
I = Lp \times F^2 \times m,
\]
where
\[
Lp = \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta}.
\]

F is the structure factor,
and m is the multiplicity of the reflection.

The selected reflections and their calculated intensities are given in Table 14. As molybdenum Kα radiation was used in the determination of the molecular and crystal structure of B₉Cl₉, the sin θ/λ values given in the original data were converted to the sin θ values expected for a powder diffraction photograph using copper Kα radiation by multiplication by 1.542 (the wavelength of copper Kα radiation). The multiplicity factors (which are an inevitable feature of the powder diffraction method since all reflections with the same Bragg angle θ are superimposed in the same diffraction arc) for each reflection were obtained from the known degeneracies of the monoclinic system.

These intensities were then tabulated in Table 15 in order of increasing θ. It can be seen that at some angles, more than one reflection occurs, leading to one ring at this angle, of intensity equal to the sum of all its components.

After obtaining this prediction of a powder diffraction photograph of B₉Cl₉, the film produced by B₉Br₉ was measured to give values of θ. The camera
Table 14. Principle Structure Factors of $\text{P}_9\text{Sr}_8$

<table>
<thead>
<tr>
<th>hkl</th>
<th>F</th>
<th>$\sin \theta / \lambda$</th>
<th>$\sin \theta \text{(Cu)}$</th>
<th>m</th>
<th>$L_p$</th>
<th>Intensity($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>020</td>
<td>75</td>
<td>.0790</td>
<td>.122</td>
<td>2</td>
<td>151.4</td>
<td>1478</td>
</tr>
<tr>
<td>040</td>
<td>50</td>
<td>.1580</td>
<td>.244</td>
<td>2</td>
<td>30.74</td>
<td>154</td>
</tr>
<tr>
<td>060</td>
<td>110</td>
<td>.2370</td>
<td>.365</td>
<td>2</td>
<td>12.40</td>
<td>300</td>
</tr>
<tr>
<td>002</td>
<td>110</td>
<td>.0744</td>
<td>.113</td>
<td>2</td>
<td>148.3</td>
<td>3589</td>
</tr>
<tr>
<td>004</td>
<td>154</td>
<td>.1488</td>
<td>.229</td>
<td>2</td>
<td>35.29</td>
<td>1674</td>
</tr>
<tr>
<td>024</td>
<td>155</td>
<td>.1684</td>
<td>.260</td>
<td>4</td>
<td>26.78</td>
<td>2574</td>
</tr>
<tr>
<td>053</td>
<td>181</td>
<td>.1627</td>
<td>.251</td>
<td>4</td>
<td>28.92</td>
<td>3790</td>
</tr>
<tr>
<td>104</td>
<td>243</td>
<td>.1629</td>
<td>.251</td>
<td>2</td>
<td>28.92</td>
<td>5415</td>
</tr>
<tr>
<td>226</td>
<td>112</td>
<td>.2686</td>
<td>.414</td>
<td>4</td>
<td>9.178</td>
<td>460</td>
</tr>
<tr>
<td>142</td>
<td>158</td>
<td>.1848</td>
<td>.285</td>
<td>4</td>
<td>21.85</td>
<td>2182</td>
</tr>
<tr>
<td>213</td>
<td>130</td>
<td>.1672</td>
<td>.258</td>
<td>4</td>
<td>27.23</td>
<td>1841</td>
</tr>
<tr>
<td>202</td>
<td>161</td>
<td>.1370</td>
<td>.211</td>
<td>2</td>
<td>42.05</td>
<td>2180</td>
</tr>
<tr>
<td>333</td>
<td>114</td>
<td>.2572</td>
<td>.366</td>
<td>4</td>
<td>12.32</td>
<td>640</td>
</tr>
<tr>
<td>131</td>
<td>160</td>
<td>.1369</td>
<td>.211</td>
<td>4</td>
<td>42.05</td>
<td>4506</td>
</tr>
<tr>
<td>302</td>
<td>166</td>
<td>.1850</td>
<td>.285</td>
<td>2</td>
<td>21.85</td>
<td>1204</td>
</tr>
<tr>
<td>300</td>
<td>188</td>
<td>.1628</td>
<td>.251</td>
<td>2</td>
<td>28.92</td>
<td>2044</td>
</tr>
<tr>
<td>100</td>
<td>28</td>
<td>.0543</td>
<td>.167</td>
<td>2</td>
<td>280.5</td>
<td>440</td>
</tr>
<tr>
<td>200</td>
<td>33</td>
<td>.1086</td>
<td>.084</td>
<td>2</td>
<td>68.79</td>
<td>150</td>
</tr>
<tr>
<td>440</td>
<td>113</td>
<td>.2685</td>
<td>.414</td>
<td>4</td>
<td>9.178</td>
<td>469</td>
</tr>
<tr>
<td>140</td>
<td>127</td>
<td>.1670</td>
<td>.258</td>
<td>4</td>
<td>27.23</td>
<td>1757</td>
</tr>
<tr>
<td>311</td>
<td>159</td>
<td>.1680</td>
<td>.260</td>
<td>4</td>
<td>26.78</td>
<td>2708</td>
</tr>
<tr>
<td>231</td>
<td>239</td>
<td>.1627</td>
<td>.251</td>
<td>4</td>
<td>28.92</td>
<td>6006</td>
</tr>
<tr>
<td>302</td>
<td>155</td>
<td>.1728</td>
<td>.266</td>
<td>2</td>
<td>25.47</td>
<td>1224</td>
</tr>
<tr>
<td>111</td>
<td>107</td>
<td>.0743</td>
<td>.115</td>
<td>4</td>
<td>148.3</td>
<td>6792</td>
</tr>
<tr>
<td>222</td>
<td>152</td>
<td>.1487</td>
<td>.229</td>
<td>4</td>
<td>35.29</td>
<td>3261</td>
</tr>
<tr>
<td>262</td>
<td>105</td>
<td>.2684</td>
<td>.414</td>
<td>4</td>
<td>9.178</td>
<td>405</td>
</tr>
</tbody>
</table>
Table 14. (Continued)

<table>
<thead>
<tr>
<th>hkl</th>
<th>F</th>
<th>( \sin \delta/\lambda )</th>
<th>( \sin \theta (\text{Cu}) )</th>
<th>( \theta )</th>
<th>( Lp )</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>115</td>
<td>0.2104</td>
<td>0.324</td>
<td>2</td>
<td>16.35</td>
<td>432</td>
</tr>
<tr>
<td>204</td>
<td>133</td>
<td>0.1761</td>
<td>0.272</td>
<td>2</td>
<td>24.24</td>
<td>858</td>
</tr>
<tr>
<td>306</td>
<td>102</td>
<td>0.2641</td>
<td>0.407</td>
<td>2</td>
<td>9.564</td>
<td>199</td>
</tr>
<tr>
<td>215</td>
<td>117</td>
<td>0.2104</td>
<td>0.324</td>
<td>4</td>
<td>16.35</td>
<td>895</td>
</tr>
<tr>
<td>133</td>
<td>152</td>
<td>0.1684</td>
<td>0.260</td>
<td>4</td>
<td>26.78</td>
<td>2475</td>
</tr>
<tr>
<td>124</td>
<td>153</td>
<td>0.1728</td>
<td>0.266</td>
<td>4</td>
<td>25.47</td>
<td>2385</td>
</tr>
<tr>
<td>102</td>
<td>35</td>
<td>0.0959</td>
<td>0.145</td>
<td>2</td>
<td>92.18</td>
<td>226</td>
</tr>
<tr>
<td>111</td>
<td>78</td>
<td>0.0791</td>
<td>0.122</td>
<td>4</td>
<td>131.4</td>
<td>3190</td>
</tr>
<tr>
<td>120</td>
<td>34</td>
<td>0.0958</td>
<td>0.148</td>
<td>4</td>
<td>88.37</td>
<td>409</td>
</tr>
<tr>
<td>013</td>
<td>14</td>
<td>0.118</td>
<td>0.182</td>
<td>4</td>
<td>57.47</td>
<td>45</td>
</tr>
<tr>
<td>022</td>
<td>32</td>
<td>0.108</td>
<td>0.167</td>
<td>4</td>
<td>68.79</td>
<td>282</td>
</tr>
<tr>
<td>122</td>
<td>11</td>
<td>0.124</td>
<td>0.191</td>
<td>4</td>
<td>51.92</td>
<td>25</td>
</tr>
<tr>
<td>211</td>
<td>16</td>
<td>0.118</td>
<td>0.182</td>
<td>4</td>
<td>57.47</td>
<td>59</td>
</tr>
<tr>
<td>203</td>
<td>63</td>
<td>0.126</td>
<td>0.194</td>
<td>2</td>
<td>50.25</td>
<td>399</td>
</tr>
<tr>
<td>125</td>
<td>17</td>
<td>0.118</td>
<td>0.182</td>
<td>4</td>
<td>57.47</td>
<td>66</td>
</tr>
<tr>
<td>113</td>
<td>63</td>
<td>0.126</td>
<td>0.194</td>
<td>4</td>
<td>50.25</td>
<td>798</td>
</tr>
<tr>
<td>hkl</td>
<td>sin θ</td>
<td>I</td>
<td>2θ</td>
<td>Corresponding B&lt;sub&gt;9&lt;/sub&gt;Br&lt;sub&gt;9&lt;/sub&gt; powder line</td>
<td>Ratio B&lt;sub&gt;9&lt;/sub&gt;Br&lt;sub&gt;9&lt;/sub&gt;: B&lt;sub&gt;9&lt;/sub&gt;Cl&lt;sub&gt;9&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
<td>----</td>
<td>----</td>
<td>-----------------------------------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.440</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>002</td>
<td>0.3589</td>
<td>6.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>0.6792</td>
<td>6.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>020</td>
<td>0.1478</td>
<td>7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>0.3190</td>
<td>7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>0.226</td>
<td>8.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.409</td>
<td>8.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.150</td>
<td>9.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>022</td>
<td>0.282</td>
<td>9.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>013</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>0.182</td>
<td>10.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>122</td>
<td>0.191</td>
<td>11.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>202</td>
<td>0.194</td>
<td>11.2</td>
<td>10.9 (w)</td>
<td></td>
<td>0.975</td>
<td></td>
</tr>
<tr>
<td>113</td>
<td>0.211</td>
<td>11.8 (m)</td>
<td></td>
<td></td>
<td>0.969</td>
<td></td>
</tr>
<tr>
<td>202</td>
<td>0.211</td>
<td>12.2</td>
<td></td>
<td></td>
<td>0.967</td>
<td></td>
</tr>
<tr>
<td>131</td>
<td>0.4306</td>
<td>12.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>004</td>
<td>0.229</td>
<td>13.2</td>
<td>12.8 (m)</td>
<td></td>
<td>0.971</td>
<td></td>
</tr>
<tr>
<td>222</td>
<td>0.229</td>
<td>13.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>040</td>
<td>0.244</td>
<td>14.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>033</td>
<td>0.251</td>
<td>14.5</td>
<td>14.1 (s)</td>
<td></td>
<td>0.971</td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>0.251</td>
<td>14.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.251</td>
<td>14.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>231</td>
<td>0.251</td>
<td>14.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 15. (Continued)

<table>
<thead>
<tr>
<th>hkl</th>
<th>Sin θ</th>
<th>I</th>
<th>θ</th>
<th>Corresponding B&lt;sub&gt;9&lt;/sub&gt;Br&lt;sub&gt;9&lt;/sub&gt; powder line</th>
<th>Ratio B&lt;sub&gt;9&lt;/sub&gt;Br&lt;sub&gt;9&lt;/sub&gt;: B&lt;sub&gt;9&lt;/sub&gt;Cl&lt;sub&gt;9&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>213</td>
<td>.258</td>
<td>1841</td>
<td>15.0</td>
<td>14.6 (s)</td>
<td>.977</td>
</tr>
<tr>
<td>140</td>
<td>.258</td>
<td>1757</td>
<td>15.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>024</td>
<td>.260</td>
<td>2574</td>
<td>15.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>.260</td>
<td>2708</td>
<td>15.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>153</td>
<td>.260</td>
<td>2475</td>
<td>15.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>302</td>
<td>.266</td>
<td>1224</td>
<td>15.4</td>
<td>15.0 (w)</td>
<td>.973</td>
</tr>
<tr>
<td>124</td>
<td>.266</td>
<td>2385</td>
<td>15.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>204</td>
<td>.272</td>
<td>858</td>
<td>15.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>142</td>
<td>.285</td>
<td>2182</td>
<td>16.6</td>
<td>16.1 (m)</td>
<td>.973</td>
</tr>
<tr>
<td>302</td>
<td>.285</td>
<td>1204</td>
<td>16.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>.324</td>
<td>432</td>
<td>18.9</td>
<td>18.3 (m)</td>
<td>.969</td>
</tr>
<tr>
<td>215</td>
<td>.324</td>
<td>895</td>
<td>18.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>060</td>
<td>.365</td>
<td>300</td>
<td>21.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>.366</td>
<td>640</td>
<td>21.5</td>
<td>20.8 (m)</td>
<td>.968</td>
</tr>
<tr>
<td>306</td>
<td>.407</td>
<td>199</td>
<td>24.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>226</td>
<td>.414</td>
<td>460</td>
<td>24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>440</td>
<td>.414</td>
<td>469</td>
<td>24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>262</td>
<td>.414</td>
<td>405</td>
<td>24.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2θ</td>
<td>9</td>
<td>Estimated Intensity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>---------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.8</td>
<td>10.9</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.7</td>
<td>11.8</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25.7</td>
<td>12.8</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.3</td>
<td>14.1</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.2</td>
<td>14.6</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>15.0</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.2</td>
<td>16.1</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.2</td>
<td>16.6</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.0</td>
<td>17.5</td>
<td>vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36.7</td>
<td>18.3</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.0</td>
<td>19.5</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.7</td>
<td>20.8</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44.6</td>
<td>22.3</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46.1</td>
<td>23.0</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47.4</td>
<td>23.7</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50.8</td>
<td>25.4</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
diameter of 5.73 cm. conveniently gives the conversion 1 cm. = 10° for 2θ. These rings and their intensities were then tabulated in table 16 for comparison with the values calculated for B₉Cl₉. It can be seen by comparing table 15 with table 14, that if the first B₉Br₉ powder line which can be measured at θ = 10.9° is taken to correspond with the B₉Cl₉ line at 11.2°, then most of the remaining observed B₉Br₉ lines can similarly be matched both in position and intensity with the calculated B₉Cl₉ values at larger angles. Indeed the variation in the ratios between the pairs of lines is within 8.5%.

These data are in agreement with the originally stated expectations for isostructural compounds. The B₉Br₉ lines are consistently at slightly lower angles than the B₉Cl₉ reflections, and the intensity distributions also appear to be very similar. Since these observations are in agreement with the conditions to be expected if B₉Cl₉ and B₉Br₉ were isostructural, then it can be stated conclusively that this is so, and thus B₉Br₉ is certainly a boron cage compound.

6.2 Mass Spectrum

On comparison of diagram 32 and diagram 17 (page 48), which are representations of the mass spectra of B₉Br₉ and B₉Cl₉, certain similarities are easily seen. The molecular ion is prominent in both
Table 17.
Species detected in the partial mass spectrum of $B_9\text{Br}_9$ (see diagram 32; the m/e values listed are those of the most intense peak observed in any group).

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/e value</th>
<th>Ion</th>
<th>m/e value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_9\text{Br}_9^+$</td>
<td>817</td>
<td>$B_2\text{Br}_3(?)$</td>
<td>261</td>
</tr>
<tr>
<td>$B_9\text{Br}_8^+$</td>
<td>787</td>
<td>$B_8\text{Br}_2^+$</td>
<td>247</td>
</tr>
<tr>
<td>$B_8\text{Br}_7^+$</td>
<td>646</td>
<td>$B_7\text{Br}_2^+$</td>
<td>236</td>
</tr>
<tr>
<td>$B_8\text{Br}_6^+$</td>
<td>566</td>
<td>$B_6\text{Br}_2^+$</td>
<td>225</td>
</tr>
<tr>
<td>$B_8\text{Br}_5^+$</td>
<td>486</td>
<td>$B_5\text{Br}_2^+$</td>
<td>214</td>
</tr>
<tr>
<td>$B_7\text{Br}_6^+$</td>
<td>476</td>
<td>$B_4\text{Br}_2^+$</td>
<td>204</td>
</tr>
<tr>
<td>$B_8\text{Br}_4^+$</td>
<td>406</td>
<td>$B_3\text{Br}_2^+$</td>
<td>193</td>
</tr>
<tr>
<td>$B_7\text{Br}_4^+$</td>
<td>396</td>
<td>$B_2\text{Br}_2^+$</td>
<td>182</td>
</tr>
<tr>
<td>$B_8\text{Br}_3^+$</td>
<td>326</td>
<td>$B\text{Br}_2^+$</td>
<td>170</td>
</tr>
<tr>
<td>$B_7\text{Br}_3^+$</td>
<td>316</td>
<td>$B_7\text{Br}^+$</td>
<td>156</td>
</tr>
<tr>
<td>$B_6\text{Br}_3^+$</td>
<td>305</td>
<td>$B_6\text{Br}^+$</td>
<td>145</td>
</tr>
<tr>
<td>$B_5\text{Br}_3^+$</td>
<td>294</td>
<td>$B_5\text{Br}^+$</td>
<td>134</td>
</tr>
<tr>
<td>$B_4\text{Br}_3^+$</td>
<td>283</td>
<td>$B\text{Br}^+$</td>
<td>90</td>
</tr>
<tr>
<td>$B_3\text{Br}_3^+$</td>
<td>272</td>
<td>$\text{Br}^+$, $\text{HBr}^+$</td>
<td>80</td>
</tr>
</tbody>
</table>

152.
32. REPRESENTATION OF THE PARTIAL MASS SPECTRUM OF THE SAMPLE.
PECTRUM OF $B_9 Br_9$
spectra, and both compounds also contain \( B_8X_6^+ \), the ion formed by loss of \( BX_3 \) from the parent. Evidence that this process does occur for \( B_9Br_9 \) is given by a broad metastable peak at approximately \( m/e 392 \), which corresponds to the reaction

\[
B_9Br_9^+ \rightarrow B_8Br_6^+ + BBr_3.
\]

An important difference between the two spectra is that whereas the base peak in the spectrum of \( B_9Cl_9 \) (in common with all other cage subchlorides so far investigated), corresponds to \( B_8Cl_6^+ \), the ion formed by loss of "BCl_5" from the parent, in the mass spectrum of \( B_9Br_9 \), the molecular peak is also the base peak. This is yet another indication of the extremely high stability of \( B_9Br_9 \).

6.3 Infra-red Spectrum

The infra-red spectrum of \( B_9Br_9 \), recorded using a sample held in a pressed potassium bromide disc, is very similar to that of \( B_9Cl_9 \) (ref. diagram 37), except that all the bands in the bromide occur at lower frequencies. This similarity again suggests that the two molecules have the same molecular shape. The fact that all the \( B_9X_9 \) spectral vibrations appear to be sensitive to the change of halogens may be due to the occurrence of a considerable amount of \( \pi \)-bonding between the \( B_9 \) cage and the halogen ligands. Such a
33. COMPARISON OF THE INFRA-RED SPECTRA OF $\text{Br}_g\text{Cl}_g$ & $\text{Br}_g\text{Br}_g$
cage-ligand interaction is thought to be partially responsible for the stability of the B₄Cl₄ molecule.

It was expected that a strong spectral band at about 1010 cm⁻¹ due to the cage vibrations, would have been present in the spectrum of B₉Br₉. The presence in the infra-red spectra of both B₄Cl₄ and B₉Cl₉ of a broad band in this region may be due to both the boron cage and the boron-chlorine vibrations. Diagram 35 shows that there is only a broad band at 957 cm⁻¹ in the infra-red spectrum of B₉Br₉ with no indication of resolution into separate peaks due to cage vibrations and boron-bromine vibrations.

6.4 Ultraviolet and Visible Spectrum

The ultraviolet and visible spectra of B₉Cl₉ and B₉Br₉ are also similar to each other. They both show two bands, the higher energy one being the more intense in both cases. The ultraviolet and visible spectrum of B₉Br₉ is shown in diagram 34, the absorption at 452 nm, being responsible for the red colour of the compound. As would be expected from the deeper red colour of B₉Br₉ than B₉Cl₉, the bands of the bromide have longer wavelengths (305 and 380 nm for B₉Cl₉; 337 and 452 nm for B₉Br₉).

6.5 Raman Spectrum

Attempts were made to obtain the Raman spectrum
34. ELECTRONIC SPECTRUM OF B₉Br₉ DISSOLVED IN BBr₃

![Graph showing the electronic spectrum of B₉Br₉ dissolved in BBr₃. The graph displays absorbance on the y-axis and wavelength (nm) on the x-axis. Peaks at 337 nm and 452 nm are indicated.]
of \( \text{B}_9\text{Br}_9 \). This was done using solutions of varying concentrations of \( \text{B}_9\text{Br}_9 \) dissolved in boron tribromide. However, no solution could be made up that was sufficiently pale coloured so as not to absorb the blue laser light, consequently no spectrum could be measured.

6.6 Handling Properties

\( \text{B}_9\text{Br}_9 \) is a particularly stable molecule. Samples can be sublimed around all-glass vacuum lines using the free flame. It can also be handled for brief periods in the open air either in form of large crystals or as a relatively fine powder. The latter seems to be the easiest way in which to carry out complex manipulations of the compound. Hydrolysis occurs rapidly in water, but if the latter is thoroughly degassed, and either vacuum conditions or an inert atmosphere used, \( \text{B}_9\text{Br}_9 \) will survive contact with water for periods of up to an hour or more.

6.7 Solvents

The best solvents are boron tribromide, and the chlorinated carbon compounds carbon tetrachloride, chloroform and dichloromethane. As \( \text{B}_9\text{Br}_9 \) also dissolves without change in boron trichloride, this solvent was normally used for work involving the high vacuum line in preference to boron tribromide, since when the latter comes into contact with moisture it produces hydrogen bromide, which reacts with any mercury in the system.
B₉Br₉ is also soluble to a limited extent in liquid hydrocarbons such as n-hexane. It slowly decomposes in the presence of ethers, but when added to benzene, in which it is extremely soluble, a stable, very dark coloured solution is produced. As this is similar to the behaviour of iodine when dissolved in benzene, where these is believed to be interaction between the two, there seems to be a possibility that such an interaction may also take place between the B₉Br₉ molecule and the benzene ring. Whatever the nature of this effect it in no way destabilises the B₉Br₉, which was recovered unchanged after the removal of the benzene.

6.8 Reactions of B₉Br₉

As a method was now available to prepare relatively large quantities of pure B₉Br₉, a rare opportunity was presented to carry out a series of chemical reactions on a member of the neutral boron halide cage series. Very little is known about the chemistry of these compounds. Three main contributing factors seem to have impeded investigations in the neutral boron cage subhalide field:

(1) There are major difficulties in isolating the pure compounds;

(11) These compounds show strong tendencies to undergo rapid hydrolysis or decomposition under possible reaction conditions;

159.
The cage compounds, once made, are very stable and resist halogen substitution reactions. For example, $\text{B}_9\text{Cl}_9$ has been found not to exchange halogens (63) on being heated to $100^\circ$ with boron tribromide, and conversely $\text{B}_9\text{Br}_9$ does not react with boron trichloride at $80^\circ$.

The first of these difficulties has been overcome with the use of the silent electric discharge preparation to produce pure $\text{B}_9\text{Br}_9$. This compound appears to be the most stable neutral boron cage monohalide yet encountered, and it was found to withstand more severe reaction conditions than other similar compounds, so enabling the bromine atoms to be substituted by different atoms or groups of atoms. Several different reactions have been performed using $\text{B}_9\text{Br}_9$ in attempts to replace the bromine atoms with other atoms or substituent groups. Some of these attempts have resulted in the partial, and in some cases, the total replacement of the bromine atoms.

6.9 Chlorination Reactions

a. Reaction between titanium tetrachloride and $\text{B}_9\text{Br}_9$

Titanium tetrachloride (approximately 15ml., obtained from Fison's Scientific Apparatus) was condensed onto a small amount of $\text{B}_9\text{Br}_9$ in a breakseal
tube of the type shown in diagram 15a. The tube was sealed off from the vacuum line and placed overnight in an oven at 250°. When the tube was removed from the oven, the colour of the solution was found to have changed from orange-red to orange-yellow. After adapting the tube by the addition of further glassware, the volatile liquid was removed and its vapour examined by infra-red spectroscopy. The results of these examinations, coupled with the yellow appearance of the liquid, suggested that the titanium tetrachloride now contained some "Br", probably in the form of TiCl$_3$Br. After removing the liquid, a yellow-orange solid remained in the reaction vessel. This solid product was slightly volatile at room temperature, and was sublimed into a narrow tube for mass spectral analysis. On examination of the resulting mass spectrum, it was found that a partial replacement of the bromine atoms on B$_9$Br$_9$ had in fact occurred. The most abundant molecular ion was B$_9$Cl$_7$Br$_2^+$, which was identified by comparing the observed intensities of the various isotopomers of B$_9$Cl$_7$Br$_2^+$ with the calculated values; see diagram 35. The following molecular ions were identified in the mass spectrum of the volatile yellow-orange solid (they are arranged in order of decreasing abundance):

$$B_9\text{Cl}_7\text{Br}_2^+ > B_9\text{Cl}_6\text{Br}_7^+ > B_9\text{Cl}_8\text{Br}_4^+ > B_9\text{Cl}_9^+ > B_9\text{Cl}_5\text{Br}_4^+ > B_9\text{Cl}_4\text{Br}_5^+ > B_9\text{Cl}_3\text{Br}_6^+.$$
35. COMPARISON OF OBSERVED & THEORETICAL INTENSITIES FOR THE

MOLECULAR ION \( \text{Br}_9\text{Cl}_7\text{Br}_2^+ \)

Observed Intensities

Theoretical Intensities
Metastable peaks corresponding to the following transitions were observed:

\[
\begin{align*}
B_9\text{Cl}_7\text{Br}_2^+ & \rightarrow B_8\text{Cl}_5\text{Br}^+ + \text{BCl}_2\text{Br} \quad (234) \\
B_9\text{Cl}_6\text{Br}_3^+ & \rightarrow B_8\text{Cl}_4\text{Br}_2^+ + \text{BCl}_2\text{Br} \quad (274) \\
B_9\text{Cl}_5\text{Br}_4^+ & \rightarrow B_8\text{Cl}_3\text{Br}_3^+ + \text{BCl}_2\text{Br} \quad (311)
\end{align*}
\]

Other additional metastable transitions may have taken place, but ions due to break-down fragments of high abundance were located in positions where it was estimated that the corresponding metastable peaks would have been centred.

Having discovered that titanium tetrachloride was successful in effecting the substitution of the bromine atoms on \(B_9\text{Br}_9\), the reaction was repeated in an attempt to obtain pure \(B_9\text{Cl}_9\). It was hoped to produce the total replacement of the bromine atoms on \(B_9\text{Br}_9\) by holding the reactants at 250° for a longer period (10 days). Apart from this time period the reaction procedure was carried out exactly as described previously, and the solid products were again analysed mass spectroscopically. The mass spectrum showed the yellow-orange solids again to consist of a mixture of \(B_9\text{Cl}_9\) and the partially brominated \(B_9\) cages, although in this particular case \(B_9\text{Cl}_9^+\) was the most abundant molecular ion. The following molecular ions were identified (arranged as before in order of decreasing
abundance): 

\[ B_9\text{Cl}_9^+ \rightarrow B_9\text{Cl}_7\text{Br}_2^+ \rightarrow B_9\text{Cl}_6\text{Br}_3^+ \rightarrow B_9\text{Cl}_5\text{Br}_4^+ \rightarrow B_9\text{Cl}_4\text{Br}_5^+ \]

On comparing this series of molecular ions with the series obtained in the first experiment, it can be seen that the conditions used in the second reaction were successful in producing a greater degree of substitution. However, even with the very large excess of titanium tetrachloride and the relatively high temperatures used in these reactions, no success was achieved in forcing the equilibrium 

\[ 9\text{TiCl}_4 + 4B_9\text{Br}_9 \rightarrow 9\text{TiBr}_4 + 4B_9\text{Cl}_9 \]

completely over to the right hand side.

b. Reaction between tin tetrachloride and $B_9\text{Br}_9$

Tin tetrachloride is known to be an excellent reagent for transforming boron-bromine bonds into boron-chlorine bonds, and this reaction was performed in another attempt to chlorinate fully the $B_9\text{Br}_9$. Again the procedure adopted was similar to that described for titanium tetrachloride and $B_9\text{Br}_9$, with the reactants (tin tetrachloride was obtained from Fison's Scientific Apparatus) being kept at 250° for 10 days. However the composition of the products (determined mass spectrometrically) was found to be similar to that produced in the reactions.
between titanium tetrachloride and $B_9 Br_9$. A representation of part of the mass spectrum of the products is shown in diagram 36.

These reactions were not successful in producing the complete chlorination of all the molecules of $B_9 Br_9$. It seems that the exchange reaction is quite slow, and that possibly further extended treatment of the partially chlorinated products with pure titanium tetrachloride or tin tetrachloride, and at even higher temperatures, would lead to the complete replacement of bromine substituents by chlorine atoms. No solid debris was produced in any of these reactions. It is therefore apparent that neither titanium tetrachloride nor tin tetrachloride has a tendency to disrupt the $B_9$ cage, and merely participates in the halogen exchange.

No attempts were made to separate the chlorobromide mixture into its components. When subliming the mixture around the all glass apparatus, no separations were observed, and it appeared at all times completely homogeneous.

6.10 Fluorination Reactions

In spite of extensive efforts in many laboratories, no neutral boron cages in which fluorine is attached to the boron atoms have yet been isolated. Attempts,
Species detected in the partial mass spectrum of the products of the reaction between $\text{B}_9\text{Br}_9$ and tin tetrachloride (see diagram 36; the m/e values listed are those of the most intense peak observed in any group).

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/e value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_9\text{Cl}_4\text{Br}_5^+$</td>
<td>639</td>
</tr>
<tr>
<td>$\text{B}_9\text{Cl}_5\text{Br}_4^+$</td>
<td>594</td>
</tr>
<tr>
<td>$\text{B}_9\text{Cl}_6\text{Br}_3^+$</td>
<td>550</td>
</tr>
<tr>
<td>$\text{B}_9\text{Cl}_7\text{Br}_2^+$</td>
<td>505</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_2\text{Br}_4^+$</td>
<td>477</td>
</tr>
<tr>
<td>$\text{B}_9\text{Cl}_8\text{Br}^+$</td>
<td>461</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_3\text{Br}_3^+$</td>
<td>433</td>
</tr>
<tr>
<td>$\text{B}_9\text{Cl}_9^+$</td>
<td>416</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_4\text{Br}_2^+$</td>
<td>388</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_5\text{Br}^+$</td>
<td>334</td>
</tr>
<tr>
<td>$\text{B}_8\text{Cl}_6^+$</td>
<td>299</td>
</tr>
</tbody>
</table>
36. REPRESENTATION OF THE PARTIAL MASS SPECTRUM OF THE PRODUCTS

- Peak at 299
- Peak at 334
- Peak at 368
- Peak at 416
- Peak at 433
- Peak at 461
- Peak at 477
- Peak at 505

Mass scale: 300 - 500
PARTIAL MASS SPECTRUM OF THE PRODUCTS OF THE REACTION BETWEEN SnCl₄ & BgBrg
described below, were made to produce such fluorine-substituted compounds by replacing the bromine atoms on the $B_9$ cage of $B_9Br_9$ with fluorine atoms.

a. Reaction between antimony trifluoride and $B_9Br_9$

The first fluorination attempt made use of antimony trifluoride as the fluorinating agent. This reagent was chosen because it has been widely used in the fluorination of non-metal compounds. For example, antimony trifluoride was used to bring about the first preparation (61) of diboron tetrafluoride, which involved the halogen exchange reaction with diboron tetrachloride.

$$3B_2Cl_4 + 4SbF_3 \rightarrow 3B_2F_4 + 4SbCl_3.$$ 

In the attempt to fluorinate $B_9Br_9$, the latter was added to resublimed antimony trifluoride (a general purpose reagent supplied by Hopkin and Williams) in a breakseal reaction vessel of the type normally used. After evacuation, the tube was sealed off from the vacuum line and held at room temperature for about two weeks. As no alteration in the appearance of the reagents was apparent after this period, the vessel was placed in an oven at 200° for two hours. On removal from the oven, the vessel was found mainly to contain grey solids with only a small amount of red material. Other than unchanged
antimony trifluoride, no volatile solids could be sublimed from the reaction vessel; the red material decomposed when heated.

There seem to be two possible explanations which could account for these observations — either the reaction conditions were too severe to permit the survival of the B₉ cage, or that any fluorinated cage compounds were too involatile to allow for their extraction and analysis using usual methods.

b. Reaction between titanium tetrafluoride and B₉Br₉

Following the success of titanium tetrachloride in inducing the replacement of the bromine atoms on B₉Br₉ with chlorine atoms, the second fluorination reaction made use of titanium tetrafluoride (obtained from Alfa Inorganics Ventron) in an attempt to produce a parallel with the chlorination reactions. After placing the two solid reactants in a breakseal reaction vessel using a glove bag, the vessel was attached to the vacuum line and n-hexane condensed in. The tube was sealed off from the vacuum line and placed in an oven at 80° for two weeks. On removal from the oven, no difference in the appearance of the contents of the reaction vessel could be observed, and the red solids sublimed from the tube were found by mass spectral analysis mainly to consist of unchanged B₉Br₉. The spectrum was found to contain a cluster of peaks centred
at m/e 756, which is the position where the central peak of $B_9FBr_8$ would be expected to occur. However, the intensity of this group of peaks was only 45% of the $B_9Br_9^+$ cluster, so that any assignment of the cluster centred at m/e 756 to $B_9FBr_8$ must be rather doubtful. No other peaks could be assigned to fluorine-substituted boron compounds.

6.11 Reaction Between Dimethylamine and $B_9Br_9$

This reaction was performed in an attempt to produce amine-substituted derivatives of the neutral polyhedral boron halides. Such amine-substituted polyhedral boron hydride ions can be made\(^{(31)}\), and if the neutral compounds were capable of existence, then they would be more easily formed from the boron subhalides. These are known to undergo substitution reactions with secondary amines, with the consequent production of amino boron compounds. For example, the reaction between dimethylamine and diboron tetrachloride,

$$B_2Cl_4 + 8(CH_3)_2NH \rightarrow B_4[N(CH_3)_2]_4 + 4(CH_3)_2NH_2Cl,$$

produces diboron tetrakisdimethylamide\(^{(69)}\), a compound of higher stability than diboron tetrachloride. This type of reaction is also thought to occur when dimethylamine is added to $B_4Cl_4$, where the research workers\(^{(69)}\) identified the product as $B_4(NMe_2)_4$. However they made
no attempt to reform the initial subchloride by the addition of hydrogen chloride to confirm the nature of the proposed B₉ amino compound.

In an attempt to produce similar B₉ amino compounds, a large excess of dimethylamine was added to B₉Br₉ in a breakseal reaction vessel. Upon warming the mixture of reactants from liquid nitrogen temperatures, the red colour of the B₉Br₉ disappeared near the melting point of the dimethylamine, followed by the appearance of a pale yellow solid. The reaction vessel was held at -65°C for approximately two hours before being opened to the vacuum line for the removal of excess dimethylamine. Following this evacuation, the breakseal tube was sealed off from the vacuum line and the pale yellow solid tested for its volatility. As it was found to be involatile when heated, the possibility was considered that it consisted of the dimethylamino B₉ compound B₉[N(CH₃)₂]₉. To test this hypothesis, hydrogen chloride at a pressure of one atmosphere was condensed into the reaction vessel. Despite leaving the reaction vessel at room temperature for several weeks, no trace of B₉Cl₉ was produced.

Obviously this sequence of reactions was unsuccessful in producing the series of conversions

$$B₉Br₉ \rightarrow B₉[N(CH₃)₂]₉ \rightarrow B₉Cl₉.$$
and it appears that the $B_9$ cage decomposed at some stage, but it is not clear at which stage this decomposition occurred. Perhaps the greatest significance of this experiment is the discovery of the reaction between $B_9Br_9$ and dimethylamine, suggesting the possible existence of a new field of boron-amine chemistry.

6.12 Attempts to Produce Hydrogen-Containing Neutral Polyhedral Boron Compounds

Although the neutral polyhedral boron hydrides are unstable, some neutral $(BR)_n$ compounds have been described. For example, a yellow, air-sensitive powder with the formula $(BC_6H_5)_9-10$ was produced by the reduction of phenylboron dichloride with sodium in toluene. If this is a polyhedral compound, then the aromatic substituents must be capable of bringing about the same type of stabilisation as the halogen atoms in the boron subhalides. Although the nature of this interaction is not fully understood, it is known that the stability of the $B_9$ cage is unaffected when one of the halogen substituents is replaced by a hydrogen atom, for in 1964 Muettterties and his co-workers succeeded in preparing and identifying the air-sensitive cage compound $B_9Cl_8H$. This material, which was isolated following the pyrolysis of the boron chloride ion $B_{10}Cl_{10}^{2-}$, gave an infra-red spectrum almost identical to that given by $B_9Cl_9$. Proton and $^{11}$B.n.m.r. and mass spectral evidence also confirmed that $B_9Cl_8H$ was a polyhedral
molecule, and suggested that the hydrogen atom was directly bonded to one boron atom, with the other eight boron atoms attached to chlorines.

Similar hydrogenated compounds were produced during attempts to separate the boron subchlorides $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$ and $\text{B}_{12}\text{Cl}_{12}$ by gas-liquid chromatography. Detailed analysis of mass spectra showed that the yellow material eluted from the column was not pure $\text{B}_9\text{Cl}_9$ as expected, even with helium as carrier gas, but that on some occasions it contained only about 5-10% of $\text{B}_9\text{Cl}_9$, with the majority being $\text{B}_9\text{Cl}_8\text{H}$ and $\text{B}_9\text{Cl}_7\text{H}_2$. Identification of these partially hydrogenated compounds was obtained from mass spectra taken of samples collected from the g.l.c. Metastable peaks aid in the assignments, since peaks have been observed corresponding to the following pathways:

![Chemical Diagram]

173.
The source of hydrogen in the experiments was assumed to be traces of moisture either on the column packing or in the helium carrier. It is not known whether these hydrogenated B₉ compounds originated from B₉Cl₉ in the injected material or from the break-down of the larger cages B₁₀Cl₁₀, B₁₁Cl₁₁ and B₁₂Cl₁₂, as was the case in Muetterties’ isolation of B₅Cl₈H.

In order to discover if any of the halogen substituents on the B₉Br₉ cage could similarly be substituted without destabilising the molecule, an attempt was made to replace some of the bromine atoms with firstly hydrogen atoms and secondly methyl groups.

a. Reaction between lithium aluminium hydride and B₉Br₉

The two solid reactants (lithium aluminium hydride was obtained from Fisons Scientific Apparatus) were placed in a reaction vessel using a glove bag. After attaching the vessel to the vacuum line and condensing in n-hexane, the tube was sealed off and held at 80° for two weeks. On removal from the oven, the tube was found still to contain some red material. However after evaporating the solvent, the orange-red material was found to decompose when being heated in order to try to force a sample into a small tube for the purposes of mass spectral analysis.
b. Reaction between tin tetramethyl and $B_9Br_9$

Tin tetramethyl (supplied in sealed 5ml. ampoules by B.D.H. Chemicals Ltd) was condensed onto $B_9Br_9$ in a glass breakseal vessel, cooled in liquid nitrogen. The reactants were allowed to warm up by removing the liquid nitrogen-filled Dewar. On melting, the tin tetramethyl was found to dissolve the $B_9Br_9$. The tube was held at room temperature for three days. At the end of this interval, no change was apparent in the appearance of the reactants, as the solution was still red in colour. After removing via the vacuum line all material volatile at room temperature, benzene was condensed onto the remaining solids in case any methyl substituted boron cages formed in the reaction should prove involatile or unstable when heated. Some of the benzene-soluble material was collected into a narrow tube for mass spectral analysis, and, after removing the benzene by means of freezing, a further sample of the product was sublimed into another narrow tube.

The mass spectra of these two samples indicated that the reaction was indeed successful in replacing some of the bromine atoms on $B_9Br_9$ by methyl groups, for the sample soluble in benzene gave rise to the molecular ions $B_9MeBr_8^+$, $B_9Me_2Br_7^+$ and $B_9Me_3Br_6^+$. 

175.
(although the sum of the intensities of these molecular ions was only 20% of the intensity of the $\text{B}_9\text{Br}_9^+$ ion). The mass spectrum of the sample forced into the narrow tube by heating contained no $\text{B}_9\text{Me}_3\text{Br}_6^+$ and little $\text{B}_9\text{Me}_2\text{Br}_7^+$, suggesting that these compounds may decompose under these conditions, but the intensity of the group of peaks produced by the $\text{B}_9\text{MeBr}_8^+$ ion was 44% of the intensity of the fully brominated $\text{B}_9\text{Br}_9$ species. These results indicate that some of the halogen atoms on a boron sub-bromide may be substituted without the total decomposition of the cage.
7. BORON SUB-BROMIDES & RELATED COMPOUNDS
7. BORON SUB-BROMIDES AND RELATED COMPOUNDS

B₉Br₉ is not the only neutral polymeric boron monobromide known to exist, for Kane and Massey \(^{(63)}\) have reported the preparation and identification of an air-sensitive material containing a mixture of B₇Br₇, B₈Br₈ and B₉Br₉. They suggested from their research that B₈Br₈ and B₉Br₉ could be expected to have closed cage structures similar to the corresponding boron monohalides; and they pointed out that if, in fact, B₇Br₇ was found to possess a closed B₇ cage, it would be the first example of that particular type (although a few B₅C₂ carboranes are known to have seven atom cages). The monobromides were isolated from the thermal decomposition products of diboron tetrabromide (leaving much solid debris behind) by the same method that the neutral polymeric boron monochlorides are obtained following the thermal decomposition of diboron tetrachloride. Some success was achieved in separating the mixture by fractional sublimation in a long sealed tube. Two compounds were identified using this separation procedure; one was a dark-coloured, crystalline B₇Br₇, and the other, a red crystalline B₉Br₉. A small proportion of B₈Br₈ was found in only one of the samples investigated. No other evidence of any other monobromides was obtained.

A major part of this research work has concentrated
on analysing the implications of this discovery, so as to provide a deeper insight into the mechanism of the decomposition of diboron tetrabromide and its resultant sub-bromide mixture. The composition of the products of the thermal decomposition reaction was found to be mainly dependent on temperature. It was found that diboron tetrabromide decomposes more quickly than the tetrachloride. However, when it was allowed to stand at room temperature in a sealed reaction vessel, traces of the undecomposed diboron tetrabromide could be recovered after a period of several weeks, despite the production of large quantities of mainly involatile dark-coloured decomposition products. At higher temperatures, the total decomposition of diboron tetrabromide occurred within 48 hours. The diboron tetrabromide was allowed to decompose in glass bankseal vessels similar to the type used in the thermal decomposition of diboron tetrachloride (ref. diagram 15a), and volatile products removed by sublimation after the adaption of the reaction vessel (ref. diagram 15b). As usual, all volatile solid products were analysed and identified mass spectrometrically. The best results (ie., where the least involatile material was produced), were obtained by heating the reaction vessel at 80-100°. At this temperature, the volatile material was found to consist mainly of the dark-coloured $B_7Br_7$. In addition, $B_9Br_9$, $B_8Br_8$ and a new compound $B_{10}Br_{10}$ were detected.
in the mass spectrum of the volatile solid products. Only $B_9Br_9$ was formed at higher temperatures (at $150^\circ$ or more); and it was possible to isolate this compound from the other polymeric monobromides by heating the mixture to temperatures as high as $400^\circ$. However, none of the other sub-bromides could be either prepared separately or totally isolated from each other by fractional sublimation in a long sealed tube.

Any diboron tetrabromide used in these reactions was prepared by the halogen exchange reaction between diboron tetrachloride and boron tribromide:

$$3B_2Cl_4 + 4BBBr_3 \rightleftharpoons 3B_2Br_4 + 4BBBr_3.\]

Care has to be taken to ensure that enough boron tribromide is added to enable the equilibrium to move to the right hand side. If this is not done, the $B_nBr_m$ compounds are easily contaminated with mixed chlorobromides, and indeed on the isolation of $B_9Br_9$ from the other polymeric boron monobromides, it has proved almost impossible to prevent the occurrence of the substituted $B_9ClBr_8$ species. The method of indirect halogen exchange preparation of diboron tetrabromide, devised by Schlesinger(13), was used in this research because for diboron tetrabromide, unlike diboron tetrachloride, no method has been devised whereby the tetrahalide can be synthesised directly from the
corresponding trihalide. Pflugmacher and Diener\(^{(66)}\) reported their attempts to accomplish this using an electrical glow discharge between either nickel or mercury electrodes, but they found even when using a carrier gas that the bulk of the boron tribromide was converted into an amorphous brown-black powder of composition \(\text{BBr}_{0.4}\) to \(\text{BBr}_{0.2}\). Similar results to this were obtained during the course of this research using the microwave discharge through boron tribromide vapour.

The nature of the halogen present in the monohalides appears to be a dominant factor in the stability of the boron cages. No conclusive evidence has been found for the existence of any fluorine-containing cages, and the stabilising effect of bromine and chlorine substituents is not identical. For example, no chlorine analogue of \(\text{B}_7\text{Br}_7\) appears to exist, and conversely the thermal decomposition of diboron tetrabromide produces no \(\text{B}_{11}\text{Br}_{11}\) or \(\text{B}_{12}\text{Br}_{12}\) and only traces of \(\text{B}_{10}\text{Br}_{10}\). The smaller \(D_4\) cage also demonstrates the different stabilising effects of chlorine and bromine substituents, for despite the stability of \(D_4\text{Cl}_4\) only partial replacement of the chlorines by bromine is possible. \(D_4\text{Cl}_4\) will exchange halogens with boron tribromide, and although the main product was a rust-like involatile solid, small amounts of \(D_4\text{Cl}_3\text{Br}\) and traces of \(D_4\text{Cl}_2\text{Br}_2\) were indentified\(^{(63)}\),
but, significantly, no $B_4Br_4$.

In an attempt to discover the extent to which the nature of the substituents determines the stability of the neutral boron cages, mixed chloro-bromides were synthesised. Two different preparative methods were used. In the first preparations, various proportions of the mixed diboron tetrahalides were allowed to decompose, so that both chlorine and bromine atoms were substituted onto the cages as the latter were built up. In the second preparations, the mixed chlorobromides were prepared from subchloride or subbromide cages by the halogen exchange reactions with aluminium bromide ($Al_2Br_6$) or with tin tetrachloride. Such reactions do not occur on treating the $B_9X_9$ cage compounds with boron trihalides at temperatures around $100^\circ$, although $B_9Br_9$ is the major volatile product when the subchloride mixture $B_{10}Cl_{10}$, $B_{11}Cl_{11}$ and $B_{12}Cl_{12}$ is heated with boron tribromide at temperatures above the decomposition point of the subchloride cage mixture.

Once the $B_9$ cage has formed, it seems that simple halogen exchange reactions, of the type which occur smoothly among the boron trihalides, are impossible. The halogen exchange between two trihalides is normally explained by assuming a halogen-bridged intermediate:

\[
BX_3 + BY_3 \rightleftharpoons X \overset{B}{\rightarrow} Y + BX_2Y + BX_2Y \rightleftharpoons \text{etc.}
\]
When some of the boron atoms are part of a B₉ cage, either the lack of available orbitals on these borons for the formation of a bridged intermediate, or steric crowding, may result in a kinetic block to the halogen exchange (the "co-ordination number" of a boron atom in B₉X₉ is either 5 or 6 depending on its position in the cage). In contrast, B₄Cl₄, in which the co-ordination of the borons is only four, will slowly exchange halogens with boron tribromide at room temperature.

No effort was made to isolate the mixed halides in view of the difficulties found in trying to separate the cage subchlorides B₁₀Cl₁₀, B₁₁Cl₁₁ and B₁₂Cl₁₁. The following methods were used in a series of abortive attempts to effect these separations: fractional sublimation, heat treatment, partial hydrolysis and chromatographic techniques.

7.1 Fractional Sublimation

A description of this technique is given on page 69. The volatilities of the boron monochlorides were found to be too similar for any separation using fractional sublimation to succeed. Only compounds with very different volatilities (such as Si₂Br₆ and the boron monobromide mixture, see page 194) have been successfully separated by this method.
7.2 Heat Treatment

This method was used\(^{(20)}\) to isolate B\(_9\)Cl\(_9\), which is the only volatile solid left when a mixture of B\(_8\)Cl\(_8\) and B\(_9\)Cl\(_9\) is strongly heated. B\(_9\)Br\(_9\) is also isolated from a mixture of the monobromides under these conditions. However, none of the heavier monochlorides exhibited any preferential stability, even when the mixture was heated to 450\(^\circ\) for up to 45 minutes in a sealed tube. In fact, mass spectral analysis of the remaining volatile solids showed that all the heavier subchlorides were equally stable under these conditions.

7.3 Partial Hydrolysis

This was also investigated, in the hope that one of the subchlorides would prove more stable than the others to hydrolysis. Unfortunately, it was found to be impossible to add sufficiently small amounts of water to prevent the degradation of all the monohalides present.

7.4 Thin Layer Chromatography

Their extreme sensitivity to moisture prevented any separation of the boron monochlorides using thin layer chromatography (T.L.C.). Despite working in a leak-free dry-box, using dry solvents and inert plates (coated with Kieselgur G, supplied by Merck Laboratory Chemicals), the boron subchlorides decomposed within a
few minutes of their application to the T.L.C. plates.

7.5 Gas-Liquid Chromatography

The method of separation which was thought to have the greatest chance of success was gas-liquid chromatography (g.l.c.), since the heavier boron monochlorides are relatively volatile and can withstand high temperatures when contained in a sealed tube. However, the only subchlorides collected after injections on to the column of solutions of mixtures containing almost entirely $B_{10}Cl_{10}$, $B_{11}Cl_{11}$ and $B_{12}Cl_{12}$ were traces of $B_{10}Cl_{10}$ and $B_{8}Cl_{8}$ and $B_{9}Cl_{9}$. The hydrogenated compounds $B_{9}Cl_{7}H$ and $B_{9}Cl_{7}H_{2}$ were also identified in material collected following injections onto the g.l.c. column.

An additional factor which would inhibit any proposed separation of the mixed subhalides is that a normal preparation yields so complex a mixture of compounds, with no large proportion of any one. Any separation would therefore produce only very small amounts of the separated material, should a successful method be devised.

7.6 Preparation of Mixed Chloro-Bromide Cages From the Mixed Diboron Tetrahalides

This preparation not only produces cage compounds containing varying numbers of the two
substituents, but also produces cages of different sizes. With such a large variety of components, the mass spectral analysis of the products is complicated, and indeed the usefulness of this reaction in producing identifiably distinct mixed subhalides is limited. This may be illustrated by referring to three separate decomposition reactions of the mixed diboron tetrahalides:

(i) When only a small amount of "Br" is added, cage subchlorides containing a small number of bromine substituents may be formed. Yet it is impossible to identify such mixed halides since many of them have very similar molecular weights. For example, the largest peaks of the molecular ions $B_8Cl_6Br_2^+$, $B_9Cl_8Br^+$ and $B_{10}Cl_{10}^+$, which might all be expected to be present in the products of this type of reaction, lie at m/e 459, 461 and 463 respectively;

(ii) When the decomposing tetrahalide mixture contains approximately equal amounts of diboron tetrachloride and diboron tetrabromide, the overlap of the different mixed subhalides in the decomposition products is still more complete and no single molecular ion may be identified;

(iii) When only a small amount of "Cl" is present in the decomposing tetrabromide, all peaks in the
Species detected in the partial mass spectrum of a mixture of mixed chloro-bromides (see diagram 37; the m/e values listed are those of the most intense peaks observed in any group).

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/e value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_9Br_9^+$</td>
<td>817</td>
</tr>
<tr>
<td>$B_9ClBr_8^+$</td>
<td>773</td>
</tr>
<tr>
<td>$B_9Br_8^+$</td>
<td>737</td>
</tr>
<tr>
<td>$B_8Br_8^+$</td>
<td>726</td>
</tr>
<tr>
<td>$B_8ClBr_7^+$</td>
<td>682</td>
</tr>
<tr>
<td>$B_8Br_7^+$</td>
<td>646</td>
</tr>
<tr>
<td>$B_7Br_7^+$</td>
<td>636</td>
</tr>
<tr>
<td>$B_7ClBr_6^+$</td>
<td>591</td>
</tr>
<tr>
<td>$B_8Br_6^+$</td>
<td>566</td>
</tr>
<tr>
<td>$B_7Br_6^+$</td>
<td>555</td>
</tr>
<tr>
<td>$B_7Cl_2Br_5^+$</td>
<td>546</td>
</tr>
<tr>
<td>$B_8ClBr_5^+$</td>
<td>522</td>
</tr>
<tr>
<td>$B_8Br_5^+$</td>
<td>486</td>
</tr>
<tr>
<td>$B_7Br_5^+$</td>
<td>476</td>
</tr>
<tr>
<td>$B_6Br_5^+$</td>
<td>465</td>
</tr>
<tr>
<td>$B_5Br_5^+$</td>
<td>454</td>
</tr>
<tr>
<td>$B_7Br_4^+$</td>
<td>396</td>
</tr>
<tr>
<td>$B_6Br_4^+$</td>
<td>385</td>
</tr>
<tr>
<td>$B_5Br_4^+$</td>
<td>375</td>
</tr>
<tr>
<td>$B_4Br_4^+$</td>
<td>364</td>
</tr>
<tr>
<td>$B_7ClBr_3^+$</td>
<td>351</td>
</tr>
<tr>
<td>$B_6ClBr_3^+$</td>
<td>340</td>
</tr>
</tbody>
</table>
37. REPRESENTATION OF THE PARTIAL MASS SPECTRUM
Spectrum of a mixture of mixed boron cage subhalides
mass spectrum of the products can easily be identified as no overlap occurs. A partial representation of the mass spectrum of a mixture containing mixed chloro-bromides is illustrated in diagram 37, the species which have been assigned to each m/e value are given in table 19. From the products of this type of reaction, conclusive mass spectral evidence has been obtained for the mixed subhalides $B_7\text{ClBr}_6$, $B_7\text{Cl}_2\text{Br}_5$, $B_8\text{ClBr}_7$, $B_9\text{ClBr}_8$, $B_9\text{Cl}_2\text{Br}_7$ and $B_{10}\text{ClBr}_9$.

The mixed halides formed during the decomposition of chlorine-contaminated diboron tetrabromide would suggest that the $B_2\text{ClBr}_3$ impurity acts as a source of BCl:

$$B_2\text{ClBr}_3 \rightarrow \text{BCl} + \text{BBr}_3.$$  

This is then incorporated into the postulated nido-$(\text{BBr})_n$ polymers before the closing occurs.

7.7 **Preparation of Chloro-Bromide Cages by Halogen Exchange Reactions**

a. **Reaction between tin tetrachloride and the $(\text{BBr})_n$ mixture.**

The substitution of many, if not all of the bromine atoms in $B_9\text{Br}_9$ with chlorine has been achieved by treatment of $B_9\text{Br}_9$ with either titanium tetrachloride
or tin tetrachloride. As this reaction produces a mixture of the chlorobromides $B_9 Br_n Cl_{9-n}$, where $n$ ranges from 0 up to 6, the entire range of $B_9 Cl_{9-x}Br_x$ ($x = 0-9$) has been observed. In an attempt to discover the extent to which the other monobromides would sustain a similar substitution of the halogen atoms, a mixture of the diboron tetrabromide decomposition products containing a high proportion of $B_7 Br_7$ was treated with excess tin tetrachloride. Unlike the halogen exchange reactions of $B_9 Br_9$, where no insoluble, involatile products were formed, in this reaction a heavy brown deposit appeared in the reaction vessel after only four hours at 80°. The majority of the solids left after removing the material volatile at room temperature, did not sublime when heated. Mass spectral analysis of the volatile solid material showed it to consist of a mixture of all the $B_9$ chloro-bromide cages. No $B_7$ compounds could be detected. This suggests that a seven-membered boron cage may be unstable with less than the five bromine substituents of the previously observed $B_7 Cl_2 Br_5$ species. Further substitution of the bromine atoms may lead to the decomposition of the $B_7$ cage and the consequent production of the observed involatile brown deposits.

b. Reaction between aluminium bromide and the (BCl)$_n$ mixture.

In a similar attempt to produce cage compounds not normally formed in the thermal decomposition of the
diboron tetrahalides, a mixture of the larger $B_nCl_n$ compounds (the mixture was known to consist mainly of $B_{11}Cl_{11}$) was dissolved in boron tribromide and added to a large excess of resublimed anhydrous aluminium bromide (supplied by Fison's Scientific Apparatus). This reaction was carried out because no $B_{11}Br_{11}$ or $B_{12}Br_{12}$ and only traces of $B_{10}Br_{10}$ have been detected in the products of the thermal decomposition of diboron tetrabromide. It was hoped that these larger cages would undergo bromination in a halogen exchange reaction between the aluminium bromide and the mixture of boron-chlorine cage compounds.

The reaction vessel was held at room temperature for approximately two weeks. At the end of this time, the solvent was removed and the volatile solids remaining sublimed into narrow tubes for mass spectral analysis. The remaining aluminium bromide, which was more volatile than the subhalide mixture, was separated by rough fractional sublimation without resorting to the long sealed tube method. All the solid material was volatile, suggesting that the boron cages remained intact. Analysis of the mass spectrum of the reaction products showed that halogen exchange had indeed occurred, since the heaviest molecular ion (centred at m/e 865) was identified as $B_{11}Cl_5Br_8$. The following $B_{11}$ compounds were also identified: $B_{11}Cl_4Br_7$, $B_{11}Cl_5Br_6$, $B_{11}Cl_6Br_5$, $B_{11}Cl_7Br_4$, $B_{11}Cl_8Br_3$ and $B_{11}Cl_9Br_2$. The molecular ion present
in highest abundance was $\text{B}_{11}\text{Cl}_{7}\text{Br}_{4}^+$: Metastable peaks corresponding to the following transitions were observed:

$$
\text{B}_{11}\text{Cl}_{8}\text{Br}_{3}^+ \rightarrow \text{B}_{10}\text{Cl}_{5}\text{Br}_{3}^+ + \text{BCl}_3 \\
\text{B}_{11}\text{Cl}_{7}\text{Br}_{4}^+ \rightarrow \text{B}_{10}\text{Cl}_{4}\text{Br}_{4}^+ + \text{BCl}_3.
$$

More extreme conditions than those utilised in this experiment could be expected to lead to the further bromination of the $\text{B}_{11}$ cage without its decomposition. The molecular weight of $\text{B}_{11}\text{Br}_{11}$ is 999, a value well within the range of most mass spectrometers, and so the normal analytical methods would still be operative.

7.8 Stability of the $\text{B}_9$ cage

A noticeable feature of the neutral boron subchlorides and sub-bromides is the high stability of the $\text{B}_9$ cage compounds. $\text{B}_9\text{Cl}_9$ and $\text{B}_9\text{Br}_9$ are both more resistant to degradation by hydrolysis and are more thermally stable than the other members of the series. Unlike other subhalides, the $\text{B}_9$ cage compounds can be handled in air for brief periods and can also withstand temperatures as high as 450° when they are contained in a sealed tube. The $\text{B}_9$ cage is so much more stable than the larger cages that the partial decomposition of the latter in some cases appears to lead to the formation of the $\text{B}_9$ entity. This process
occurs in the pyrolysis of $\text{B}_{10}\text{Cl}_{10}^{2-}$, leading to the production of $\text{B}_9\text{Cl}_8\text{H}$. A similar cage reduction sequence may happen on the g.l.c. column where often only $\text{B}_9$ cage compounds including $\text{B}_9\text{Cl}_9$, $\text{B}_9\text{Cl}_8\text{H}$ and $\text{B}_9\text{Cl}_7\text{H}_2$ could be detected following the injection of solutions containing large amounts of the heavier subchlorides $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$ and $\text{B}_{12}\text{Cl}_{12}$. These observations seem to demonstrate that the $\text{B}_9$ cage is stable in conditions where the larger compounds are not; and that the initial decomposition of the subhalide cage is arrested if the cage can close to form the $\text{B}_9$ entity after loss of one, two or three of the boron atoms.

The reversal of this reduction in cage size, that is the insertion of a $\text{B-X}$ species into $\text{B}_9$ or smaller boron cages does not appear to be possible. The recovery of $\text{B}_4\text{Cl}_4$ from the thermal decomposition products of diboron tetrachloride was described earlier on page 132; and similarly, no insertion of $\text{BCl}$ into the $\text{B}_9$ cage of $\text{B}_9\text{Br}_9$ was detected following the thermal decomposition of diboron tetrachloride containing $\text{B}_9\text{Br}_9$. Indeed, if insertion of $\text{B-X}$ species into closed cages was possible, then only the very largest cages would be isolated.

If $\text{B}_9\text{Cl}_9$ and $\text{B}_9\text{Br}_9$ are the most stable compounds of their respective subhalide series, then
undoubtedly $\text{B}_9\text{Br}_9$ is the most stable of all the neutral boron cage subhalides, for its resistance to decomposition by hydrolysis and pyrolysis is greater than that of $\text{B}_9\text{Cl}_9$. The high stability of $\text{B}_9\text{Br}_9$ is best illustrated by referring to the reaction between a mixture of the larger $\text{B}_n\text{Cl}_n$ compounds and boron tribromide. After holding the two reagents at $300^\circ$ for several hours (conditions in which $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$ and $\text{B}_{12}\text{Cl}_{12}$ would normally remain undecomposed), mass spectral analysis showed that 75% of the volatile solids remaining after the removal of the mixed boron trihalides consisted of $\text{B}_9\text{Br}_9$. The only other molecular ions present were $\text{B}_9\text{ClBr}_8^+$ and $\text{B}_9\text{Cl}_2\text{Br}_7^+$. When the reaction was repeated with first boron trichloride and then boron trifluoride replacing the boron tribromide, the larger $\text{B}_n\text{Cl}_n$ cages remained intact.

These results suggest that the formation of $\text{B}_9\text{Br}_9$ is so favoured a process that the contraction of the larger boron cages begins before this would normally occur without the presence of boron tribromide. The almost complete bromination of the resulting cages, despite the presence of significant amounts of chlorine, is another indication of the stability of $\text{B}_9\text{Br}_9$.

The reasons for the apparently anomalous stability of the $\text{B}_9$ cage will not be understood until
its electronic structure has been worked out. This has been done for the $B_4$ cage, which has had discussed in detail not only its electronic structure, but also the nature of the ligand-boron interaction (41). However, the high symmetry of $B_4 Cl_4$ greatly simplified these calculations; performing similar operations on the far less symmetrical $B_9$ cage would be extremely difficult.

7.9 Reaction Between Diboron Tetrabromide and Disilicon Hexabromide

Many compounds containing both boron and carbon in the central cage (known as carboranes) have been prepared, but so far no similar silicon-containing molecules have been isolated. In many ways this is somewhat surprising in that carbon and silicon belong to the same group in the periodic table, and both elements form a series of carbides and silicides of boron where the non-boron atom can take up positions in the $B_{12}$ icosahedron.

An attempt was made to prepare compounds containing both boron and silicon atoms in the central cage by allowing diboron tetrabromide to decompose in the presence of $Si_2 Br_6$. The latter was produced by brominating $Si_2 Cl_6$, which itself was produced as a by-product in the electrical discharge through boron trichloride vapour. $Si_2 Br_6$ contains a direct
silicon-to-silicon bond; and it was hoped that the molecule would decompose to produce the SiBr$_2$ intermediate and silicon tetrabromide in the same way as the decomposition of diboron tetrachloride is known to lead to the production of the BCl intermediate and boron trichloride.

The reagents were prepared in a breakseal reaction vessel by means of the halogen exchange reaction between boron tribromide and the mixture of diboron tetrabromide and Si$_2$Cl$_6$. After scaling off the tube from the vacuum line, the diboron tetrabromide was allowed to decompose in an oven at 100° for two days. On removing the vessel from the oven it was modified in order that the volatile solid material could be forced into a long tube for fractional sublimation. This process, which was carried out in the way described on page 69, succeeded in separating the initial dark-coloured mass of the products into two fractions:

(1) Colourless crystals (melting point approximately 95°) sublimed approximately 9 inches up the fractionation tube from the remainder of the products;

(ii) The remainder of the material, which was very darkly coloured, and did not sublimes.
These fractions were isolated from each other by sealing off the fractionation tube and analysing them mass spectrometrically. Fraction (i) was found to consist of \( \text{Si}_2\text{Br}_6 \) and fraction (ii) of a mixture of \((\text{BBr})_n\) compounds. None of these cages contained any silicon, which suggests that any cleavage of the silicon-silicon bond in \( \text{Si}_2\text{Br}_6 \) must require more energetic conditions than those used during this reaction. Similar attempts to prepare the carbon-containing carborane subhalides might prove more successful since the preparation of the fully chlorinated \( \text{B}_{10}\text{C}_{2}\text{Cl}_{12} \) has been reported\(^{71}\).
7.10 Summary

Some of the interconversion reactions of the boron subhalides are summarised in diagram 38.

Key

a. Mercury discharge.
b. Thermal decomposition.
c. Silent electric discharge.
d. Titanium tetrachloride or tin tetrachloride at 200-250°.
e. $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$ and $\text{B}_{12}\text{Cl}_{12}$ heated with boron tribromide to 250°.
f. Boron tribromide at 20°.
38. SOME INTERCONVERSION REACTIONS OF THE DORON SUBHALIDES

\[
\begin{align*}
B_n\text{Br}_n & \quad B\text{Br}_3 \\
\text{(n=7-10)} & \quad 200^\circ \\
B_2\text{Br}_4 & \quad B_g\text{Br}_9 \\
& \quad d \\
B\text{Cl}_3 & \quad B_2\text{Cl}_4 \\
& \quad a \\
B_4\text{Cl}_4 & \quad (n=8-12) \\
& \quad 400^\circ \\
B_4\text{Cl}_3\text{Br} & \quad B_g\text{Cl}_9 \\
& \quad [H] \\
B_{10}\text{H}_{14} & \quad \rightarrow \quad (\text{H}_3\text{O})_2B_{10}\text{Cl}_{10} & \quad \rightarrow \quad B_g\text{Cl}_8\text{H}
\end{align*}
\]
8. A CHLORINE-SUBSTITUTED BORO-ADAMANTANE
8. A CHLORINE-SUBSTITUTED BORO-ADAMANTANE (BCl)$_6$(CH)$_4$

During the course of studies (72) on the thermal decomposition of 1,2-bis(dichloroboryl)-ethane, BCl$_2$CH$_2$CH$_2$BCl$_2$, at temperatures between 400° and 500°, a low yield of an unidentified white solid was obtained (73). Other products were identified as hydrogen, methane, ethane, hydrogen chloride, boron trichloride and chlorodimethylborane. The colourless crystalline solid sublimed in conditions could be reproduced at 66-67° (approximately 0.1 mm. mercury) and was very rapidly hydrolysed by water to give chloride ions. This decomposition reaction has now been repeated in an attempt to identify the solid.

8.1 Preparation of 1,2-bis(dichloroboryl)-ethane

This was prepared by the reaction of diboron tetrachloride with ethylene (15) at -78.5°,

\[
\text{B}_2\text{Cl}_4 + \text{C}_2\text{H}_4 \rightarrow \text{BCl}_2\text{CH}_2\text{CH}_2\text{BCl}_2.
\]

Since the reactants and products are all volatile at room temperature, the reaction was carried out in a U-trap on the fractionating train of the vacuum line. Ethylene does not react with boron trichloride at -78.5°, so no purification of the diboron tetrachloride from the preparative apparatus was required. The reaction was
initiated by the addition of excess ethylene to the unpurified diboron tetrachloride. The U-trap was then isolated from the rest of the system and held at -78.5° for 3-4 days until the manometer recorded no further change in the pressure of ethylene, signifying that the reaction had reached completion. On warming the reaction vessel to room temperature, the products were passed through a cold trap held at -116° to remove the volatile traces of excess ethylene. Next, the material involatile at -116° was passed into a trap held at -45° (which allowed any involatile impurities such as boron trichloride to pass through), in which the reaction product was retained as long, colourless needle-shaped crystals. These melted below ambient temperatures to form a colourless, slightly volatile liquid.

8.2 Decomposition of 1,2-bis (dichloroboryl)ethane

The product from the above reaction was condensed into an all glass reaction vessel provided with a constriction and a breakseal (of the type shown in diagram 15a). The tube was evacuated, sealed off at the constriction, and placed in an oven at 450°. After some hours, the tube, which showed signs of considerable charring, was removed from the oven, opened up to the vacuum line via the breakseal and all material volatile at room temperature pumped away. By gently fanning the tube with a free flame, the white
solid could be sublimed free of the char products in
the reaction tube and into the clean apparatus above
the breakseal; the compound was then analysed mass
spectroscopically in the usual way.

8.3 Mass Spectrum of the Volatile Solid Decomposition
Product

The complex pattern of peaks making up the
parent ion in the mass spectrum (see diagram 39)
indicated the presence of at least several atoms of
boron and chlorine; the mass number of the most
intense line in the parent ion cluster was 330. Using
a published computer program, the theoretical
isotopic patterns were calculated for all possible
combinations of boron, chlorine, carbon and hydrogen
which would give a cluster of isotopomer ions at
around m/e values of 330. The only theoretical
pattern which would fit the experimentally observed
parent ion was that for the formula \((\text{BCl})_6(\text{CH})_4\) (see
diagram 39). The close fit of the calculated and the
observed line intensities shows that there is virtually
no cleavage of single hydrogen atoms from the parent.

The only metastable peak which could be detected
in the mass spectrum of \((\text{BCl})_6(\text{CH})_4\) was an exceedingly
strong one centred at about 262 mass units (due to the
number of isotopes of the various elements, this
metastable peak was about ten mass units wide).
39. COMPARISON OF THE OBSERVED & THEORETICAL INTENSITIES FOR THE MOLECULAR ION IN (DCl)_6(CH)_4
The calculated position for the metastable peak for this transition, using m/e values for the strongest peak in both parent and daughter ions, was 262.0 mass units. This ready cleavage of hydrogen chloride from the parent ion of \((\text{BCl})_6(\text{CH})_4\) is in direct contrast to the mass spectra of the hydrogen-substituted boron-chlorine cluster compounds (i.e. \(\text{B}_9\text{Cl}_8\text{H}\) and \(\text{B}_9\text{Cl}_7\text{H}_2\)) which show no cleavage of \(\text{HCl}\) but have quite intense metastable peaks corresponding to the loss of both \(\text{BHCl}_2\) and \(\text{BCl}_3\) molecules.

A much less intense cluster of peaks centred at m/e 534 was identified as the methyl-substituted molecular ion \((\text{BCl})_6(\text{CH})_3\text{CCH}_3^+\). This species possessed only about one tenth of the intensity of \((\text{BCl})_6(\text{CH})_4\), but the methyl-substituted compound was present in all samples investigated.

### 8.4 Structure of \((\text{BCl})_6(\text{CH})_4\)

From its formula, two possible structures could be suggested for \((\text{BCl})_6(\text{CH})_4\):
The first possibility is that this compound could be the B-perchloro derivative of an unknown but predicted \(74\) nido-carborane \(B_6H_6C_4H_4\), having a framework based on the \(B_{10}\) cage of decaborane;

The second possibility is that the compound could be the B-perchloro derivative of the adamantane-like compound \((BCH_2)_6(CH)_4\) (see diagram 40, \(X=CH_2\)). This compound, a colourless, crystalline air-sensitive material, is the major product \(75\) of the sealed-tube pyrolysis of trimethylborane (25\% yield based on starting material consumed). Such a high yield is remarkable for a reaction of this type. The initial isolable product is \((CH_2)_2BCH_2B(CH_2)_2\), which is not unlike the starting material used in the production of \((BCl)_6(CH)_4\). Other pyrolysis products include methane and various \(B_3\) and \(B_5\) closo-carboranes isolable by g.l.c. such as \((CH)_2(BMe)_3\) and \((CH)_2(BMe)_4BH\).

The adamantane-like compound seems to be unique in having a stoichiometry expected of a carborane and yet not possessing the usual carborane type of structure. Its method of preparation, however, resembles that of the sila-adamantane \((SiCH_3)_4(CH_2)_6\) obtained \(76\) in very low yields from the pyrolysis of
40. The Boro-Adamantane Structure
tetramethyl-silane, although here the silicon atoms are in the bridgehead positions. A similar type of cage has been proposed for the compound (AlCH$_3$)$_6$(CCH$_3$)$_4$, although structural evidence is lacking.

The formula of (BCl)$_6$(CH)$_4$, its very high thermal stability (it remained undecomposed after four days at 450$^\circ$), the mass spectral behaviour and the extreme sensitivity towards water led to the conclusion that the compound had the adamantane-like structure of diagram 40, in which X = Cl.

8.5 The Raman Spectrum

The exceptional sensitivity of (BCl)$_6$(CH)$_4$ towards air and moisture made a spectral study of the compound very difficult. A Raman spectrum of the solid sealed in a pyrex tube was the easiest to obtain, and this revealed the C-H stretching vibration at a shift of 3000 cm$^{-1}$; the strong similarity between this Raman spectrum and that of (BCH$_3$)$_6$(CH)$_4$ (see diagram 42), proves that the two compounds have a common skeleton. As can be seen, the spectra are very similar, with some of the absorptions, caused by the cage alone, overlapping. Other absorptions move to lower Raman shifts on substitution of methyl groups for the heavier chlorine atoms. The Raman spectrum of (BBr)$_6$(CH)$_4$ is also given.
8.6 The Infra-red Spectrum

A sample of the "boroadamantane" was sealed in a small evacuated vessel, and the material sent to the Physico-Chemical Measurement Unit at Harwell for examination.

The infra-red spectrum was recorded as a mull with suction-dried nujol over the range 4000-200 cm\(^{-1}\); as a fluorolube mull over the range 4000-200 cm\(^{-1}\); and as a wax disc over the range 600-40 cm\(^{-1}\). The peaks obtained and their intensities are given in table 20. It should be noted that the spectra obtained from the fluorolube and nujol mulls were consistent except for the region 3600-2500 cm\(^{-1}\); where some ambiguities arose due to a possible aliphatic hydrocarbon impurity. In this region, the following peaks were obtained in the nujol spectrum:

- 3580 (m., broad), 3400 (m., broad), 2973 (m., nujol),
- 2870 (m., shoulder), 2838 (m.).

The following peaks were obtained in the fluorolube mull in the same region:

- 3560 (weak, very broad), 3410 (w., very broad),
- 2980 (w.), 2964 (w.), 2930 (w.), 2853 (w.)

To prevent the hydrolysis of the "boroadamantane", the samples were prepared in a dry bag filled with dry...
Table 20.

Infra-red and Raman peaks of (BCl)₆(CH)₄

<table>
<thead>
<tr>
<th>Infra-red spectrum (cm⁻¹)</th>
<th>Raman spectrum (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>71 (m.)</td>
<td>65 (m.)</td>
</tr>
<tr>
<td></td>
<td>94 (sh.)</td>
</tr>
<tr>
<td>168 (m.)</td>
<td>165 (m.)</td>
</tr>
<tr>
<td></td>
<td>315 (v.s.)</td>
</tr>
<tr>
<td>381 (m.)</td>
<td></td>
</tr>
<tr>
<td>562 (m.)</td>
<td></td>
</tr>
<tr>
<td>576 (m.)</td>
<td>681 (w.)</td>
</tr>
<tr>
<td>739 (m.)</td>
<td></td>
</tr>
<tr>
<td>780 (w.sh.)</td>
<td>775 (w.)</td>
</tr>
<tr>
<td>821 (s.)</td>
<td>841 (s.)</td>
</tr>
<tr>
<td>910 (v.s.)</td>
<td>907 (w.,br.)</td>
</tr>
<tr>
<td></td>
<td>1045 (w.,br.)</td>
</tr>
<tr>
<td>1130 (s.,br.)</td>
<td></td>
</tr>
<tr>
<td>1180 (s.,br.)</td>
<td></td>
</tr>
<tr>
<td>1350 (s.)</td>
<td></td>
</tr>
<tr>
<td>1588 (w.)</td>
<td></td>
</tr>
<tr>
<td>1670 (w.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3000 (s.)</td>
</tr>
</tbody>
</table>

(see text for remainder of infra-red peaks)
nitrogen and containing a tray of phosphorus pentoxide. The mulls were held between silver chloride plates, in a gas cell fitted with silver chloride plates, containing a nitrogen atmosphere. For the far infra-red work, the wax disc was prepared in the dry bag and the spectrum recorded in an evacuated instrument.

Finally, for comparison purposes, the spectrum of the nujol mull of a hydrolysed sample was recorded. The sample exposed to the atmosphere gave a completely different result from the unhydrolysed sample (see table 20), giving peaks at 3500 (v.s., broad), 1335 (v.s., broad), 1250 (v.s., broad), 1105 (m.), 1040 (s.), 980 (w., shoulder), 840 (s.), 810 (w., shoulder), 775 (w.), 728 (w.), 655 (w.), 468 (m.), 385 (w.). This suggests that any decomposition taking place in the glove bag was either slight or different from the atmospheric reaction.

8.7 The Proton n.m.r. Spectrum

Further confirmation that \((\text{BCl})_6(\text{CH})_4\) does indeed possess the "adamantane" structure was obtained from its proton n.m.r. spectrum. As the compound was insoluble in deuterio-chloroform (\(\text{CDCl}_3\)), and it was considered that it would decompose in other available organic solvents such as deuterated acetone\((\text{CD}_3)_2\text{CO}\), an attempt was made to dissolve a sample in boron trichloride. The advantage of using this material as a solvent is that it would shield the chlorine
substituted boro-adamantane from attack by hydrolysis, but as boron trichloride boils at 120° under atmospheric pressure and reacts with air, its use as a solvent in n.m.r. work presents certain problems. These were solved using the equipment shown in diagram 41. The sample of (BCl)6(CH)4 was initially contained in the breakseal tube A. After evacuation through cone B, the breakseal was broken and boron trichloride was condensed into finger C via the vacuum line. The apparatus was sealed off from the vacuum line at D and the boron trichloride allowed to melt; fortunately the solid dissolved completely, and the solution was washed from the breakseal tube, which was then sealed off from the remainder of the apparatus at E. In the final step, a strong solution of (BCl)6(CH)4 in boron trichloride was sealed off in the n.m.r. tube whilst both limbs of the equipment were held in ice baths to maintain the internal pressure below atmospheric pressure (otherwise, the tubing would blow out when melted).

The sample was run on a Perkin Elmer R32 at 90MHz. Two single peaks at 5.91 λ and 8.56 λ with integrated intensities 7:1 were given in the n.m.r. spectrum (dioxan used as external reference). The downfield signal at 5.91 λ is close to the value of 6.02 λ reported for (BCH3)6(CH)4, the slight difference being in the correct direction for the substitution of
41. APPARATUS USED TO OBTAIN SAMPLES FOR N.M.R. ANALYSIS
methyl groups by the more electronegative chlorine atoms. The singlet at 8.56\( \tau \) may be assigned to the methyl protons in the impurity compound \((\text{BCl})_6(\text{CH})_2\text{CCH}_3\) in \((\text{BCl})_5(\text{CH})_4\), the methyl hydrogens, now bonded to boron atoms, give a singlet (75) at 9.43\( \tau \).

8.8 Reactions of \((\text{BCl})_6(\text{CH})_4\)

For \((\text{BCl})_6(\text{CH})_4\) to be formed, there must have been some cleavage of the carbon-carbon bonds in 1,2-bis(dichloroboryl)ethane; the presence of methane and chlorodimethylborane among the products previously identified\(^{(73)}\) shows that carbon-carbon cleavage certainly occurs at some stage during the decomposition.

If a better synthesis can be found for this compound, the reactivity of the boron-chlorine bonds should allow the preparation of a whole range of substituted compounds. Only a limited amount of the chlorine-substituted boroadamantane was, however, available, and so only two reactions were attempted.

a. Reaction between \((\text{BCl})_6(\text{CH})_4\) and boron tribromide

The excess boron tribromide was condensed onto \((\text{BCl})_6(\text{CH})_4\) in a breakseal reaction vessel, which was sealed off from the vacuum line and placed in an oven at 80\(^{\circ}\) for ten days. At the end of this period, material volatile at room temperature was removed, and the remaining product, a colourless crystalline
Solid with appreciably lower volatility than the solid starting material, was sublimed into the appropriate tubes and subjected to analysis by both laser Raman and mass spectroscopy. Both of the resulting spectra indicated that the bromination reaction had been successful. As shown in diagram 42, the Raman spectrum is very similar to both the chlorine and methyl-substituted boroadamantanes; the absorptions which move to lower Raman shifts on substitution of methyl groups for the heavier chlorine atoms are found at even lower shifts in the hexabromo-derivative \((\text{BBr})_6(\text{CH})_4\). The Raman shifts of the most intense peaks in the three different boroadamantanes are given in table 21. This tabulation gives an indication of the movement of the various absorptions. The sample of the hexamethyl derivative was kindly provided by Dr. M.P. Brown of Liverpool University.

The predominant molecular ion in the mass spectrum of the brominated boro-adamantane was indeed found to be \((\text{BBr})_6(\text{CH})_4\); only a small amount of the partially chlorinated \(\text{B}_6\text{ClBr}_5(\text{CH})_4\) was present. As in the chloroadamantane spectrum, the partially methylated impurity \((\text{BBr})_6(\text{CH})_3\text{CCH}_3\) was detected, and again the molecular ion \((\text{BBr})_6(\text{CH})_4^+\) exhibited the metastable loss of the hydrogen halide:

\[
(\text{BBr})_6(\text{CH})_4^+ \rightarrow \text{B}_6\text{Br}_5\text{C}_4\text{H}_7^+ + \text{HBr}.
\]
### Table 21.

Most intense peaks in the Raman spectra of the three boro-adamantanes

<table>
<thead>
<tr>
<th></th>
<th>$(BCH_3)_6(CH)_4$</th>
<th>$(BCl)_6(CH)_4$</th>
<th>$(BBr)_6(CH)_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>84 (s.)</td>
<td>65 (m.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107 (sh.)</td>
<td>94 (sh.)</td>
<td>104 (m.)</td>
<td></td>
</tr>
<tr>
<td>271 (m.)</td>
<td>165 (m.)</td>
<td>149 (m.)</td>
<td></td>
</tr>
<tr>
<td>445 (v.s.)</td>
<td>315 (v.s.)</td>
<td>203 (v.s.)</td>
<td></td>
</tr>
<tr>
<td>830 (s.)</td>
<td>841 (s.)</td>
<td>842 (s.)</td>
<td></td>
</tr>
<tr>
<td>2890 (m.br.)</td>
<td>3000 (s.)</td>
<td></td>
<td>3010 (s.)</td>
</tr>
<tr>
<td>2930 (s.)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2950 (s.)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
42. PRINCIPAL PEAKS IN THE RAMAN SPECTRA OF SOLID SAMPLES OF BORO-ADAMANTANES
This bromination reaction illustrates the difference between these adamantane-like compounds, and the polyhedral subhalides, where such substitution reactions involving the boron trihalides do not operate. The difference in reactivity must be due either to the lower co-ordination of the boron atoms in the boro-adamantanes or to the presence of available orbitals, and their resulting ability to participate in the halogen-bridged intermediates thought to be responsible for halogen exchange in the boron trihalides. Unlike the polyhedral subhalides, where the co-ordination number of the boron atoms can be as high as six, the bonding in the adamantane-like structure may be readily explained in terms of 2-electron boron-carbon bonds as in the organoboranes (although the possibility of electron-deficient delocalised bonding cannot be discounted), and the co-ordination number of the boron atoms is only three.

b. Reaction between \((\text{BCl})_6(\text{CH})_4\) and tetramethylstannane
This reaction was carried out in an attempt to produce the methyl derivative \((\text{BCH}_3)_2(\text{CH})_4\) obtained following the pyrolysis of trimethylborane. Tetramethylstannane (supplied in sealed 5ml. ampoules by B.D.H. Chemicals Ltd.) was condensed onto \((\text{BCl})_6(\text{CH})_4\) in a glass breakseal vessel, which was then sealed off from the vacuum line. When the tetramethylstannane melted, it was found not to dissolve
the boro-adamantane. The tube was placed in an oven at 80°C for 16 hours, then removed, and material volatile at room temperature was taken off in the normal way via the breakseal. The remaining products appeared to consist of more than one component as both solids and a slightly volatile liquid were present. Mass spectral analysis of a sample of low volatility proved that the reaction was partially successful, for the mixed chloro-methyl compounds B₆(CH₃)₃Cl₃(CH)₄ and B₆(CH₃)₄Cl₂(CH)₄ were identified.

8.9 Summary

The formation of each of the proposed adamantane-like compounds (BCH₃)₆(CH)₄, (SiCH₃)₄(CH₂)₆ and (AlCH₃)₆(CCH₃)₄ is thought to involve free radicals. In the pyrolysis of trimethylborane, the initiation steps are believed to involve the formation of the radicals (CH₃)₂B and (CH₃)₂BCH₂·

\[
\begin{align*}
(\text{CH}_3)_2\text{B}-\text{CH}_3 & \rightarrow (\text{CH}_3)_2\text{B} + \cdot\text{CH}_3 \\
(\text{CH}_3)_2\text{B}-\text{CH}_2-\text{H} & \rightarrow (\text{CH}_3)_2\text{BCH}_2\cdot + \text{H}\cdot
\end{align*}
\]

The coupling of these radicals would lead to the formation of (CH₃)₂BCH₂B(CH₃)₂, which is in fact the main initial reaction product. Some confirmation of the involvement of free radicals has been obtained by the addition of dimethyl mercury to the trimethylborane.
Since the dimethyl mercury readily generates methyl radicals, this enables the pyrolysis to take place at 350° (100° lower than usual), and \((\text{CH}_3)_2\text{BCH}_2\text{B(CH}_3\text{)}_2\) was again isolated. As the procedure used in the formation of the chloro-substituted boro-adamantane is so similar to those used to prepare the methyl-substituted \((\text{BCH}_3)_6\text{(CH)}_4\) from trimethylborane and the sila-adamantane \((\text{SiCH}_3)_4\text{(CH}_2\text{)}_6\) from tetramethyl silicon (i.e. sealed tube pyrolysis at elevated temperatures), free radicals may also be involved in the decomposition of the 1,2bis(dichloroboryl)ethane.

To develop the full chemistry of the chloro-adamantane, however, a better synthesis must be devised, for although the pyrolysis produces no other volatile solids, only very small amounts are obtained, the vast majority of the products consisting of the volatile components (hydrogen, methane, ethane, hydrogen chloride, boron trichloride and boron alkyl chlorides) and the unidentified involatile black charred mass. In parallel with the pyrolysis of trimethylborane, a better preparation might be thought to involve the pyrolysis of dichloromethylborane or chlorodimethylborane. However these are much more stable than the fully methylated compound; dichloromethylborane will withstand temperatures as high as 450° for long periods.\(^{(78)}\)

The high thermal stability of the chloro-
adamantane suggests that the chemistry of this class of compounds may prove to be of great interest. A greater resistance to degradation by hydrolysis is conferred by the substitution of the chlorine atoms for methyl groups (the methyl-substituted adamantane was separated from the other trimethylborane pyrolysis products by treatment with water\(^{79}\)). Different substituents on the boron atoms may produce still more inert compounds.
9. CONCLUSIONS.
9. CONCLUSIONS

As a result of the successful preparation of $B_9Br_9$ and the development of reactions in which it participates, the field of boron subhalide chemistry may subsequently be developed one stage further to include a proper understanding of its relationship with the polyhedral borohydride ions and carboranes.

A comparison of $B_9Br_9$ with $B_9H_9^{2-}$ shows there to be a number of similarities between the two cage compounds:

(i) The boron cage in both $B_9Br_9$ and $B_9H_9^{2-}$ is thought$^{(78)}$ to consist of a symmetrically tricapped trigonal pyramid.

(ii) Both $B_9Br_9$ and $B_9H_9^{2-}$ possess high thermal stability. The thermal stability of alkali metal salts of $B_9H_9^{2-}$ is said to be comparable$^{(78)}$ to the salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$; $B_9Br_9$ can withstand temperatures as high as 500°.

(iii) Both $B_9$ cage compounds are hydrolytically unstable. The $B_9H_9^{2-}$ ion is unstable in acidic media$^{(78)}$; and whilst $B_9Br_9$ is unaffected by treatment with degassed water at room
temperature, degradation by hydrolysis proceeds rapidly using less mild conditions.

(iv) Both $B_9^\text{Br}_9$ and $B_9^\text{H}_9^2-$ produce measurable electronic spectra, the latter being the only polyhedral borohydrde ion known to do this. However the $B_9^\text{H}_9^2-$ ion absorbs radiation (78) only in the far ultra violet at 2260Å, so that it is colourless. In contrast, the neutral sub-bromide is deep red in colour and gives absorption peaks at 370Å and 4520Å, suggesting that in $B_9^\text{Br}_9$ the energy difference between the highest filled molecular orbital and the lowest unfilled molecular orbital must be much less than in the borohydrde ion.

It may be possible to promote interconversion reactions between the neutral cages and the ions by the simple addition or removal of electrons. It should be noted that Muetterties (58) has claimed to have isolated $\left[(\text{CH}_3)_4\text{N}\right]_2B_9\text{Cl}_8\text{H}$, the alkyl ammonium salt of $B_9^\text{H}_8^2-$, following the addition of a solution of an alkyl ammonium halide to a mixture of $B_9\text{Cl}_8\text{H}$ and water. The reversal of this process, that is the removal of electrons from the cage ions, may possibly be accomplished by the electrolysis of halogenated cage ions in a conducting medium such as acetonitrile:
Such a method may prove to be the only feasible way of producing the larger subchlorides pure. Despite mass spectral evidence having indicated that the glassy red material produced in the thermal decomposition of diboron tetrachloride is not one compound as stated by Urry(17), rather it is a mixture of $\text{B}_{10}\text{Cl}_{10}$, $\text{B}_{11}\text{Cl}_{11}$ and $\text{B}_{12}\text{Cl}_{12}$, all attempts to separate the mixture into its components have failed.

It is interesting to note that some of the samples analysed using mass spectrometry have appeared to contain the compounds $\text{B}_{13}\text{Cl}_{13}$ and $\text{B}_{14}\text{Cl}_{14}$. If these are found to be cage compounds, they will constitute the subchloride equivalents of the 13 and 14 vertex polyhedral metallocarboranes described by Hawthorne(36,37).

Prior to this research, little was known about the chemistry of the neutral boron cage subhalides, since difficulties had been found both in preparing adequate quantities of the pure compounds to carry out reactions and also in producing reaction conditions which would prove sufficiently mild to prevent the decomposition of the boron cage. As described in Chapter 6, the silent electric discharge preparation of $\text{B}_{9}\text{Br}_{9}$ has yielded sufficiently large amounts of the pure sub-bromide to enable investigations.
of its physical properties and some chemical reactions to be carried out. It would be beneficial if the silent electric discharge method could be modified so that the preparation became continuous (as in the production of diboron tetrachloride), in order to avoid the trap-to-trap distillation procedure, which requires continual attention. However, as the silent electric discharge preparation of $B_9\text{Br}_9$ is thought to take place via the intermediate formation of diboron tetrabromide, to produce the cage compound, the proposed intermediate must also be circulated through the discharge cavity. This circulation is normally achieved using the method of trap-to-trap distillation; but it is difficult to conceive a continuous method which could similarly draw diboron tetrabromide together with the much more volatile boron tribromide through the discharge cavity.

In the attempts to replace the bromine atoms on $B_9\text{Br}_9$ with other substituent atoms or groups of atoms, only a restricted range of reactions was carried out. Chlorination reactions were the most successful, where the products of the reaction between $B_9\text{Br}_9$ and the chlorinating agent (either titanium tetrachloride or tin tetrachloride) were found to contain $B_9\text{Cl}_9$, as well as partially brominated molecules. Further treatment of the partially brominated product with a chlorinating agent may be necessary to produce
the total substitution of $B_9Br_9$ with chlorine atoms.

Attempts to fluorinate the $B_9Br_9$ were less successful. Better results may have been obtained using antimony trifluoride aided by the addition of an inert solvent and allowing the mixture of reagents to stand at room temperature. If halogen exchange is found to occur between the antimony trifluoride and the $B_9Br_9$ under these conditions, the products of the reaction would constitute the first known examples of fluorine-substituted boron cage compounds.

No efforts were made to substitute iodine atoms onto the cage in $B_9Br_9$. However, since the action of aluminium bromide on the $(BCl)_n$ ($n = 10-12$) compounds was found to lead to a partial replacement of the chlorine atoms with bromine atoms, then it would seem reasonable to expect that treating $B_9Br_9$ with aluminium iodide would lead to the production of iodine-substituted $B_9$ compounds.

As it has been established that halogen atoms attached to the boron cages of the neutral boron subhalides may be substituted for different halogen atoms without the consequent disruption of the boron cage, the question naturally arises as to whether non-halogen atoms may similarly be substituted onto the cage. The psuedohalogenes seem to be potential
boron cage substituents. It may also be possible to produce from \( B_9 Br_9 \), \((BR)_n\) compounds similar to those described by Kuchen (79) (where \( R = C_6 H_5 \)) or Kraus (80) (where \( R = C_4 H_9 \)). Certainly the identification of the methyl-substituted compounds \( B_9 Br_9 - x Me_x \) (\( x = 1-3 \)) following the reaction between tin tetramethyl and \( B_9 Br_9 \) suggests that neutral boron cage compounds substituted with organic groups are capable of existence.

A further series of possible reactions is suggested following the identification of the partially hydrogenated subchlorides \( B_9 Cl_8 H \) and \( B_9 Cl_7 H_2 \). In parallel with the reaction between n-butyl lithium (69) and \( B_{10} C_2 Cl_{11} H \), where the only hydrogen atom is replaced by lithium leading to the production of \( B_{10} C_2 Cl_{11} Li \), the action of n-butyl lithium on the partially hydrogenated subhalide would be expected to lead to the metallation of the subhalide, producing \( B_9 Cl_8 Li \). This type of compound might react in the same way as organo-lithium compounds. If this was indeed the case, treatment of \( B_9 Cl_8 Li \) with boron trichloride could lead to the production of \( B(B_9 Cl_8)_3 \); and the action of mercuric bromide on the lithiated cage compound would be expected to yield \( Hg(B_9 Cl_8)_2 \).

The halogen atoms of the chlorine-substituted boro-adamantane have been shown to be more reactive.
than halogen atoms attached to the polymeric monohalides, since, unlike the latter, the chlorine atoms of the boro-adamantane readily exchange with boron tribromide. It is therefore possible that a series of reactions similar to those proposed for the polymeric monohalides may also produce analogous replacements on the boro-adamantane.

In addition to the type of reaction mentioned above for the boron cage compounds, the chlorine atoms of boro-adamantane may react with magnesium to produce the Grignard reagent, which would then have the potential to yield an almost infinite number of derivatives. Any linkages of the boro-adamantane unit produced perhaps by reacting the Grignard derivative with boron trichloride might produce a polymer retaining the high thermal stability of the chlorine-substituted boro-adamantane. The reactivity of the boron-chlorine bonds may in fact make the chemistry of the molecule of greater interest than the methyl-substituted boro-adamantane isolated following the pyrolysis of trimethylboron, of which no reactions have yet been reported.

Experiments described in this thesis represent some of the first attempts to perform reactions with the neutral boron cage halides. Since such reactions have now been shown to be successful, it is hoped that
the chemistry of these compounds will be further developed, and that the suggestions of possible future reactions may be of use to further research workers.
REFERENCES


42. J.D. Lee, Talanta 20, 1029 (1973).


68. Private communication from Dr. M.B. Hursthouse, Queen Mary College.


