STUDY OF MOLECULAR MOTION ON MAIN GROUP III AND V ADDITION COMPLEXES BY BROADLINE AND PULSED NMR

by

TIAN TSE ANG

B.Sc., Nanyang University, Singapore, 1967

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY in the Department of Chemistry

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

August, 1972.
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date Aug 19/72
Abstract

The proton magnetic resonance absorption and spin-lattice relaxation measurements have been carried out on $\text{Me}_3\text{N-BMe}_3$, $\text{Me}_3\text{N-AlMe}_3$, $\text{Me}_3\text{P-AlMe}_3$, $\text{Me}_3\text{P-BMe}_3$, $\text{Me}_3\text{P-Me}_3\text{B}$, $\text{Me}_2\text{NH-BMe}_3$, $\text{Me}_2\text{NH-AlMe}_3$, $\text{Me}_3\text{NBCl}_3$, $\text{Me}_3\text{NBBBr}_3$, and trimethylamine-halogen complexes in order to study the molecular motion and phase transitions of these complexes in the solid state between 77 K to their melting points. The activation energies and rate parameters associated with these motional processes are reported.

The second moment data of all the trimethylamine addition complexes indicate the methyl groups attached to nitrogen are all rigid (as far as the nmr second moment is concerned) at liquid nitrogen temperature and at higher temperature the methyl groups as well as the trimethylamine moiety rotate with a frequency greater than about 10 kHz. The methyl groups rotate prior to the rotation of the trimethylamine moiety in all but the $\text{Me}_3\text{N-Br}_2$ and $\text{Me}_3\text{N-BMe}_3$ complexes. The present study concludes that if the intermolecular contributions to the activation energies for methyl group reorientations are of the same order, the activation energies for the methyl groups follow the trend of the stability of the trimethylamine complexes.

The second moment data show that the methyl groups attached to boron, phosphorus and aluminium are all reorientating at 77 K at a rate faster than about 10 kHz. The relaxation studies conclude that the activation energies for the three methyl groups attached to various central atoms decrease in the order $\text{N} > \text{C} > \text{B} > \text{Si} > \text{Al}$. 

Comparison of the calculated and experimental $T_1$ minimum for methyl group reorientation suggests that there is small distortion of the $C_3$ potential well, and comparison of the calculated and experimental pre-exponential factors suggests that the activation energy for rotation of the whole molecule or the moiety is temperature dependent.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>xvii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td></td>
</tr>
<tr>
<td>CHAPTER I INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>A. Introduction to Addition Complexes</td>
<td>1</td>
</tr>
<tr>
<td>B. Various Studies on Addition Complexes</td>
<td>2</td>
</tr>
<tr>
<td>C. NMR Studies on Addition Complexes</td>
<td>3</td>
</tr>
<tr>
<td>References (Chapter I)</td>
<td>4</td>
</tr>
<tr>
<td>CHAPTER II INTRODUCTION TO NMR THEORY</td>
<td>6</td>
</tr>
<tr>
<td>A. Elementary Resonancy Theory</td>
<td>6</td>
</tr>
<tr>
<td>B. The Line Shape Function</td>
<td>7</td>
</tr>
<tr>
<td>C. Second Moment of Absorption Line Shape</td>
<td>10</td>
</tr>
<tr>
<td>D. Spin-lattice Relaxation Time</td>
<td>15</td>
</tr>
<tr>
<td>E. Distribution of Correlation Times and their Effect on $T_1$ and $E_a$</td>
<td>20</td>
</tr>
<tr>
<td>F. Activation Energy</td>
<td>23</td>
</tr>
<tr>
<td>References (Chapter II)</td>
<td>24</td>
</tr>
</tbody>
</table>
CHAPTER III  APPARATUS AND METHODS OF MEASUREMENT--------- 27
A.  Continuous Wave (CW) Measurements---------------------- 27
   1. CW Spectrometer---------------------------------------- 27
   2. Calibration of Spectrometer----------------------------- 27
   3. Line Width and Second Moment Measurements------------- 28
   4. Variable Temperature Assembly-------------------------- 29
B.  Spin-lattice Relaxation Measurements--------------------- 30
   1. Pulsed Spectrometer------------------------------------ 30
   2. Linearity of Receiver----------------------------------- 32
   3. Variable Temperature Assembly-------------------------- 32
   4. Measurement of Spin-lattice Relaxation Time------------ 33
C.  The Dry Box--------------------------------------------- 35
References (Chapter III)------------------------------------ 36

CHAPTER IV  AN NMR STUDY OF TRIMÉTHYLAMINE OR PHOSPHINE
            COMPLEXED WITH TRIMETHYLBORANE OR ALUMINIUM----- 37
A.  Introduction--------------------------------------------- 37
B.  Experimental-------------------------------------------- 37
   B.1 Materials--------------------------------------------- 37
   B.2 Preparation of Addition Complexes---------------------- 37
   B.3 Measuring Procedures----------------------------------- 38
C.  Trimethylamine-trimethylborane--------------------------- 38
   C.1 Line Widths and Secqnd Moments------------------------- 38
   C.2 Calculation of Second Moment and
        Discussion of Molecular Motion----------------------- 39
C.3 Interpretation of the Observed Second Moment ----------------------------- 41
C.4 Spin-lattice Relaxation----------------------------------------------- 47
D. Trimethylamine-trimethylaluminium Complex------------------------------- 52
D.1 Line Width and Second Moment--------------------------------------- 52
D.2 Calculation of Second Moment and Discussion of Molecular Motion-------- 54
D.3 Spin-lattice Relaxation----------------------------------------------- 56
E. Trimethylphosphine-trimethylaluminium--------------------------------- 63
E.1 Line Widths and Second Moments-------------------------------------- 63
E.2 Calculation of Second Moment---------------------------------------- 63
E.3 Spin-lattice Relaxation Time----------------------------------------- 67
F. Trimethylphosphine-trimethylborane----------------------------------- 69
F.1 Experimental Line Width and Second Moment----------------------------- 69
F.2 Calculation of Second Moment and Discussion of Molecular Motion---------- 71
F.3 Spin-lattice Relaxation Times---------------------------------------- 73
References (Chapter IV)----------------------------------------------- 79

CHAPTER V AN NMR STUDY OF TRIMETHYLPHOSPHINE AND TRIMETHYL-
BORANE------------------------------------------------------------- 81
A. Introduction---------------------------------------------------------- 81
B. Experimental---------------------------------------------------------- 81
B.1 Materials----------------------------------------------------------- 81
B.2 Measuring Procedures----------------------------------------------- 82
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. Trimethylphosphine</td>
<td>82</td>
</tr>
<tr>
<td>C.1 Experimental Line Widths and Second Moments</td>
<td>82</td>
</tr>
<tr>
<td>C.2 Calculation of Second Moment and Discussion of Molecular Motion</td>
<td>82</td>
</tr>
<tr>
<td>C.3 Spin-lattice Relaxation Times</td>
<td>86</td>
</tr>
<tr>
<td>D. Trimethylborane</td>
<td>90</td>
</tr>
<tr>
<td>D.1 Experimental Second Moments and Line Widths</td>
<td>90</td>
</tr>
<tr>
<td>D.2 Calculation of Second Moment and Discussion of Molecular Motion</td>
<td>90</td>
</tr>
<tr>
<td>D.3 Spin-lattice Relaxation Times</td>
<td>95</td>
</tr>
<tr>
<td>References (Chapter V)</td>
<td>96</td>
</tr>
</tbody>
</table>

**CHAPTER VI AN NMR STUDY OF DIMETHYLAMINE COMPLEXED WITH TRIMETHYLALUMINIUM OR TRIMETHYLBORANE**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Introduction</td>
<td>97</td>
</tr>
<tr>
<td>B. Experimental</td>
<td>97</td>
</tr>
<tr>
<td>B.1 Preparation of Complexes</td>
<td>97</td>
</tr>
<tr>
<td>B.2 Procedure of measurement</td>
<td>98</td>
</tr>
<tr>
<td>C. Dimethylamine-trimethylaluminium</td>
<td>98</td>
</tr>
<tr>
<td>C.1 Experimental Line Widths and Second Moments</td>
<td>98</td>
</tr>
<tr>
<td>C.2 Calculation of Second Moments and Determination of Molecular Motion</td>
<td>98</td>
</tr>
<tr>
<td>C.3 Spin-lattice Relaxation Times</td>
<td>102</td>
</tr>
<tr>
<td>D. Dimethylamine-trimethylborane</td>
<td>106</td>
</tr>
</tbody>
</table>
C.2 Trimethylamine-iodine Chloride Complex----------------------------- 128
C.3 Trimethylamine-bromine Complex----------------------------- 129
D. Summary------------------------------------------------------------- 129
References (Chapter VIII)------------------------------------------ 131

CHAPTER IX CONCLUSION AND SUGGESTIONS FOR FURTHER WORK------------------ 132
A. Conclusion of the Present Work------------------------------------- 132
B. Suggestions for Further Work-------------------------------------- 137
References (Chapter IX)------------------------------------------ 139

APPENDIX A Computer Programme to calculate $T_1$ from experimental data ----------------- 141

APPENDIX B Computer Programme to calculate second moment from experimental data--------------------------------------------------------------- 143

APPENDIX C Computer Programme to fit the experimental $T_1$ data using two BPP curves----------------------------------------------- 144
## List of Tables

<table>
<thead>
<tr>
<th>TABLE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Theoretical second moment for trimethylamine-trimethylborane (in $G^2$) and comparison with experimental values</td>
<td>44</td>
</tr>
<tr>
<td>4.2</td>
<td>Theoretical second moment for trimethylamine-trimethylaluminium (in $G^2$) and comparison with experimental values</td>
<td>55</td>
</tr>
<tr>
<td>4.3</td>
<td>Theoretical second moment for trimethylphosphine-trimethylaluminium (in $G^2$) and comparison with experimental values</td>
<td>65</td>
</tr>
<tr>
<td>4.4</td>
<td>Energy and Rate Parameters for trimethylphosphine-trimethylaluminium</td>
<td>69</td>
</tr>
<tr>
<td>4.5</td>
<td>Theoretical second moment for trimethylphosphine-trimethylborane (in $G^2$) and comparison with experimental values</td>
<td>72</td>
</tr>
<tr>
<td>4.6</td>
<td>Energy and Rate Parameters for trimethylphosphine-trimethylborane</td>
<td>77</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.1</td>
<td>Comparison of theoretical and experimental second moments of trimethylphosphine (second moment in $G^2$)</td>
<td>85</td>
</tr>
<tr>
<td>5.2</td>
<td>Comparison of theoretical and experimental second moments of trimethylborane (second moment in $G^2$)</td>
<td>92</td>
</tr>
<tr>
<td>6.1</td>
<td>Calculation of second moments for dimethylamine-trimethylaluminium complex and comparison with the experimental values (second moment in $G^2$)</td>
<td>101</td>
</tr>
<tr>
<td>6.2</td>
<td>Calculation of second moments for dimethylamine-trimethylborane complex and comparison with the experimental values (second moment in $G^2$)</td>
<td>108</td>
</tr>
<tr>
<td>7.1</td>
<td>Results of combustion analysis on trimethylamine-boron trihalides complexes</td>
<td>115</td>
</tr>
<tr>
<td>8.1</td>
<td>Results of combustion analysis on trimethylamine-halogens complexes</td>
<td>125</td>
</tr>
<tr>
<td>9.1</td>
<td>Activation energies (in kcal/mole) and rate parameters for various motions in addition complexes</td>
<td>133</td>
</tr>
</tbody>
</table>
9.2 Values of $T_1$ minimum for methyl group reorientation

134
List of Figures

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Relation of input signal and output voltage of the receiver operating at 30 MHz</td>
<td>33</td>
</tr>
<tr>
<td>4.1</td>
<td>Line width and second moment of trimethylamine-trimethylborane as a function of temperature</td>
<td>40</td>
</tr>
<tr>
<td>4.2</td>
<td>The spin-lattice relaxation time, $T_1$, of trimethylamine-trimethylborane as a function of inverse temperature</td>
<td>48</td>
</tr>
<tr>
<td>4.3</td>
<td>Plot of $\omega_0 T_C$ versus inverse of temperature of trimethylamine-trimethylborane (a) for rotation of the methyl groups attached to boron (b) for rotation of the methyl group attached to nitrogen plus the reorientation of the whole molecule about the B-N bond</td>
<td>49</td>
</tr>
<tr>
<td>4.4</td>
<td>Line width and second moment of trimethylamine-trimethylaluminium as a function of temperature</td>
<td>53</td>
</tr>
</tbody>
</table>
4.5 The spin-lattice relaxation time of trimethylamine-trimethylaluminium as a function of inverse temperature

4.6 Plot of $\omega_0 \tau_C$ versus reciprocal of temperature of trimethylamine-trimethylaluminium (a) for rotation of the methyl groups attached to nitrogen (b) for reorientation of the whole molecule about the N-A bond

4.7 Temperature dependence of line width and second moment of trimethylphosphine-trimethylaluminium

4.8 The spin-lattice relaxation time of trimethylphosphine-trimethylaluminium as a function of reciprocal of temperature

4.9 Temperature dependence of line width and second moment of trimethylphosphine-trimethylborane

4.10 Spin-lattice relaxation time of trimethylphosphine-trimethylborane as a function of inverse temperature
5.1 Line width and second moment of trimethylphosphine as a function of temperature------------------ 83

5.2 Spin-lattice relaxation time of trimethylphosphine as a function of inverse temperature------------------ 87

5.3 Plot of $\omega_0^2 T$ versus reciprocal of temperature of trimethylphosphine------------------ 88

5.4 Line width and second moment of trimethylborane as a function of temperature------------------ 91

5.5 Spin-lattice relaxation time of trimethylborane as a function of inverse of temperature------------------ 94

6.1 Line width and second moment of dimethylamine-trimethylaluminium as a function of temperature---- 99

6.2 Spin-lattice relaxation time of dimethylamine-trimethylaluminium as a function of inverse of temperature------------------ 103

6.3 Plot of $\omega_0^2 T_c$ versus inverse of temperature for the rotation of the methyl groups attached to nitrogen in dimethylamine-trimethylaluminium------------------ 104
6.4 Line width and second moment of dimethylamine-trimethylborane versus temperature

6.5 Spin-lattice relaxation time of dimethylamine-trimethylborane versus inverse of temperature

7.1 Spin-lattice relaxation time of trimethylamine boron tribromide complex as a function of inverse of temperature

7.2 Spin-lattice relaxation time of trimethylamine boron trichloride complex as a function of inverse temperature

7.3 DSC curve for trimethylamine boron trichloride complex

8.1 Spin-lattice relaxation time of trimethylamine-iodine chloride complex as a function of inverse of temperature

8.3 Spin-lattice relaxation time of trimethylamine-bromine complex as a function of inverse of temperature
Acknowledgments

I would like to express my sincere gratitude to Professor B.A. Dunell who introduced me to the field of broadline and pulsed NMR. I am greatly indebted to him for his kind help, guidance, research facilities and constant encouragement. The help and courage he gave to me and my family during my critical illness is beyond repayment.

Also I would like to express my sincere gratitude to Drs. K.S. Chan, W.A. Young and his medical group, H. Chuan, I.H. Plenderleith, A.I. Munro and his medical group who have saved my life. Special thanks are due to Dr. A.I. Munro and his medical group who performed an excellent thoracotomy.

Further I would like to thank Professor C.A. McDowell for his continuing interest in the field of broadline and pulsed NMR, his kind help and his generous research facilities.

I would like to thank Dr. A. Storr for providing Me₃N-BMe₃, Drs. R. Ikeda, A.W. Khanzada, S.E. Ulrich and W.R. Janzen for their helpful discussions, friendship and cheer, and members of the electronic shop for their ideal service and advice in keeping the spectrometers in good operating condition.

My debt to my wife for her constant encouragement and especially for the courage and care she gave me during my critical illness is beyond repayment.
Finally, I would like to acknowledge the receipt of an assistantship from the Department of Chemistry, a University of British Columbia Graduate Fellowship.
献给
蓝鲸君
CHAPTER I

Introduction

A. Introduction to Addition Complexes

Addition complex formation is an association with definite stoichiometry between two or more molecules. This association is stronger than an ordinary van der Waals interaction. Addition complexes are frequently formed when electron acceptor molecules interact with electron donor molecules. These complexes are recognized by the almost invariable appearance of new intense broad spectral bands in the visible or ultraviolet spectrum, generally accompanied by perturbations of the spectral bands arising from electronic transitions of the component molecules and by indications of compound formation in phase diagrams. Most complexes have small heats of formation and definite formation constants. Dipole moments and semiconductivity are different from those of the component molecules, and marked anisotropies in light absorption, conductivity, compressibility and other physical properties are frequently observed.

Addition complexes may be classified into three classes. They are $\sigma-\sigma$, $\sigma-\pi$ and $\pi-\pi$, referring to complexes where the orbitals are involved in formation of complexes are both $\sigma$ orbitals, one $\sigma$ and one $\pi$, both $\pi$ orbitals respectively. Examples are:

1. $\sigma$ orbital donors: amines, phosphines, arsines, etc.
2. $\pi$ orbital donors: aromatic hydrocarbons.
3. \(\sigma\) orbital acceptors: \(BF_3\), \(BCl_3\), \(Me_3B\) etc.

4. \(\pi\) orbital acceptors: aromatic or ethylenic hydrocarbons

with electron-withdrawing substituents such as \(NO_2\) and \(CN\) groups.

The present study involved only \(\sigma-\sigma\) addition complexes. Therefore only relevant topics will be discussed.

B. Various Studies on Addition Complexes

The earlier work on addition complexes has concerned the preparation of the complexes and studies on the physical chemistry and thermodynamic properties of complexes. There have been several reviews concerned with addition complexes, largely complex compounds formed by one specific acceptor molecule, or by one class of acceptor molecules, usually boron-containing, e.g. boron tribromide [1.1], boron trichloride [1.2], boron trifluoride [1.3 - 1.5], borane [1.6 - 1.7] and trialkylboranes [1.8]. The stability relationships among analogous molecular addition compounds of Group III elements have been reviewed by Stone [1.9]. Mulliken [1.10] in 1952 gave a theoretical basis for interpreting molecular complex formation, and the treatment immediately provided the theoretical basis for interpretation of spectroscopic and formation constant data, and initiated research on semiconductivity and magnetic properties of molecular complexes [1.11]. Various methods have been used to study the structure of addition complexes. They are: X-ray diffraction, in which the crystal structure in the solid state can be studied, Electron Diffraction and Microwave
Spectroscopy, in which the molecular structure can be studied in the gaseous phase, vibrational spectroscopy, in which the force constant of the bond formed can be determined and the stabilities of complexes can be compared, and electrochemical studies and equilibrium properties. All these methods have been reviewed by Coyle and Stone [1.12] for boron complexes.

C. NMR Studies on Addition Complexes

Nuclear Magnetic Resonance measurements have been performed on a number of \( \pi-\sigma, \pi-\pi \) and \( \sigma-\sigma \) addition complexes [1.13 - 1.20] to study the molecular motion in the solid state. \(^{35}\text{Cl}\) NQR has been studied to investigate the \( \sigma- \) and \( \pi- \) character in the B-Cl bonds [1.21] and temperature variation study on \(^{35}\text{Cl}\) NQR was used in an attempt to study the reorientation of the BC\( \text{Cl}_3 \) moiety in trimethylamine-boron trichloride complexes [1.22]. The earlier nmr work is mostly limited to linewidth and second moment measurement. The present study involves the addition complexes of main Groups III and V. Besides making linewidth and second moment measurements to determine the molecular motion for those complexes, we have also used pulsed nmr to study the kinetics of the molecular motion in the solid state. Most of this work involves the addition complexes of alkylamines and alkylphosphines with alkylboranes and alkylaluminiums. Since most of them are air and moisture sensitive, they must be handled in an extremely dry and oxygen free atmosphere.
References


CHAPTER II

Introduction to NMR Theory

It is the intention of this chapter to give a brief introduction to the theory of nuclear magnetic resonance. A detailed theory is beyond the scope of this thesis and will not be given, but there are many excellent books [2.1 - 2.5] and reviews [2.6, 2.7] on the nmr theory and results. The work involved in this thesis concerns the study of protons in diamagnetic solids and therefore only relevant sections of theory are reviewed.

A. Elementary Resonance Theory

When a nucleus possessing a non-zero spin angular momentum is placed in a magnetic field, the spatial degeneracy of the angular momentum is removed, yielding \( 2I + 1 \) equally spaced energy levels with a splitting \( \Delta E = \gamma H_0 \). Here \( I \) is the nuclear spin quantum number, \( \gamma \) is a scalar quantity relating the nuclear spin and magnetic moment vectors, \( \hbar \) is Planck's constant divided by \( 2\pi \) and \( H_0 \) is the applied magnetic field. When the nuclear spins are in thermal equilibrium with the lattice, the relative populations \( n_i, n_j \), of adjacent levels are governed by the Boltzmann distribution

\[
\frac{n_i}{n_j} = e^{\Delta E / kT}
\]  

Thus there will be a population difference between adjacent states. If an oscillating rf field perpendicular to \( H_0 \) is now applied to the system such that \( \hbar \nu = \Delta E = \gamma H_0 \), absorption of energy occurs.
Equation (2.1) shows that if $H_0 = 0$, $n_i = n_j$. The establishment of thermal equilibrium between the two states after application of $H_0$ must inevitably require that there are interactions between the nuclei and their surroundings; these interactions cause the spin orientation to change, while the excess magnetic energy is transferred to other degrees of freedom. This process is called spin-lattice relaxation and the time constant to establish the thermal equilibrium between states after application of $H_0$ is called the spin-lattice relaxation time $T_1$.

Besides interacting with the magnetic field, the rf field and the lattice, the nuclear spins also interact with each other. The interactions within the spin system will broaden the resonance line shape and also dephase the nuclear magnetization in the xy plane. A measure of the phase memory time of the nuclear magnetization in the xy plane is usually termed the spin-spin relaxation time $T_2$.

**B. The Line Shape Function**

Calculation of the nmr line shape is a most difficult task in the solid state where the resonance lines are broadened by the local field produced by neighboring spins and by the corresponding spin-flip process among spins of the same nuclear species. Of all the different causes of broadening of resonance lines, the one important one for our case (protons) is the dipolar broadening. The Hamiltonian of interest can be written as

$$H = H_z + H_d$$ (2.2)
where $H_z$ is the Zeeman Hamiltonian and is given by

$$H_z = -\gamma \mathbf{h} H_0 \sum_i I^i_z$$

(2.3)

Here $H_0$ is the applied magnetic field in the z-direction and $I^i_z$ is the quantum number for the Z component of the $i$th nuclear spin. $H_d$ is the dipolar Hamiltonian and for two nuclei $i$ and $j$ with magnetic moments $\mu_i$ and $\mu_j$ respectively and joined by a vector $\mathbf{r}_{ij}$ is given by

$$H_d = \sum_{i<j} \left[ \frac{\mu_i \cdot \mu_j}{r_{ij}^3} - \frac{3(\mu_i \cdot \mathbf{r}_{ij})(\mu_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right]$$

(2.4)

where

$$A_{ij} = I^i_z I^j_z (1 - 3 \cos^2 \theta_{ij}) r_{ij}^{-3}$$

$$B_{ij} = \frac{1}{4} (I^i_z + I^j_z)(1 - 3 \cos^2 \theta_{ij}) r_{ij}^{-3}$$

$$C_{ij} = \frac{3}{2} \left( I^i_z I^j_z + I^i_z I^j_z \right) \sin \theta_{ij} \cos \theta_{ij} \exp(-i \phi_{ij}) r_{ij}^{-3}$$

$$E_{ij} = \frac{3}{4} (I^i_z) \sin^2 \theta_{ij} \exp(-2i \phi_{ij}) r_{ij}^{-3}$$

$$D_{ij} = C_{ij}^*, F_{ij} = E_{ij}^*$$

where $F_{ij}, \theta_{ij}, \phi_{ij}$ are the polar coordinates of the vector between spin $i$ and $j$, $I^i_z, I^j_z$ etc. are the usual raising and lowering operators for eigenfunction of $I^i_z$ etc., and the * signs denote the complex conjugates of the function.

In $H_d$, the terms $A$ and $B$ commute with $H_z$ and are called the secular terms.
They give the so-called truncated dipolar Hamiltonian \( H_d' \), i.e.

\[
H_d' = r^2 \hbar^2 \sum_{i<j} A_{ij} + B_{ij} \\
= -(\gamma \hbar^2/2) \sum_{i<j} (I_i \cdot I_j - 3I_i^z I_j^z) (1 - 3 \cos^2 \theta_{ij}) r_{ij}^{-3} \tag{2.5}
\]

It is the Zeeman and truncated dipolar Hamiltonians that determine the position and shape of the resonance line.

The resonance line shape for two-spin systems was first studied for gypsum \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O})\) by Pake [2.8], and extensive work on a wide range of crystal hydrates has recently been reviewed [2.9]. Theoretical studies of line shape in three-spin systems have also been made. Systems studied include compounds containing the \( \text{CH}_3 \) group, without and with taking account of the tunnelling effect for the \( \text{CH}_3 \) group [2.10 - 2.12], and the \( \text{H}_3\text{O}^+ \) [2.13] and \( \text{HF}_2^- \) [2.14] ions. Some four-spin systems have been studied, as, for example, \( \text{NH}_4^+ \) ion [2.15, 2.16] and barium bromide dihydrate [2.17]. One five-spin system yielding a highly structured spectrum has been examined in detail. That is the \( \text{H}_2\text{F}_3^- \) ion in its sodium and potassium salts [2.18]. Some promising results have been obtained for \( \text{SF}_6 \) clathrate deuterate, where because of very weak intermolecular interactions, the \(^{19}\text{F} \) absorption line shows a good fine structure [2.19] at liquid helium temperature. For complicated systems, for which exact line shape calculation is too difficult, the well known Van Vleck formula [2.20] for second moment of absorption line shape is very useful in obtaining structural information.
C. Second Moment of Absorption Line Shape

C.1 Second Moment from Absorption Line Shape.

We define the $n$th moment, $M_n$, of a resonance absorption curve (normalized to unit area by the relation [2.2, p. 106])

\[ M_n = \int_{-\Delta}^{\Delta} \Delta^n g(\Delta) d\Delta \quad (2.6) \]

where $\Delta = \omega_0 - \omega$

The second moment $M_2$ is then given by

\[ M_2 = \int_{-\Delta}^{\Delta} \Delta^2 g(\Delta) d\Delta \quad (2.7) \]

For polycrystalline material, the second moment is [2.1, p. 160]

\[ M_2 = \frac{6}{5} I(I+1)g^2B^2N^{-1} \sum_{i,j} r_{ij}^{-6} + \frac{4}{15} g^2N^{-1} \sum_{i,j} (I_{ij}+1)g^2r_{ij}^{-6} \quad (2.8) \]

where $I$ is the nuclear spin number for nuclei at resonance, $g$ is the nuclear $g$ factor, $B$ is the nuclear magneton, and $r_{ij}$ is the distance between $i$th and $j$th nuclei. Subscript $f$ refers to other nuclei not at resonance.

The second moment can be calculated by numerical integration of the absorption curve, from the line width of the dispersion mode of the adiabatic rapid passage (ARP) signal [2.21, 2.22] or from the free induction decay obtained by pulse methods. Calculation of second moment from the absorption
curve is a long and tedious procedure and caution must also be exercised to avoid saturation from $H_1$ and the modulation field [2.4, p. 109]. Calculation of second moment from the ARP dispersion signal is a rapid method, the signal-to-noise ratio is much better than that in conventional wide-line nmr, and, in addition, saturation and modulation effects are eliminated. However, if the spin-lattice relaxation time in the rotating frame, $T_1\rho$, is short, the relaxation in the rotating frame diminishes the signal to an unusable level. Therefore it is not applicable to the whole temperature range of interest [2.22, 2.23]. It is well known that the signal voltage of the FID curve can be expanded in terms of even powered moments of the resonance absorption curve [2.24, 2.2, p. 110] i.e.

$$V(t) = 1 - \frac{t^2}{2T_1} M_2 + \frac{t^4}{4T_1^2} M_4 -$$ (2.9)

Equation (2.9) shows that the moments of even number can be calculated from the FID curve. But the main difficulty here is that the important initial part of $V(t)$ is buried in the dead time of the receiver. A method has been described by Barnaal and Lowe [2.25] to correct the beginning of the FID curve for the distortion due to slow recovery of the receiver from saturation, but it is a laborious procedure. Powles and Strange [2.26], and Mansfield [2.7] have developed a method to overcome this situation by using two $90^\circ$ pulses, the second pulse being $90^\circ$ out of rf phase with the first $(90^\circ - \tau - 90^\circ)$, to produce a solid echo. They have shown that the signal voltage of the solid echo after a time $\tau'$ from the second pulse is
\[ V(\tau + \tau') = \left\{ 1 - \frac{(\tau - \tau')}{2i} M_2 + \frac{(\tau - \tau')^2}{4i} M_2 - \cdots \right\} + \left\{ -\frac{6i^2\tau'^2}{4i} M_{4x} + \cdots \right\} \] (2.10)

where the last term \( M_{4x} \) is an attenuation term of the FID. This method has been used successfully in polymethylbenzenes [2.28] where the second moment is smaller than 20 G². Rhim, Pines and Waugh [2.29] have recently developed a new method using a sequence of pulses to produce a "magic echo". The "magic echo" method seems to be the best since it is practically free of the nonlinear attenuation effects unavoidable in the case of the solid echo.

C.2 Effect of Molecular Motion on Second Moment and Line Width.

The second moment was shown by Pake [2.30] and Andrew and Newing [2.31] to be invariant to molecular motion. Further it was shown in the latter paper that rotation produces in the spectrum weak side bands which are usually unobservable experimentally, because they are buried in the noise in the wings and hence a reduced second moment is observed. A line narrowing transition is expected to be completed when [2.2, p. 425]

\[ (\Delta \omega_0^2)^{1/2} \tau_c \ll 1 \] (2.11)

where \( \Delta \omega_0^2 \) is the rigid lattice second moment expressed as an angular frequency and \( \tau_c \) is the correlation time for the random motional process.
If the motion is thermally activated and the line shape is the same before and after the motional narrowing (which is usually not exactly the case), a relation between line width and correlation time is given by [2.32]

$$\tau_c = \tan \left( \frac{\pi (\delta H^2 - B^2)/2(C^2 - B^2)}{\alpha Y \delta H} \right)$$

(2.12)

where $\alpha$ is an ill-defined constant and is approximately equal to unity, $\delta H$ is the line width in the narrowing region, $B$ is the narrowed line width and $C$ is the unnarrowed line width. $\tau_c$ obeys the Arrhenius activation energy and temperature relationship

$$\tau_c = \tau_c^0 \exp \left( \frac{E_a}{RT} \right)$$

(2.13)

where $E_a$ is the activation energy for the barrier hindering the rotation. Equations (2.12) and (2.13) can provide an estimate of the activation energy from the line width versus temperature measurement.

The effect of molecular rotation on second moment can be calculated from Gutowsky and Pake's formula [2.33]

$$M_2' = M_2 \left[ \frac{1}{4} (3 \cos^2 \gamma - 1) \right]$$

(2.14)

where $\gamma$ is the angle between the internuclear vector $r$ and the axis of rotation, $M_2'$ and $M_2$ are the reduced and rigid lattice second moments respectively. If the motion is oscillatory, Andrew's expression [2.34] should be used:
\[(M^2)_{\text{osc}} = M^2_o \]

where \( \rho = 1 - \frac{3}{4} \left[ (1 - J_0^2(\alpha)) \sin^2 \gamma + (1 - J_0^2(2\alpha)) \sin^4 \gamma \right] \] \hspace{1cm} (2.15)

where \( J_0 \) is a Bessel function of first kind, \( \alpha \) is the amplitude of oscillation, and \( \gamma \) is the angle between the pair direction and the axis of rotational oscillation. For small angle \( \alpha, \rho \) reduces to

\[ \rho = 1 - \frac{3}{2} \alpha^2 \sin^2 \gamma \] \hspace{1cm} (2.16)

**C.3 Tunnelling Effect on the Second Moment.**

Studies on polymethyl benzenes [2.28, 2.35, 2.36] and ammonia [2.37] have indicated that second moments keep their reduced values down to very low temperature, which means \( (\Delta \omega^2)^{1/2} \tau_c \ll 1 \), whereas the spin-lattice relaxation time studies show \( (\Delta \omega^2)^{1/2} \tau \gg 1 \). This apparent contradiction has been interpreted as indicating the existence of a tunnelling assisted phenomenon in the liquid helium temperature range.

Allen [2.38] has derived an expression for \( M^2 \) for an isolated tunnelling \( \text{CH}_3^- \) group accounting for the reduced second moment at low temperature. For a barrier height of 3 kcal/mole, the second moment is just 1/4 of the rigid lattice value. For a higher barrier (3 - 3.5 kcal/mole) his expression is

\[ M^2 = \frac{9}{40} \left( \frac{\gamma^2 R^2}{r^6} \right) \left[ 1 - 0.11(\Gamma/\Delta)^{1/2} - 0.64(\Gamma/\Delta) \right] \] \hspace{1cm} (2.17)

where \( \Gamma = (r^2 R^2/r^3) \) and \( \Delta \) is the tunnelling splitting of torsional ground state.

In a more recent paper Clough [2.29] has shown by calculation that the
tunnelling effect can decrease the rigid lattice second moment but the second moment due to tunnelling is higher than the second moment reduced by classical reorientation about the C₃ axis; i.e. it is more than 1/4 of the rigid lattice value. He has shown that the increase of second moment from the classical reduced value may be as great as 5 G².

D. Spin-lattice Relaxation Time

In general, two conditions are necessary for a successful spin-lattice relaxation mechanism. Firstly, there must be some interaction which acts directly on the spins; secondly, it must be time dependent. It can be shown [2.5, Chap. 4] that any interaction which fluctuates strongly at the resonance frequency produces powerful spin-lattice relaxation.

A number of physical interactions have been found to be important in coupling the nuclei to the lattice and hence providing a link through which energy can be changed between the spins and lattice. These processes are:

1. magnetic dipole-dipole interaction
2. electric quadrupole interaction
3. chemical shift anisotropy interaction
4. scalar-coupling interaction
5. spin-rotation interaction.

To describe the motion and/or the position of a rigid body it is customary, helpful and convenient to introduce functions related to the spherical harmonics.
They are defined as follows:

\[ Y_0 = r^{-3} (1 - 3 \cos^2 \theta) \]

\[ Y_1 = r^{-3} \sin \theta \cos \theta \exp(i\phi) \]

\[ Y_2 = r^{-3} \sin^2 \theta \exp(2i\phi) \]  
\[ (2.18) \]

where \( r, \theta, \phi \) are the usual spherical coordinates. As the molecule moves, the \( r, \theta, \phi \) become functions of time and so do the functions \( Y_i \) (\( i = 0, 1, 2 \)). Since the relaxation times \( T_1 \) and \( T_2 \) are related to the average behaviour of a collection or ensemble of nuclei, we are particularly interested in the average way in which the nuclei move about. The so-called correlation functions \( K_i(\tau) \) (\( i = 0, 1, 2 \)) give us this information; they are defined as

\[ K_i(\tau) = \langle Y_i(\tau) Y_i^*(\tau + \tau) \rangle \]  
\[ (2.19) \]

where \( Y_i^* \) is the complex conjugate of \( Y_i \) and \( \langle \rangle \) denotes the ensemble average. A common and frequently used correlation function is of exponential form, i.e.

\[ K_i(\tau) = Y_i(\tau) Y_i^*(\tau) \exp(-\tau/\tau_c^i) \]  
\[ (2.20) \]

where \( \tau_c \) is the correlation time characteristic of the motion. The intensity of the motion at frequency \( \omega \), the so-called spectral density function, can be obtained by Fourier Transformation of the correlation function, i.e.
The spin-lattice relaxation rate, $T_1^{-1}$, therefore depends on the value of $J(\omega_0)$ and also the strength of the coupling between the spin system and the lattice. In a diamagnetic solid, the dipole-dipole interactions are important and the spin-lattice relaxation time $T_1$ was shown [2.2, p. 291] to be

$$\frac{1}{T_1} = \frac{3}{2} I(I + 1) \gamma^2 h^2 \sum_j \left[ J_{ij}(\omega_0) + J_{ij}(2\omega_0) \right]$$

where $i$ and $j$ are now the nuclei of interest.

For two-spin systems $T_1$ due to isotropic rotation was given by [2.2, p.300]

$$\frac{1}{T_1} = \frac{2}{5} \frac{4\hbar^2 I(I + 1)}{r^6} \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]$$

The spin-lattice relaxation time for 3-spin systems has been studied extensively. The calculation of relaxation time involves two correlation functions for each mutual dipole-dipole interaction. If we are examining the relaxation of proton 1 in a three proton system, the correlation function for interactions 1, 2 and 1,3 is called the "auto-correlation function" and the correlation function for interactions 2,3, which also affects the relaxation of proton 1, is called the "cross-correlation function". Hilt and Hubbard [2.40]
have shown that in the case of 3-spin systems undergoing hindered rotation, if cross correlations are neglected, the relaxation function is exponential, and for polycrystalline material they derived an expression for $T_1$

$$\frac{1}{T_1} = \frac{9}{20} \frac{\gamma^4 h^2}{r^6} \left[ \frac{T_c}{1 + \omega_0^2 \tau_c^2} + \frac{4T_c}{1 + 4\omega_0^2 \tau_c^2} \right]$$

The result is the same as that obtained by O'Reilly and Tsang [2.41] who used a much simpler approach.

Hilt and Hubbard [2.40] also treated the 3-spin system by considering both the cross-correlation and auto-correlation functions. They found the magnetization $M_z(t)$ after a pulse of width $\Theta$ is not exponential, but a sum of 4 exponentials given by

$$M_z(t) - M_0 = (\cos \Theta - 1) M_0 \sum_{j=1}^{4} C_j \exp(-q_j t / T') \quad (2.23)$$

where $C_j$, $q_j$ are complicated functions of $\omega_0 T_c$ and the angle $\beta$ between the $C_3$-axis and $H_0$, and $T'$ is a measure of the strength of interaction between the magnetic dipoles given by

$$\frac{1}{T'} = (\gamma^2 h / r^3)^2 \frac{1}{\rho_o} \quad (2.24)$$

where $r$ is the interproton distance in the CH$_3$-group. For polycrystalline
material and a 180° - τ - 90° pulse sequence, Equation (2.23) becomes

\[ R_{AV}(t) = \frac{[M - M_z(t)]}{2M_0} \int_{0}^{\pi} \sum_{j=1}^{4} C_j \exp(-\alpha_j \tau/T') \sin \theta \, d\theta \] (2.25)

More recently Allen and Clough [2.42] have calculated the temperature dependence of \( T_1 \) taking into account the tunnelling splitting of the torsional-oscillator ground state of the hindered CH₃-group. This tunnelling splitting accounts for more than one minimum at very low temperature (below 100 K). The expression obtained by these authors is [2.42, 2.43]

\[ \frac{1}{T_1} = \frac{9}{20} \frac{4\pi^2}{r^6} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} + \pi f(\omega_0) + 4\pi f(2\omega_0) \right) \] (2.26)

where \( f(\omega) = 8\pi/\{6\pi \} X^4 + 2X^2(2Y^2 - 1) + 1 \) with \( X = \omega/3J, Y = (3Jx)^{-1} \). In \( X \) and \( Y, 3J\bar{R} \) is the tunnelling splitting and \( \tau_c \) is a correlation time obeying the equation \( \tau_c = \tau_0 \exp(E_a/RT) \). At high temperature where the tunnelling effect is not important, the last two terms can be omitted and one obtains the BPP equation [2.44, 2.45]

\[ \frac{1}{T_1} = C \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \] (2.27)
E. Distribution of Correlation Times and Their Effect on $T_1$ and $E_a$

The modified BPP Equation (2.27) is only satisfactory for one correlation time, $\tau_c$. The activation energy can be extracted from the slopes of a $\ln T_1$ vs $T^{-1}$ plot on either side of the minimum, where

1. in the low temperature region ($\omega_0 \tau_c >> 1$), $\ln T_1 \propto E_a/RT$

2. in the high temperature region ($\omega_0 \tau_c << 1$), $\ln T_1 \propto -E_a/RT$

It can also be obtained from a plot of $\omega_0 \tau_c$ versus inverse of temperature where $\omega_0 \tau_c$ at temperature $T$ can be obtained from the experimental $T_1$ minimum and the experimental value of $T_1$ at temperature $T$. However, if there is a lack of a unique correlation time, a broad and flat $T_1$ minimum exists, in contrast with a sharp $T_1$ minimum predicted by the BPP Equation (2.27). The presence of more than one correlation time may arise in three different ways.

The first case is where we may have a number of independent types of rotation proceeding at nearly the same temperature but with different rates and each contributing towards $T_1$. A known example of this case is the tert-butyl group, which may exhibit both methyl and tert-butyl group rotation. The first work to separate these two specific contributions is that of Allen and Johnson [2.46] on 1-tert-butyl-4-methyl-benzene.

The second case is that there exists the same type of motion proceeding at different rates in a limited number (of the order of three or four) of different environments and contributing towards $T_1$ at the same temperature.
This may come about because the rotating groups are attached to different central atoms, or the rotating groups are located at different crystal sites. The different contributions of each motion to $T_1$ may be separated under favorable circumstances. Examples will be seen in the following Chapters.

The third case is that there exists a distribution of correlation times, perhaps all due to the same type of motion, for example, methyl group reorientation. This distribution results from a continuous distribution of environments within the sample attributable to static crystal inhomogeneities or thermal fluctuation of environment. This case, which is characteristic of polymer systems, has been reviewed by Odajima [2.47] and Connor [2.48] and we will summarize the main points of their review here.

In order to explain the broad $T_1$ minimum, the modified BPP equation has been further modified [2.49] to include a continuous distribution of correlation times, described by a density function $G(\tau_C)$ where

$$\int_0^\infty G(\tau_C)d\tau_C = 1 \quad (2.28)$$

to give [2.50]

$$\frac{1}{T_1} = C \left[ \int_0^{\tau_o} \frac{G(\tau_C)d\tau_C}{1+\omega_0^2 \tau_C^2} + 4 \int_0^{\tau_o} \frac{G(\tau_C)d\tau_C}{1+4\omega_0^2 \tau_C^2} \right] \quad (2.29)$$

The density function can be expressed in terms of a logarithmic correlation time scale. If $\tau_0$ is the center of the distribution on the logarithmic scale,
then define

\[ S = \ln \left( \frac{\tau_C}{\tau_0} \right) \]

\( G(\tau_C) \) can then be replaced by \( F(S) \) with conditions

\[
\int_{\infty}^{\infty} F(S)dS = 1, \quad G(\tau_C)d\tau_C = F(S)dS, \quad \tau_C G(\tau_C) = F(S) \quad (2.30)
\]

There are various types of distribution functions which give rise to a symmetric curve of \( \ln T_1 \) versus \( T^{-1} \). They are: the rectangular density function, Gaussian distribution function, Lorenztian density function, Fuoss and Kirkwood, and Cole and Cole distribution functions. The \( \ln T_1 \) versus \( T^{-1} \) curves derived from the first three functions have the following properties: the limiting slopes are the same as those obtained from the BPP equation, but the curve generally shows a broad \( T_1 \) minimum. The \( \ln T_1 \) versus \( T^{-1} \) curves derived from Fuoss and Kirkwood and Cole and Cole distributions have, in general, a broad \( T_1 \) minimum, and the limiting slopes are smaller than those obtained from the BPP equation. The only distribution function which gives an asymmetric curve of \( \ln T_1 \) versus \( T^{-1} \) is the Cole-Davidson function. The higher temperature limiting slope is the same as that from the BPP equation, whereas the lower temperature slope is modified by the width of the distribution, and \( T_1 \) minimum is shifted slightly downward. The \( T_1 \) minimum in this case is not very broad.
F. Activation Energy

Even in the gaseous state, it is difficult to make correct empirical predictions of barrier heights because many factors can affect the potential barrier. These include the bond length associated with the rotational motion, molecular symmetry, electronegativity of the substituents and the type of bonding (for example, the possible existence of $\pi$-bonding). In the solid state, there are also intermolecular forces, which affect the activation energy for the rotational motion. The strength of intermolecular forces depends on the type of crystal. Ionic and covalent network crystals may have the binding energy as high as 300 kcal/mole. Metallic crystals may have the binding energy as high as 100 kcal/mole. Hydrogen-bonded crystals like ice have about 12 kcal/mole binding energy. The compounds studied in this thesis are molecular crystals whose binding energies are normally less than 10 kcal/mole.

A point worth mentioning is that in a molecule like $\text{Me}_3A \cdot \text{BMe}_3$ or $\text{Me}_3A \cdot \text{BX}_3$, where A, B are central atoms and X is a halogen atom, we are unable to distinguish between the $C_3$ reorientation of the molecule as a whole and uncorrelated reorientation of each half of the molecule about the A-B bond using the nmr technique. However, the activation energy for the $C_3$ reorientation of the molecule as a whole involves merely intermolecular interactions whereas uncorrelated reorientation of each half of the molecule about the A-B bond involves both intermolecular and intramolecular interactions. Thus the activation energy for the latter case should be higher than that for the former case if other parameters of the systems being compared are very similar or if one can distinguish both motions in the same system.
References


J.W. McGrath, J. Chem. Phys. 43 (1965) 3746


M.B. Dunn and C.A. McDowell (to be published)

J.H. Van Vleck, Phys. Rev. 74 (1948) 1168


[2.46] P.S. Allen and L.W. Johnson (to be published)
CHAPTER III
Apparatus and Methods of Measurement

This chapter is intended to give some details of apparatus used and methods of measurement of second moment, $M_2$, and spin-lattice relaxation time, $T_1$. The preparative methods for addition complexes are not discussed here, because they will be given in detail in later chapters.

A. Continuous Wave (CW) Measurements

1. CW Spectrometer

The spectrometer used for CW measurements was a conventional cross-coil Varian VF-16 wideline spectrometer equipped with a Varian six inch magnet. The transmitter and receiver unit was a Varian V4210A variable frequency rf unit operating at 16 MHz in all experiments. The usual lock-in detection method was used. The modulating field was supplied by a Varian V4250B sweep unit and a V4240 sweep amplifier unit, and in all experiments the modulation frequency was kept at 80 Hz. The first derivative of the absorption mode signal was recorded by means of Varian V4270B lock-in amplifier unit. Spectra were recorded by a HP Model 680 strip chart recorder.

2. Calibration of Spectrometer

The $'H$ resonance field $H_0$ was located from the position of the absorption signal obtained from a doped water sample. A side band technique was used for
calibration of the scanning rate. To produce these side bands, the rf carrier frequency (16 MHz) was modulated by a known audiofrequency generated from a H.P. Model 200CD wide range oscillator, the frequency of which was measured by a H.P. Model 3734A electronic counter. The scan rate was calibrated in gauss per cm. along the base line of the recorder. The modulation amplitude was calibrated by directly recording the first derivative of the overmodulated doped water sample. The observed peak-to-peak line width was taken equal to 2Hm, where Hm is the modulation amplitude in gauss.

3. Linewidth and Second Moment Measurements

The linewidth was taken as the distance between the extreme maximum and minimum of the recorded spectrum. The second moment of the experimental absorption derivative curve after subtracting the well-known modulation correction due to Andrew [3.1] is

\[ M_2 = \frac{1}{3} \left[ \int_{-\infty}^{\infty} h^3 \frac{dg}{dh} dh / \int_{-\infty}^{\infty} h \frac{dg}{dh} dh \right] - \frac{1}{4Hm} \]  

(3.1)

where \( g(h) = g(H_o - H) = \gamma^{-1} g(\omega_o - \omega) = \gamma^{-1} g(\Delta) \), \( H_o \) is the resonance field, \( H \) the field away from resonance and \( Hm \) is the modulation amplitude.

For numerical integration purposes Equation (3.1) reduces to

\[ M_2 = \frac{S^2}{3} \cdot \frac{1}{\sum_{n=1}^{n=N} nY_n} \cdot \frac{1}{\sum_{n=1}^{n=N} n^3Y_n} - \frac{1}{4Hm} \]  

(3.2)
where \( n \) is the number of sections on the x-axis, \( Y_n \) is the y-axis height of the derivative curve, \( N \) is the maximum number of sections on the x-axis and \( S \) is the scanning rate in G/section.

A computer programme was used to calculate the second moments using Equation (3.2). At least two spectra were recorded at each temperature and the average second moment and linewidth was obtained. The rf field used was 0.005 mG to 0.10 mG depending on the \( T_1 \) and \( T_2 \) of the sample. The reported second moment has in most cases a deviation of less than 10%. The important source of error comes from the signal at each wing where the signal/noise ratio is smaller than 1. The modulation amplitude was always kept much smaller than 1/3 of the linewidth to avoid modulation broadening and to satisfy the first two conditions of Provotorov's Theory [3.2]. However, when self-diffusion occurs, the modulation frequency may exceed the linewidth, and the signal is overmodulated. The inhomogeneity of the magnetic field \( H_0 \) becomes significant when the linewidth is less than about 0.5G. Consequently the linewidth in the region of self-diffusion is affected by field inhomogeneity.

4. Variable Temperature Assembly

Temperature control was achieved by immersing the sample directly in liquid nitrogen to attain 77\(^{0}\)K. Temperatures below 77\(^{0}\)K were obtained by pumping on liquid nitrogen, and temperatures can be adjusted by changing the rate of pumping. For temperatures from 110\(^{0}\)K to room temperature cold gas flow methods were used. The liquid nitrogen was boiled off with a 400 Watt heater immersed in a 50 liter tank. The cold nitrogen gas was led from a.
Dewar system to the probe. The temperature was varied either by varying the voltage across the heater or, for faster response, by heating the cold gas with an additional heater placed inside the Dewar system. To get minimum temperature gradient, the voltage on the heater immersed in liquid nitrogen was held fixed at a value which gives a good high flow rate of cold gas and negligible thermal gradient. The temperature of the sample was measured using a copper-constantan thermocouple placed approximately 1-2 cm. below the sample, and a Leeds and Northrup Type G strip chart recorder, or a potentiometer. For temperatures between 77°K and 110°K, the cold gas from the 50 liter tank was first passed through a copper heat exchanger placed in liquid nitrogen before reaching the Dewar system. The temperatures were controlled by a Versa-Therm proportional electronic temperature controller Model 2156 with a Veco 05A1 thermistor. For temperatures from room temperature upwards, hot air was used. The stability of the temperature with this system is about ±0.5°. The sample was allowed to equilibrate for at least forty minutes before the spectra were taken.

B. Spin-Lattice Relaxation Measurements

1. Pulsed Spectrometer

The pulsed spectrometer used for $T_1$ measurements was a Bruker variable frequency (16 to 62 MHz) pulsed spectrometer. The frequency at which all our $T_1$ measurements were performed was 30 MHz.

This spectrometer contains a basic 1 MHz quartz oscillator with a frequency stability lying between $10^{-8}$ - $10^{-9}$. All the measurement times
are derived digitally from this oscillator and their accuracy is of the same order as that of the oscillator frequency. Three separate pulse channels are available to gate the high frequency in the oscillator unit. The basic 1 MHz frequency from the main oscillator is taken into a frequency synthesizer, where half of the resonance frequency is produced. This half high frequency is then fed to three channels after amplification. The first channel is gate channel I, where the high frequency signal is fed after being phase shifted, doubled and amplified. In the second channel, which is gate channel II, the high frequency is fed directly after being doubled and amplified. In the third channel, termed the reference channel, the high frequency serves as a phase coherent frequency for the phase sensitive detector. The gate channel I is opened only by pulse I and the gate channel II is opened by pulses II and III. The high frequency in the form of pulses is led, after passing through the gates opened by d.c. pulses I, II and III, through a five-stage rf power amplifier which is capable of delivering a power of 2-3 μsec for a 180° pulse to the transmitter coil in the probe where it excited the nmr frequency signal. This nmr signal combined with the signal produced by rf pulses is passed through a preamplifier and after attenuation is detected by the receiver either by diode or phase sensitive detection.

The maximum bandwidth of the receiver in the spectrometer is 1 MHz. The dead time of the receiver after an rf pulse is approximately 5-6 μsec at 30 MHz. Most of the experiments in this work were done using a bandwidth of 1 MHz, but in some cases where noise level was high and the T₂ was long, a bandwidth of 300 kHz was used.
The magnet used for the polarizing magnetic field $H_0$ was a Varian 12-inch high resolution electromagnet. The signal amplitudes were recorded on a Tektronix Type 549 storage oscilloscope with Type 1A1 Dual Trace plug-in unit. The oscilloscope has a band width of 30 MHz.

2. Linearity of Receiver

In all experiments we have used a diode detector. To calibrate the linearity of the receiver at 30 MHz we used a H.P. Model 606A signal generator operating at 30 MHz. The output of the signal generator was fed to the input of the receiver preamplifier. The output voltage from the receiver was measured with a Tektronix Type 549 oscilloscope. The input voltage was read from the meter of the signal generator. The oscilloscope was calibrated by the built in voltage calibrator. Fig. 3.1 shows the output voltage as a function of the input voltage from the H.P. signal generator at 30 MHz. Most of the $T_1$ measurements were taken in the range of linearity. Those which were outside were corrected for non-linearity of the diode detector.

3. Variable Temperature Assembly

The quartz variable temperature insert was different from the Bruker insert and was designed by Allen*. With the redesigned insert, the temperature of the sample can be taken as low as the liquid nitrogen temperature. To prevent condensation in the probe, the used nitrogen gas was recycled, heated to about 50°C, and blown into the probe. The cooling system is similar to the system used in CW measurement except that temperatures above 105°K were controlled by a B-ST 100/700 temperature controller in the pulse work.

* Visiting Professor from Department of Physics, University of Nottingham, England.
Fig. 3.1. Relation of input signal and output voltage of the receiver operating at 30 MHz.
To obtain the necessary accuracy in temperature measurement, temperatures between 77° and 105°K were monitored and measured by copper-constantan thermocouple connected with a potentiometer. The sample was allowed to equilibrate for at least twenty minutes before measurement was made.

4. Measurement of Spin-Lattice Relaxation Time

Spin-lattice relaxation time was measured by either a $180^\circ - \tau - 90^\circ$ pulse sequence or a $90^\circ - \tau - 90^\circ$ pulse sequence. If the relaxation is exponential, the relaxation function $R(\tau)$ is given by

$$R(\tau) = \frac{[M_0 - M_z(\tau)]}{2M_0} = \exp\left(-\frac{\tau}{T_1}\right)$$

for a $180^\circ - \tau - 90^\circ$ pulse sequence. Where $M_0$ is proportional to the voltage after a single $90^\circ$ pulse, and $M_z(\tau)$ is proportional to the voltage after a $180^\circ - \tau - 90^\circ$ pulse sequence. For different $\tau$'s, we get different values of $M_z(\tau)$ and a plot of $\ln R(\tau)$ versus $\tau$ should give a straight line with slope $(-1/T_1)$. Alternatively one can choose $\tau$ in the sequence $180^\circ - \tau - 90^\circ$ in such a way so as to give, at $\tau = \tau_0$, $M_z(\tau) = 0$. In that case (Null method) Equation (3.3) gives

$$R(\tau_0) = 1/2 \quad \text{and} \quad T_1 = \frac{\tau_0}{\ln 2} = 1.443\tau_0$$

However, this method is not very accurate, especially when the rf field is not homogeneous and a diode detector is used for signal detection. A method for correcting the $H_1$ inhomogeneity has been proposed by van Putte [3.3]. The
$T_1$ obtained from the slope of the plot of $R(\tau)$ versus $\tau$ always gives a reliable value [3.4]. However, as a matter of good experimental practice, it is always desirable to achieve good $H_1$ homogeneity. For a sample with long $T_1$, it is more convenient to use a $\pi 90^\circ - \tau - 90^\circ$ pulse sequence. For this sequence the relaxation function $R(\tau)$ is given by

$$R(\tau) = \frac{[M_0 - M_z(\tau)]}{M_0} = \exp(-\tau/T_1)$$  \hspace{1cm} (3.4)

A plot of $R(\tau)$ versus $\tau$ should also give a straight line with slope $(-1/T_1)$. A computer programme with least square fitting was used to calculate $T_1$. The standard deviation of the slope of the straight line was found to be less than 5% for all the samples studied.

C. The Dry Box

Since alkylaluminium and alkylborane compounds and their complexes are air sensitive, they must be handled in a dry and oxygen free atmosphere. A glove bag, obtained from Instruments for Research and Industry, was used as a dry box. The oxygen free dry nitrogen gas was blown into the glove bag for at least twenty minutes before the glove bag was sealed. After sealing, two small holes were punched on the top of the glove bag so that nitrogen gas could be blown continuously into the glove bag to maintain highest purity of the nitrogen atmosphere.
References


CHAPTER IV

An NMR Study of Trimethylamine or phosphine complexed with Trimethylborane or aluminium

A. Introduction

This chapter describes the details of an nmr study of the addition complexes of trimethylamine and trimethylphosphine with trimethylborane and trimethylaluminium. The addition complexes have been reviewed by Stone [4.1] and have been discussed in Chapter I. The complexes are on the one hand very similar to hexamethylethane and hexamethyldisilane in molecular structure and on the other hand, they provide variation of the length of the bond between the methyl groups and the central atoms. It is possible to use the nmr technique to study the molecular motion of these addition complexes and the effect of the central atoms on molecular motion.

B. Experimental

B.1 Materials

Trimethylamine (anhydrous) was obtained from Eastman Kodak. Trimethylphosphine was obtained from Pfaltz and Bauer, Inc. Trimethylborane and trimethylaluminium were purchased from Alfa Inorganics. Trimethylamine-trimethylborane was kindly provided by Dr. A. Storr.

B.2 Preparation of Addition Complexes

The complex trimethylamine-trimethylaluminium [4.2] was prepared by introducing an excess of trimethylamine to trimethylaluminium which was at
liquid nitrogen temperature. The transfer was made in a vacuum system, the mixture of compounds warmed slowly from liquid nitrogen temperature to room temperature, and the excess trimethylamine pumped off at room temperature. The product which remained was sublimed into a vacuum and collected on a cold finger which was at about 10°C. The cold finger was then warmed slowly to room temperature and the sample was kept under vacuum overnight. Trimethylphosphine-trimethylaluminium [4.2] was prepared by mixing trimethylphosphine and trimethylaluminium at room temperature with trimethylphosphine slightly in excess and was then purified by vacuum sublimation. Trimethylphosphine-trimethylborane [4.3, 4.4] was prepared by introducing a small amount of trimethylborane to trimethylphosphine which was trapped at liquid nitrogen temperature. The mixture of the compounds was warmed to dry ice acetone temperature. The procedure was repeated until a manometer showed the reaction was completed. The residual gas was pumped off and the product which remained was purified by vacuum sublimation.

Samples were transferred in a dry box to 10 mm O.D. sample tubes for CW measurement and to 7.5 - 8.0 mm O.D. thin wall tubes for spin-lattice relaxation time measurement.

B.3 Measuring Procedures

Both CW and T₁ measurements have been described in Chapter III.

C. Trimethylamine-trimethylborane

C.1 Line widths and Second Moments

The experimental second moments and line widths are plotted vs. temperature
in Figure 4.1. The second moment has a plateau value of $22.2 \pm 0.6 \text{ G}^2$
between 63 and 95 K. Then it decreases from $19.6 \text{ G}^2$ at 100 K to a value of
$2.6 \pm 0.3 \text{ G}^2$ at 138 K, and continues to decrease very slowly to $2.0 \pm 0.3 \text{ G}^2$
at the highest observed temperature, 350 K. The shape of the line width vs.
temperature is similar to that of the second moment vs. temperature.

C.2 Calculation of Second Moment and Discussion of Molecular Motion

C.2.1 Notation

Before calculating the theoretical second moment for various
degrees of motion in the lattice, let us introduce some notation for second
moments. We denote the rigid lattice second moments as follows: $S$, the
total second moment; $S_I$, second moment arising from interaction between protons
within the same methyl group; $S_{II}$, second moment arising from interactions
between different methyl groups in the same molecule; $S_{III}$, second moment due
to interactions between protons and nitrogen and boron atoms in the same
molecule; $S_{IV}$, intermolecular second moment. When the three methyl groups
attached to one of the central atoms are rotating rapidly, whereas the methyl
groups attached to the other are still "fixed", the second moments are
denoted by $S'$, $S'_I$, $S'_{II}$, $S'_{III}$, $S'_{IV}$, respectively, as above. When all methyl
groups in the molecule are rotating rapidly, the second moments are denoted
by $S''$, $S''_I$, $S''_{II}$, $S''_{III}$, $S''_{IV}$, respectively. When the whole molecule rotates
about its B-N bond and all the methyl groups are also rotating, the second
moments are denoted as above by $S'''$, $S'''_I$, $S'''_{II}$, $S'''_{III}$, $S'''_{IV}$ respectively.

C.2.2. Rigid lattice second moment

Since the crystal structure of trimethylamine-trimethylborane
Fig. 4.1. Line width and second moment of trimethylamine-trimethylborane as a function of temperature.
is not known, the theoretical second moment can only be estimated. The total rigid second moment, $S$, of trimethylamine-trimethylborane may be considered as the sum of four components: $S_I$, $S_{II}$, $S_{III}$, $S_{IV}$ as defined before. Of the four components, only $S_I$ can be calculated with precision. Assume that the C-H bond distance is 1.10 Å and that the carbon bonds are directed tetrahedrally. Then $S_I$ is 21.3 G$^2$. Although the atomic coordinates of trimethylamine-trimethylborane are not known at very low temperature, an estimate of bond lengths can be made by using tables of interatomic distances [4.5] or from covalent radii [4.8]. Good estimates appear to be $r$(C-N) = 1.47 Å and $r$(C-B) = 1.56 Å. The B-N bond length calculated from covalent radii is 1.55 Å, which is 0.01 Å longer than the C-C bond length. However, in hexamethylethane, the central C-C bond length is 1.58 Å according to electron diffraction studies [4.7]. From the fact that trimethylamine-trimethylborane will dissociate rather easily at high temperature [4.8], it is presumed that the B-N bond length should not be less than 1.58 Å. We assume it is 1.60 Å. This value is lower than 1.80 ± 0.15 Å obtained by microwave [4.24]. However, the conclusion of microwave has been criticized [4.25] on the grounds that this B-N bond distance is substantially greater than that observed in a number of solid complexes by X-ray diffraction. Changes in this value by about 0.05 Å will, however, affect $S_{II}$ by only 0.1 G$^2$. We assume also that at low temperature the methyl groups attached to the nitrogen atoms are staggered with respect to the methyl groups attached to boron. Smith [4.9] found that $S_{II}$ would be reduced by a factor 0.90/1.04 if he assumed that the effect of the methyl group reorientation is to concentrate the CH$_3$ protons at their centre of rotation.
In our calculation of $S_{II}$ a reverse line of reasoning was followed. Assuming that all methyl groups rotate, we calculated the contribution to the second moment by concentrating the $\text{CH}_3$ protons at their centre of rotation. Then $S_{II}$ is obtained by multiplying by a factor $1.04/0.90$, and we get $S_{II} = 4.35 \text{ G}^2$. The contribution to the second moment arising from interactions between protons and nitrogen is small, being about $0.01 \text{ G}^2$, which can be neglected. However, the contribution to the second moment arising from interactions between protons and $^{11}\text{B}$ is not negligible. Calculation gives $0.3 \text{ G}^2$ for this contribution. The contribution due to $^{10}\text{B}$ was neglected. We conclude that $S_{III}$ is approximately $0.3 \text{ G}^2$. A reasonable estimate [4.9, 4.10] for $S_{IV}$ is $7 \pm 1 \text{ G}^2$, and thus the total rigid lattice second moment is $S = 33.0 \pm 1 \text{ G}^2$.

C.2.3. Effect of rotation of three methyl groups in either the trimethyl-amine or trimethylborane moiety

From Powles and Gutowsky's formula [4.11], $S'_{I}$ is found to be $13.3 \text{ G}^2$. Smith's method [4.9, 4.12] was used to calculate $S'_{II}$, and we found it to be $S'_{II} = 4.0 \text{ G}^2$. $S'_{III}$ is the same as $S_{III}$ if the methyl groups attached to nitrogen are rotating. If the methyl groups attached to boron are rotating, $S'_{III}$ becomes $0.2 \text{ G}^2$. By linear interpolation between the value $S''_{IV} = 2.4 \pm 0.8 \text{ G}^2$ (see below) and the rigid lattice value of $7 \pm 1 \text{ G}^2$ we obtain $S'_{IV} = 4.7 \pm 0.8 \text{ G}^2$. As a result, the total calculated $S'$ is $22.3 \pm 0.8 \text{ G}^2$.

C.2.4. Effect of rotation of all methyl groups

The effect of the rotation of the methyl groups about their 3-fold axis is to reduce $S_{I}$ by a factor of 4. Thus $S''_{I} = 5.3 \text{ G}^2$. $S''_{II}$ is obtained by the method of Smith, mentioned in the section on rigid lattice second moment.
and is $3.8 \, G^2$. $S''_{III}$ is the same as $S'_{III}$. Following Smith's summary [4.9] of estimates made in the literature of finding reduction factors of 0.42 - 0.25 for second moment contributions from interactions between two rotating groups, we estimated a value for $S''_{IV}$ of $2.4 \pm 0.8 \, G^2$. Thus $S'' = 11.7 \pm 0.8 \, G^2$.

C.2.5. Effect of methyl reorientation plus reorientation about the central bond

The contribution to the second moment of a methyl group reorientating rapidly about its $C_3$ axis and also about an axis making an angle $\psi$ to the $C_3$ axis has been considered by Powles and Gutowsky [4.11]. In this case we can calculate $S''_{I} = 0.6 \, G^2$. $S''_{II}$ can be calculated by assuming all CH$_3$ protons concentrate at the centre of the circle of rotation. Thus $S''_{II} = 0.5 \, G^2$. $S''_{III}$ will be reduced to approximately zero. According to Chezeau et al. [4.10], $S''_{IV}$ should not be less than $0.9 \, G^2$ and they estimated $S''_{IV} = 1.4 \, G^2$.

We also assume $S''_{IV} = 1.4 \, G^2$ for trimethylamine-trimethylborane, and therefore conclude that $S'' = 2.5 \pm 0.5 \, G^2$.

C.3 Interpretation of the observed second moment

The calculated values for the proton resonance second moments are compared with experimental results in Table 4.1. Even at the lowest temperature attained, 63 K, the lattice is not rigid since the measured value of 22.5 $G^2$ is considerably less than the calculated value of 33 $G^2$. The plateau value observed below 95 K corresponds reasonably well with reorientation of three methyl groups. It has already been indicated that the C-B bond length is greater than C-N bond length. It seems plausible, therefore, that steric hindrance to rotation of the methyl groups attached to boron will be less than that for the methyl groups attached to
TABLE 4.1

Theoretical second moments for trimethylamine-trimethylborane (in G²) and the Comparison with experimental values

<table>
<thead>
<tr>
<th>Group</th>
<th>Motion</th>
<th>Theoretical Second Moment Contribution</th>
<th>Experimental Second Moment</th>
<th>Temperature T°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₃N</td>
<td>Me₃B</td>
<td>Inter CH₃</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Intra CH₃</td>
<td>Intramolecular</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Proton to N and B</td>
<td>Intermolecular</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>SS</td>
<td>21.3</td>
<td>4.35</td>
<td>7 ± 1</td>
</tr>
<tr>
<td>SS</td>
<td>RS</td>
<td>13.3</td>
<td>4.0</td>
<td>0.2</td>
</tr>
<tr>
<td>RS</td>
<td>SS</td>
<td>13.3</td>
<td>3.9</td>
<td>0.3</td>
</tr>
<tr>
<td>RS</td>
<td>RS</td>
<td>5.3</td>
<td>3.8</td>
<td>0.2</td>
</tr>
<tr>
<td>RR</td>
<td>RR</td>
<td>0.6</td>
<td>0.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

SS = methyl group stationary and whole moiety stationary
RS = methyl group rotating but moiety stationary
RR = methyl group rotating and whole moiety rotating
nitrogen and that reorientation of the methyl groups in the trimethylborane moiety will affect the nmr line width and second moment at lower temperatures than will reorientation of methyl groups in the trimethylamine moiety. Thus we interpret the second moment plateau of 22.5 G² below 95 K as indicating reorientation of methyl groups in the trimethylborane moiety and "fixed" methyl groups in the trimethylamine moiety.

The question can arise of whether the reorientation of methyl groups at low temperatures is assisted by quantum mechanical tunnelling [4.26 - 4.29]. As discussed in Chapter II, the second moment reduction which occurs when there is tunnelling may be different from that which occurs for classical reorientation, but according to Allen [4.13] the quantum mechanical and classical mechanisms both give a reduction factor of 1/4 when the barrier height is less than about 3 kcal/mole, a value which is in excess of most of the barriers to methyl group reorientation observed in this work. In these cases the magnitude of the second moment gives no evidence for the existence of tunnelling. For N-methyl groups, for which the barrier is more than 3 kcal/mole, we have found the observed second moments to be consistent with rigid lattice conditions at the lowest observed temperatures. Tunnelling mechanisms do not come into question, then, in the case of N-methyl groups in our compounds. Analysis of the T₁ data (see later) shows that the T₁ minimum can be explained satisfactorily by the modified BPP equation [4.16, 4.17] which assumes the dipole-dipole relaxation is thermally activated. It has been shown that the line narrowing transition is expected to be completed when [4.14]
\[(\Delta \omega^2)^{1/2} \tau_c \ll 1\]  \hspace{1cm} (4.1)

where \(\Delta \omega^2\) is the rigid lattice second moment and \(\tau_c\) is the correlation time for the motional process. Using the \(T_1\) data, a line width and second moment transition is expected to occur at about 51 K if the methyl groups attached to boron are rigid. This temperature is lower than the lowest temperature we can attain. It would be interesting to see if there is tunnelling assisted reorientation below 50 K in trimethylamine-trimethylborane.

Since no halt in the decrease of second moment between 95 K and 140 K is observed near 12 G\(^2\), one concludes that rotation of methyl groups in the trimethylamine moiety and rotation of the whole molecule about the boron-nitrogen axis occur with comparable frequencies in this temperature range. This observation corresponds to that for hexamethylethane [4.10], for which no plateau which would correspond to methyl group reorientation but no significant reorientation about the central C-C bond is observed in the second moment. This observation agrees with easier methyl group reorientation about the longer C-Si bond [4.15] and lends credibility to our interpretation of the second moment vs. temperature curve of trimethylamine-trimethylborane. The levelling off of second moment above about 140 K to a value of some 2.6 G\(^2\) agrees well with the calculated second moment for reorientation of all methyl groups as well as rotation of the whole molecule about the B-N axis. The study was not pursued above 350 K because the compound begins to sublime and dissociate to a significant extent beyond that temperature.
C.4 Spin-Lattice Relaxation

Figure 4.2 shows the temperature dependence of spin-lattice relaxation times of trimethylamine-trimethylborane. The modified [4.16] equation originally developed by Bloembergen [4.17]

\[
\frac{1}{T_1} = \frac{k_B T}{\omega_0} \sum_{\text{ij}} \left( \frac{\omega_0 \tau_c}{1 + \omega_0^2 \tau_c^2} \frac{4 \omega_0 \tau_c}{1 + 4 \omega_0^2 \tau_c^2} \right)
\]

(4.2)
is used to analyze our \( T_1 \) data. The symbols are conventional and have been defined in Chapter II. The correlation time \( \tau_c \) is assumed to have a simple Arrhenius dependence on an activation energy, \( E_a \), and on temperature

\[
\tau_c = \tau_c^0 \exp \left( \frac{E_a}{RT} \right)
\]

(4.3)

This equation can also be written as

\[
\omega_0 \tau_c = \omega_0 \tau_c^0 \exp \left( \frac{E_a}{RT} \right)
\]

(4.4)

We attribute the low temperature minimum in the \( \ln T_1 \) vs \( T^{-1} \) curve to reorientation about their \( C_3 \) axes of those methyl groups which are attached to the boron atom. Using a value \( (T_1)_{\text{min}} = 37 \text{ ms} \) to evaluate the part of Equation (4.2) outside the square brackets, we obtained a value of \( \omega_0 \tau_c \) for each experimental \( T_1 \) point between 79 and 130 K. A plot of \( \ln \omega_0 \tau_c \) vs \( T^{-1} \) is shown by line a in Figure 4.3. A least squares fit of the line gave
Fig. 4.2. The spin-lattice relaxation time, $T_1$, of trimethylamine-trimethylborane as a function of inverse temperature. The broken lines indicate the resolution of the observed $T_1$ into two mechanisms.
Fig. 4.3 Plot of $\omega_0^\infty$ versus inverse of temperature of trimethylamine-trimethylborane. (a) for rotation of the methyl groups attached to boron (b) for rotation of the methyl groups attached to nitrogen plus the reorientation of the whole molecule about the B-N bond.
\[ \ln \omega_0 \tau_C = (-9.68 \pm 0.21) + (1.89 \pm 0.04) \times 10^3 / RT \]  

(4.5)

The activation energy was thus found to be 1.89 ± 0.04 kcal/mole for reorientation of the methyl groups attached to the boron atom. We attribute the high temperature minimum in the \( \ln T_1 \) vs \( T^{-1} \) curve to reorientation of methyl groups attached to nitrogen and the reorientation of the whole molecule about the B-N axis. Between 130 and 165 K the spin-lattice relaxation time is believed to be controlled by three mechanisms; namely the reorientation of the three methyl groups attached to the boron atom, the reorientation of methyl groups attached to the nitrogen atom, and the rotation of the whole molecule about the B-N axis. The change of second moment with temperature between 100 and 138 K indicates that the latter two mechanisms cannot be separated from each other in the frequency range in which they are effective in changing the line width of the CW spectrum. We assume that these two rotational motions are likewise inseparable in their contribution to spin-lattice relaxation at the Larmor frequency of 30 MHz, and we have lumped them together as a single process with a common activation energy and a common value of \( \tau_C^0 \). In the temperature range 130 to 165 K, the observed spin-lattice relaxation time can be expressed as

\[ \frac{1}{(T_1)_{obs}} = \frac{1}{(T_1)_{CH_3}} + \frac{1}{(T_1)_{mol}} \]  

(4.6)

where \( (T_1)_{CH_3} \) is the relaxation time constant of the reorientation mechanism
for the three methyl groups attached to boron. Its value can be calculated from Equation (4.5) and (4.2), and it is shown in Figure 4.2 by the broken line of positive slope. \((T_1)_\text{mol}\) is the relaxation time constant of the reorientation mechanisms for the methyl groups attached to nitrogen combined with rotation of the whole molecule about the B-N axis. Using Equation (4.6), one can obtain it from the observed \(T_1\) and calculated values of \((T_1)_{\text{CH}_3}\). The broken line of negative slope in Figure 4.2 shows the calculated value of \((T_1)_{\text{mol}}\). Using a value of \((T_1)_{\text{min}} = 19\) ms, calculated values of \((T_1)_{\text{mol}}\) in the temperature range from 145 to 165 K, and observed \(T_1\) values above 165 K, we calculated \(\omega_0 \tau_C\) for each \(T_1\) point between 145 and 335 K. These values are plotted as line b in Figure 4.3. A least square fit of the line gave

\[
\ln \omega_0 \tau_C = (-10.71 \pm 0.08) + (3.63 \pm 0.03) \times 10^3/RT \quad (4.7)
\]

The activation energy was thus found to be 3.63 ± 0.03 kcal/mole for reorientation of methyl groups attached to nitrogen and rotation of the whole molecule about the B-N axis. The assigned relaxation mechanism can be checked from n.m.r. line width and second moment. Decrease in n.m.r. line width or second moment due to the combined rotation motion of methyl groups attached to nitrogen and whole molecule should occur in a correlation time range near \(\tau_C \sim (\gamma M_2)^{-1}\) or \((\gamma \delta H)^{-1}\) where \(M_2\) and \(\delta H\) are the second moment and line width at about the midpoint of narrowing. \(M_2 = 12\) G² (see Figure 4.1) gives \(\omega_0 \tau_C = 2.0 \times 10^3\) and \(\delta H = 11\) G gives \(\omega_0 \tau_C = 6.4 \times 10^3\). From Figure 4.3b or Equation (4.7), one predicts that the temperature of second moment or line width decrease should be at about 100 or 106 K, respectively, values which agree satisfactorily with the experimental...
temperature for line narrowing.

If in Equation (4.2), $k \sum_{ij} r^{-6}$ is put equal to $3r^{-6}/5$ for an isolated methyl group rotating about its C$_3$ axis [4.18], where $r$, the inter-proton distance, is taken as 1.80 Å, one obtains $(T_1)_{\min} = 17.8$ ms. We believe that at the lower temperature minimum in $T_1$ only the methyl groups on boron are rotating rapidly enough to contribute to spin-lattice relaxation. The other half of methyl groups in the molecule are presumably relaxed through spin-diffusion [4.19] to the B-methyl groups and the observed minimum in $T_1$ would be expected to be twice [4.19] that for the B-methyl groups alone, hence 35.6 ms, neglecting inter-group contributions to $T_1$. Despite the fact that one would expect the predicted $T_1$ minimum to be larger than the observed value (37 ms) in view of the neglect of inter-group contribution, the agreement with experiment is good enough to suggest that the low temperature minimum has been correctly assigned to rotation of three of the six methyl groups. For rotation of the whole molecule, $k \sum_{ij} r^{-6}$ becomes $8r^{-6}/45$ for an isolated methyl group [4.20]. At the temperature of the 19 ms minimum in $T_1$, relaxation by rotation of the B-methyl groups is considered negligible and the minimum in $T_1$ for the combined motion is calculated to be 22.4 ms, neglecting inter-group contribution. This compares reasonably with the experimental value of 19 ms.

D. Trimethylamine-trimethylaluminium complex

D.1 Line Width and Second Moment

The experimental line width and second moment of trimethylamine-trimethylaluminium are plotted against temperature in Figure 4.4. The second
Fig. 4.4. Line width and second moment of trimethylamine-trimethylaluminium as a function of temperature.
moment is constant at $20.3 \pm 0.5 \text{ G}^2$ between 65 and 80 K and then decreases rather rapidly to $9.8 \pm 0.3 \text{ G}^2$ at about 120 K. It remains at this value for several degrees and then decreases slowly to about $2 \text{ G}^2$ at 240 K, above which it changes only very little except near 313 K, where there is a sharp and comparatively large change in line width. Above 313 K, the second moment is essentially zero and the line width is determined by the amplitude of the modulation field and the magnetic field inhomogeneity.

D.2 Calculation of Second Moment and Discussion of Molecular Motion

Using the methods for calculating theoretical second moments which were described in detail before, we have obtained the theoretical second moments, which are listed in Table 4.2, for rigid lattice conditions and for various kinds of molecular motion. For the calculation on trimethylamine-trimethylaluminium we have taken interatomic distances as follows [4.5]: $r(\text{C-H}) = 1.10 \AA$, $r(\text{C-N}) = 1.47 \AA$, $r(\text{C-A}_{\ell}) = 2.00 \AA$ and $r(\text{N-A}_{\ell}) = 1.93 \AA$.

It is clear from Table 4.2 that even at the lowest observed temperature the rigid lattice value of the second moment of trimethylamine-trimethylaluminium has not been reached. The experimental value of the second moment between 65 and 80 K agrees very well with the value calculated on the assumption that three of the six methyl groups in the molecule are reorienting. Since the C-A$_{\ell}$ bond is much longer than the C-N bond it seems probable that the rapidly reorienting groups are those attached to aluminium. This conclusion is supported by the fact that the methyl groups in hexamethyldisilane [4.15] rotate essentially

\* $r(\text{N-A}_{\ell})$ obtained from $r(\text{C-N})$, $r(\text{C-A}_{\ell})$ and $r(\text{C-C})$
TABLE 4.2
Theoretical second moments for trimethylamine-trimethylaluminium (in G\(^2\)) and the Comparison with experimental values

<table>
<thead>
<tr>
<th>Group [Me_3N] Motion [Me_3Al]</th>
<th>Intra [CH_3] but Intramolecular</th>
<th>Proton to N and Al[^\rightarrow] Intermolecular</th>
<th>Total</th>
<th>Experimental Second Moment</th>
<th>Temperature (\text{T}^\circ\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS SS</td>
<td>21.3</td>
<td>2.5</td>
<td>0.3</td>
<td>6 ± 1</td>
<td>30.1 ± 1</td>
</tr>
<tr>
<td>SS RS</td>
<td>13.3</td>
<td>2.3</td>
<td>0.1</td>
<td>4.3 ± 0.5</td>
<td>20.0 ± 0.5</td>
</tr>
<tr>
<td>RS SS</td>
<td>13.3</td>
<td>2.2</td>
<td>0.3</td>
<td>4.3 ± 0.5</td>
<td>20.1 ± 0.5</td>
</tr>
<tr>
<td>RS RS</td>
<td>5.3</td>
<td>2.2</td>
<td>0.1</td>
<td>2.4 ± 0.5</td>
<td>10.0 ± 0.5</td>
</tr>
<tr>
<td>RR RR</td>
<td>0.6</td>
<td>0.3</td>
<td>0</td>
<td>1.0 ± 0.3</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td>diffusion</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

SS = methyl group stationary and whole moiety stationary

RS = methyl group rotating but moiety stationary

RR = methyl group rotating and whole moiety rotating
freely at liquid nitrogen temperature, whereas the methyl groups in hexamethylethane [4.10] are severely limited in their rotational freedom at 85 K, and also that the bond lengths are \( r(C-Al) > r(C-Si) \) and \( r(C-C) > r(C-N) \). This conclusion further supports the previous conclusion on trimethylamine-trimethylborane since \( r(C-Al) > r(C-B) \). The plateau at \( 9.8 \pm 0.3 \ G^2 \), which we observed between 120 and 130 K, corresponds to the second moment calculated on the assumption that all the methyl groups rotate freely about their \( C_3 \) axes. The further gradual decrease in linewidth and second moment which takes place above 130 K is attributed to reorientation of the whole molecule about the \( N-Al \) axis. The experimental second moment of \( 2.0 \ G^2 \) found over the considerable temperature range centred about 250 K agrees with the value calculated on the assumption that the methyl groups are rotating and the whole molecule rotates about its \( N-Al \) axis. Narrowing of the line width and decrease of second moment essentially to zero above the transition temperature of 313 K is believed to be caused by diffusion of the whole molecule in the crystal lattice.

D.3 Spin-lattice Relaxation

A plot of \( T_1 \) against reciprocal temperature is shown in Figure 4.5. Below 290 K two minima are observed in \( T_1 \), one at about 183 K and one at about 276 K. Sudden changes in \( T_1 \) at 290 and 313 K are attributed to phase transitions in the solid, and the sharp change at 375 K is due to melting, although it is \( 2^\circ \) below the melting point given by Davidson and Brown [4.2]. The solid down to 313 K is designated as phase I, between 313 and 290 K as phase II, and below 290 K as phase III.
Fig. 4.5. The spin-lattice relaxation time of trimethylamine-trimethylaluminium as a function of inverse temperature. The broken lines indicate the resolution of observed $T_1$. The open circles are the resolved $T_1$ for rotation about N-Al bond.
The analysis of the $T_1$ data for trimethylamine-trimethylaluminium is similar to that for trimethylamine-trimethylborane. We analyze the $T_1$ data in the various phases as follows.

**Phase III**

We attribute the increase of $T_1$ with increasing temperature in the range of 77 to 88 K to the reorientation about their $C_3$ axes of those methyl groups attached to the aluminium atom. In that temperature range the contribution to the overall relaxation time, $T_1$, made by the mechanism which produces a $T_1$ minimum at 183 K is small. Extrapolation of the linearly decreasing $\ln T_1$ with decreasing $T^{-1}$ (that portion of the curve which is due to this second mechanism) back to $T = 88$ K shows that the contribution of the second process to $T_1$ is over 30 times larger than the observed $T_1$ at 88 K. The error introduced by ignoring the contribution of the second mechanisms to the value of $T_1$ observed at and below 88 K is, therefore within the experimental uncertainty in $T_1$. The broken lines in Figure 4.5 between 88 and 125 K are the values of $T_1$ for the two resolved relaxation mechanisms. The resultant $T_1$ obtained by recombining the resolved values agrees very well with the observed $T_1$.

A least squares determination of the slope of the best straight line for the $\ln T_1$ points plotted against $T^{-1}$ between 77 and 88 K gives an activation energy of $0.7 \pm 0.1$ kcal/mole for reorientation of the methyl groups attached to aluminium. This value is smaller than that reported for methyl groups attached to silicon, $1.56 \pm 0.08$ kcal/mole [4.18], and is essentially the same as the value, uncorrected for any temperature dependence of the pre-exponential factor in $\tau$, of $653 \pm 29$ cal/mole given by Smith [4.9] for tetramethylgermane, in which
the C-Ge bond length -1.99 Å is close to the C-Al bond length in trimethyl-
aluminium [4.5].

The minimum in $T_1$ at 183 K is due to reorientation about their $C_3$
axes of methyl groups attached to the nitrogen atom. Using a value of 36 ms,
we obtained $\omega_o \tau_c$ for each $T_1$. A plot of those values of $\omega_o \tau_c$ against $T^{-1}$
is shown in line a in the Figure 4.6, and from the least squares fit of this
line

$$\ln \omega_o \tau_c = (-9.06 \pm 0.17) + (3.10 \pm 0.06) \times 10^{+3}/RT$$  \hspace{1cm} (4.8)

the activation energy for the reorientation of the methyl groups attached to
nitrogen is found to be 3.1 ± 0.1 kcal/mole.

Spin-lattice relaxation between 210 and 290 K is believed to be a
result of two principal mechanisms, namely, reorientation of the methyl groups
on nitrogen and reorientation of the whole molecule about its N-Al axis. The
observed relaxation rate, $\frac{1}{T_1}_{\text{obs}}$, can be expressed as the sum of the relaxation
rate due to reorientation of methyl groups attached to nitrogen atom, $(T_1)_{N-CH_3}^{-1}$,
and the relaxation rate due to the reorientation of the whole molecule
$(T_1)_{\text{mol}}^{-1}$

$$\frac{1}{T_1}_{\text{obs}} = (T_1)_{N-CH_3}^{-1} + (T_1)_{\text{mol}}^{-1}$$  \hspace{1cm} (4.9)

Values of $(T_1)_{N-CH_3}$ were obtained for the several temperatures corresponding
to experimental points from Equation (4.8) and (4.2) and the value $(T_1)_{\text{min}}$
36 ms. Values of $(T_1)_{\text{mol}}$ were then calculated for those temperatures by
Fig. 4.6. Plot of $\omega_0 \tau_c$ versus reciprocal of temperature of trimethylamine-trimethylaluminium (a) for rotation of the methyl groups attached to nitrogen, (b) for reorientation of the whole molecule about the N-Al bond.
Equation (4.9). These values of $(T_1)_{mol}$ are plotted as open circles and connected with a broken line in Figure 4.5. The minimum of 49 ms for $(T_1)_{mol}$ can then be used to obtain a plot of $\omega_0 \tau_c$ against $T^{-1}$, where $\tau_c$ is now the correlation time for reorientation about the $N-A^\parallel$ axis. This plot is shown in line b in the Figure 4.6, and from the least squares fit

$$\ln \omega_0 \tau_c = (-10.20 \pm 0.34) + (5.42 \pm 0.18) \times 10^{-3}/RT$$

we obtain an activation energy of $5.4 \pm 0.2$ kcal/mole for reorientation of the whole molecule about its $N-A^\parallel$ axis. The assigned relaxation mechanisms in phase II were checked with the second moment and line width data and they agree very well.

**Phase II**

The sudden change in $T_1$ at 290 K indicates that here there is a phase transition which allows a sudden change in the correlation frequencies of the relaxation processes. Line b in Figure 4.6 shows that on the low temperature side of the transition $\omega_0 \tau_c$ is approximately equal to 0.4 for reorientation of the whole molecule. Since $\nu_0$ is 30 MHz, we find that the correlation frequency just below the transition temperature is about 75 MHz for that process. This is much larger than the motional frequency which would affect the line width and second moment. Consequently no change appears in these parameters at the transition between phase II and III. Although the $\ln T_1$ against $T^{-1}$ points between 290 and 313 K can be fitted by a straight line whose slope corresponds to an activation energy of $3.9 \pm 0.4$ kcal/mole, it is probably incorrect to assign
this to the reorientation of the whole molecule in solid phase II. The value of 310 ms for $(T_1)_{N-CH_3}$ at 290 K, while $(T_1)_{obs}$ is 900 ms at 291 K, shows that there must be a sudden increase in correlation frequency for N-methyl group rotation as well as for the rotation of the whole molecule. The relative contribution of the two processes is unknown in the range 290 to 313 K. The fact that there is a discontinuous change in correlation frequency for N-methyl group rotation at the phase transition emphasizes that the reorientation process must be at least partly controlled by intermolecular interactions.

**Phase I**

There is a sudden jump in $T_1$ at 313 K. This corresponds to the rapid change in line width and second moment which was observed at this temperature, and we consider that a transition between two solid phases occurs here, and that in the higher temperature phase I diffusional jumps occur with sufficient frequency to decrease the line width and second moment to very small values. At higher temperatures in phase I the rate of diffusional jumping has increased to the point where, above about 350 K, it causes $T_1$ to decrease once again until the melting point is reached. It is not known what contribution N-methyl group reorientation makes to the observed $T_1$ in phase I. If we assume it to be negligible and consider only whole molecule rotation and diffusion as the effective relaxation mechanisms, we can resolve the $\ln T_1$ against $T^{-1}$ curve in the range 313 to 375 K into a straight line of $\ln(T_1)_{mol}$ against $T^{-1}$ (with increasing $T_1$ for increasing $T$) for the contribution of the rotation of the whole molecule about its N-Al axis to the observed spin-lattice relaxation, and a second straight line of $\ln(T_1)_{dif}$ against $T^{-1}$ (with decreasing $T_1$ for increasing $T$) for the contribution...
of diffusional motion to the relaxation, the observed $T_1$ being assumed to be of the form

$$ (T_1)_{\text{obs}}^{-1} = (T_1)_{\text{mol}}^{-1} + (T_1)_{\text{dif}}^{-1} $$

The slopes of these lines, which are shown in Figure 4.5, correspond to activation energies of $4.7 \pm 0.2$ kcal/mole for molecular rotation and $19.5 \pm 0.2$ kcal/mole for self-diffusion. The latter agrees very well with the activated energy of self-diffusion for hexamethylethane, which Chezeau et al [4.10] found from line width, $T_1$ and $T_1 \rho$ studies.

**E. Trimethylphosphine-trimethylaluminium**

**E.1 Line Widths and Second Moments**

The experimental second moment and line width are plotted vs temperature in Figure 4.7. The second moment has a value of $10.0 \pm 1.0$ G$^2$ at 65 K. It decreases slowly to a plateau value of $4.5 \pm 0.5$ G$^2$ at 132 K, and again decreases slowly above 180 K to another plateau value of $1.75 \pm 0.2$ G$^2$ at about 240 K. The shape of the line width vs temperature curve is similar to that of the second moment vs temperature.

**E.2 Calculation of Second Moment**

The molecular parameters and crystal structure of trimethylphosphine-trimethylaluminium are all unknown. The theoretical second moment has, however, been calculated by the methods described earlier in this chapter, and its values are listed in Table 4.3 for rigid conditions and various types of molecular
Fig. 4.7. Temperature dependence of line width and second moment of trimethylphosphine-trimethylaluminium.
TABLE 4.3

Theoretical second moments for trimethylphosphine-trimethylaluminium (in G²) and comparison with experimental values

<table>
<thead>
<tr>
<th>Group Motion</th>
<th>Me₃P</th>
<th>Me₃Al</th>
<th>Intra CH₃</th>
<th>Inter CH₃ but intra-molecular</th>
<th>Proton to P and Al</th>
<th>Inter-molecular</th>
<th>Total $\pm$</th>
<th>Experimental Second Moment</th>
<th>Temperature $T^\circ K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS SS</td>
<td>21.3</td>
<td>1.2</td>
<td>0.2</td>
<td>7 ± 1</td>
<td></td>
<td></td>
<td>29.8 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RS SS</td>
<td>()</td>
<td>()</td>
<td></td>
<td>13.2</td>
<td>1.1</td>
<td>0.1</td>
<td>4.5 ± 0.8</td>
<td>18.9 ± 0.8</td>
<td>-</td>
</tr>
<tr>
<td>SS RS</td>
<td>()</td>
<td>()</td>
<td>()</td>
<td>5.3</td>
<td>1.0</td>
<td>0.1</td>
<td>2.4 ± 0.8</td>
<td>8.8 ± 0.8</td>
<td>10.0 ± 1</td>
</tr>
<tr>
<td>RS RR</td>
<td>2.9</td>
<td>0.6</td>
<td>0</td>
<td>1.7 ± 0.8</td>
<td></td>
<td></td>
<td>5.2 ± 0.8</td>
<td>4.5 ± 0.5</td>
<td>132 - 180</td>
</tr>
<tr>
<td>RR RR</td>
<td>0.6</td>
<td>0.3</td>
<td>0</td>
<td>1.2 ± 0.3</td>
<td></td>
<td></td>
<td>2.1 ± 0.3</td>
<td>1.8 ± 0.2</td>
<td>240 - m.p.</td>
</tr>
</tbody>
</table>

SS = Methyl groups and the moiety are both stationary
RS = The methyl groups are rotating but the moiety is stationary
RR = Methyl groups and moiety are rotating
motion. For calculation of second moments, the following bond distances have been taken. \( r(C-H) = 1.10 \, \text{Å} \), \( r(C-P) = 1.84 \, \text{Å} \) \([4.19, 4.20, 4.21]\), \( r(C-Al) = 2.0 \, \text{Å} \) \([4.5]\), \( r(P-Al) = 2.30 \, \text{Å} \).

Table 4.3 shows that even at the lowest temperature attained, trimethylphosphine-trimethylaluminium is not rigid, nor does it behave similarly to trimethylamine-trimethylborane and trimethylamine-trimethylaluminium, in which the methyl groups in one of the moieties are effectively rigid at 77 K. The second moment obtained at 65 K corresponds to all methyl groups rotating. This is expected since \( r(C-P) > r(C-B) > r(C-N) \). The second moment above 240 K agrees very well with the value estimated on the assumption that all methyl groups are rotating about their threefold axes and the whole molecule is rotating about the P-Al bond. The plateau value between 132 and 180 K agrees quite well with the calculated value on the assumption that all methyl groups as well as one of the moieties are rotating while the other moiety is fixed. One cannot determine which moiety is rotating in this temperature region from only the results obtained for trimethylphosphine-trimethylaluminium. The best way to solve this problem would be to study a compound such as \((CD_3)_3P-Al(CH_3)_3\) or \((CH_3)_3P-Al(CD_3)_3\). Another possibility is to consider the results for \(Me_2PH-AlMe_3\) and \(Me_2NH-AlMe_3\). The second moments of \(Me_2NH-AlMe_3\) (see Chapter VI) suggest that the rotation of the trimethylaluminium moiety starts at about 240 K. Thus in the temperature region of 132 - 180 K, the moiety which rotates may possibly be trimethylphosphine.

* Obtained from \( r(C-P) \), \( r(C-Al) \) and \( r(C-C) \)
E.3 Spin-lattice Relaxation Time

Figure 4.8 shows the variation of experimental $T_1$ with inverse of temperature. It shows multiple minima, and at low temperature the $T_1$ curve is nearly flat. The analysis of the $T_1$ data is straightforward. We attribute the $T_1$ minimum at about 290 K to reorientation of the trimethylaluminium moiety, and the $T_1$ minimum at about 157 K to rotation of trimethylphosphine. If we assume a $T_1$ minimum due to some relaxation mechanism occurs well below liquid nitrogen temperature, the $T_1$ results can be resolved into three parts as shown by the broken lines. The resultant $T_1$ from this resolution is within 15% of the experimental $T_1$ values. Thus there are three relaxation mechanisms which contributed to the observed spin-lattice relaxation rate in the temperature range of 77 - 157 K. One of them must be the rotation of the trimethylphosphine moiety. The previous two studies have shown that methyl groups attached to different kinds of central atoms have different correlation times. In trimethylphosphine-trimethylaluminium, since $r(C-Al) > r(C-P)$, the methyl groups attached to aluminium are expected to rotate prior to the rotation of methyl groups attached to phosphorus. We thus assign the $T_1$ minimum at about 112 K from the resolved curve to the rotation of methyl groups attached to phosphorus and in the range 77 to 120 K, the increase of $T_1$ with increasing temperature to the rotation of methyl groups attached to aluminium. The results are summarized in Table 4.4.
Fig. 4.8. The spin-lattice relaxation time of trimethylphosphine-trimethylaluminium as a function of reciprocal of temperature. The broken curves indicate the resolution of observed $T_1$ into more than one mechanism.
TABLE 4.4

Energy and Rate Parameters for Trimethylphosphone-trimethylaluminiun

<table>
<thead>
<tr>
<th>Type of motion</th>
<th>$E_A$ (kcal/mole)</th>
<th>$\tau_c$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation of $\text{Me}_3\text{Al}$ moiety</td>
<td>$9.95 \pm 0.19$</td>
<td>$1.03 \times 10^{-16}$</td>
</tr>
<tr>
<td>Rotation of $\text{Me}_3\text{P}$ moiety</td>
<td>$3.28 \pm 0.06$</td>
<td>$7.63 \times 10^{-14}$</td>
</tr>
<tr>
<td>Rotation of methyl groups at $\text{Me}_3\text{P}$</td>
<td>$1.15 \pm 0.1$</td>
<td>$1.86 \times 10^{-11}$</td>
</tr>
<tr>
<td>Rotation of methyl groups at $\text{Me}_3\text{Al}$</td>
<td>$0.75 \pm 0.1$</td>
<td>-</td>
</tr>
</tbody>
</table>

We have checked the correlation times for the rotations of the trimethylaluminium and trimethylphosphine moieties using the $T_1$ data at their line width and second moment transition temperatures. The correlation times obtained at these temperatures from the $T_1$ data show they agree with the correlation times of narrowing the line widths and second moments. This confirms that the assignment is correct for the relaxation mechanisms in the trimethylphosphine-trimethylaluminiun complex in the temperature range of 157 K to its melting point.

F. Trimethylphosphine-trimethylborane

F.1 Experimental Line Width and Second Moment

The line widths and second moments are plotted as functions of temperature in Figure 4.9. Below 100 K the second moment increases slowly as the temperature decreases. It has a value of about $9.8 \pm 0.5 \text{ G}^2$ in the temperature
Fig. 4.9. Temperature dependence of line width and second moment of trimethylphosphine-trimethylborane.
range 100 - 125 K. It decreases slowly as the temperature is increased and then reaches a plateau value of $2.3 \pm 0.4 \text{ G}^2$ at about 200 K. At 324 K, there is a sudden change in line width and second moment and above this temperature the line width is the same as the line width of doped water. The shape of line width versus temperature curve is similar to that of second moment versus temperature.

**F. 2 Calculation of Second Moment and Discussion of Molecular Motion**

Calculation of the theoretical second moment has been made in the same way before, and with the assumption that $r(\text{C-H}) = 1.10 \text{ Å}$, $r(\text{C-P}) = 1.84 \text{ Å}$ [4.19, 4.20, 4.21], $r(\text{C-B}) = 1.56 \text{ Å}$ [4.5, 4.6], $r(\text{P-B}) = 1.83 \text{ Å}$.* The results are shown in Table 4.5.

Table 4.5 shows that even at the lowest temperature attained, the rigid second moment has not been reached. The experimental second moment in the range 100 - 125 K agrees quite well with the value calculated on the assumption that all methyl groups are rotating. The second moment between 200 - 324 K agrees very well with the calculated value assuming that all methyl groups as well as the whole molecule is rotating about its P-B bond. The second moment above 324 K is believed to be determined by the self-diffusion mechanism in the solid state. The increase of second moment with decreasing temperature below 100 K is almost certainly due to the decrease in rotational frequency of the methyl groups.

* Obtained from $r(\text{C-P}), r(\text{C-B}), r(\text{C-C})$
TABLE 4.5
Theoretical second moment (in $G^2$) for trimethylphosphine-trimethylborane and comparison with experimental values

<table>
<thead>
<tr>
<th>Group Motion</th>
<th>Me$_3$P</th>
<th>Me$_3$B</th>
<th>Theoretical Second Moment</th>
<th>Moment Contribution</th>
<th>Total</th>
<th>Experimental Second Moment</th>
<th>Temperature $^0K$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intra CH$_3$</td>
<td>Inter CH$_3$ but intra-molecular</td>
<td>Proton to P and B</td>
<td>Inter-molecular</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS SS</td>
<td>21.3</td>
<td>2.9</td>
<td>0.5</td>
<td>7 ± 1</td>
<td>31.8 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RS SS RS</td>
<td>13.2</td>
<td>2.4</td>
<td>0.5</td>
<td>4.5 ± 0.8</td>
<td>30.6 ± 0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RS RS</td>
<td>5.3</td>
<td>2.4</td>
<td>0.5</td>
<td>2.4 ± 0.8</td>
<td>10.6 ± 0.8</td>
<td>9.8 ± 0.5</td>
<td>100 - 125</td>
</tr>
<tr>
<td>RR RR</td>
<td>0.6</td>
<td>0.6</td>
<td>0.2</td>
<td>1.2 ± 0.3</td>
<td>2.6 ± 0.3</td>
<td>2.3 ± 0.4</td>
<td>200 - 324</td>
</tr>
</tbody>
</table>

Self-Diffusion: 0 0 0 0 0 0 0.1 324 - m.p.

SS = Methyl groups and the moiety are both stationary
RS = The methyl groups are rotating but the moiety is stationary
RR = Methyl groups and moiety are rotating
F.3 Spin-lattice Relaxation Times

Figure 4.10 is a plot of $T_1$ versus the inverse of temperature. There is a sudden jump of $T_1$ at 310 K and 324 K. The change in $T_1$ at 324 K is not as great as the change at 310 K. However, there is a sudden change in time constant of the FID curve which indicates there is a sudden change in line width or $T_2$ at this temperature. There are two minima in the $T_1$ curve below 310 K. The solid down to 324 K is assigned as phase I, between 324 and 310 K as phase II, and below 310 K as phase III. We will analyse the $T_1$ data in different phases.

Phase III

The spin-lattice relaxation rate between 200 and 290 K is affected by the relaxation mechanism at high temperature and by the relaxation mechanism at low temperature. The two contributions were resolved as shown by the broken lines in Figure 4.10. From the resolved $T_1$, and the $T_1$ data above 250 K as well as the $T_1$ minimum at 250 K, $\omega_0 \tau_C$ can be obtained for each temperature at which a $T_1$ value has been found, and a least squares fit gives

$$\ln \omega_0 \tau_C = (-15.5 \pm 0.1) + (8.00 \pm 0.08) \times 10^3/RT$$

Thus the activation energy for the relaxation mechanism in this temperature range is found to be $8.00 \pm 0.08$ kcal/mole. Analysis of the second moments has suggested that this relaxation mechanism be assigned to the rotation of the whole molecule about its P-B bond. Decrease in n.m.r. line width or second moment due to the rotation of the whole molecule about its P-B bond should
Fig. 4.10. Spin-lattice relaxation time of trimethylphosphine-trimethylborane as a function of inverse temperature. The broken lines show the resolution of observed $T_1$ at about 250 K. The open circles show the resolution of observed $T_1$ at each point into more than one mechanism.
occur in a correlation time range near $\tau_c = (\gamma \delta / M_2)^{-1}$ or $(\gamma \delta H)^{-1}$ where $M_2$ and $\delta H$ are the same as defined before. $M_2 = 6 \, G^2$ (see Figure 4.9) gives $\omega_0 \tau_c \sim 10^3$ and $\delta H = 5.5 \, G$ gives $\omega_0 \tau_c \sim 10^3$. Values of $\omega_0 \tau_c$ obtained from the relaxation data in the temperature range of 140 - 170 K are of the order of $10^5$ to $10^3$. This indicates that the assignment of the relaxation mechanism in the temperature range of 200 to 310 K is correct and the relaxation mechanism is the rotation of the whole molecule about its P-B bond.

The $T_1$ minimum at lower temperature is very broad and the $T_1$ curve cannot be described by a BPP equation with a single correlation time. However, a good fit can be obtained if we assume there are two correlation times and the relaxation processes can be described by two BPP equations. The solid points on the curve are the experimental points, the open points are the resolved $T_1$ points and the solid line is the resultant $T_1$ calculated from the two separate mechanisms. The calculated values agree quite well with the experimental data. The resolved curve for which the $T_1$ minimum occurs at 104 K has $T_1^{\text{min}} = 52 \, ms$ and an activation energy of 1.46 kcal/mole. The other resolved curve which the $T_1$ minimum occurs at 124 K has $T_1^{\text{min}} = 53 \, ms$ and an activation energy of 2.14 kcal/mole. The values of $T_1^{\text{min}}$ suggest that the two relaxation mechanisms are the same but differ in activation energy only.

The previous studies have shown that methyl groups attached to different central atoms have different rotational correlation times. In trimethylphosphine-trimethylborane, the methyl groups attached to phosphorus and the methyl groups attached to boron experience different environments. If these
environments do not differ too much, the correlation times for rotation of the methyl groups will not differ significantly. Therefore both correlation times make a contribution to the spin-lattice relaxation rate and a broad minimum in $T_1$ was obtained. Since the C-P bond length is greater than the C-B bond length, the activation energy of 1.47 kcal/mole can probably be assigned to the rotation of methyl groups attached to phosphorus and 2.14 kcal/mole can be assigned to the rotation of methyl groups attached to boron. This assignment of activation energies is also supported by the fact that values of activation energy for the reorientation of methyl groups attached to phosphorus in trimethylphosphine-trimethylaluminium (1.2 kcal/mole) and to boron in trimethylamine-trimethylborane (1.9 kcal/mole) are quite close to the activation energies assigned.

**Phase II**

Although an activation energy of $1.00 \pm 0.45$ kcal/mole was obtained from the three experimental points between 310 and 324 K, it is dangerous to assign this activation energy to the reorientation of the whole molecule along its P-B bond. The relaxation rate in this phase may be the result of two or more mechanisms, namely, the rotation of the whole molecule about its P-B bond, the rotation of methyl groups, and other mechanisms, which may involve isotropic rotation of the whole molecule.

**Phase I**

The spin-lattice relaxation time increases with the increasing of temperature in the temperature range of 324 - 358 K. The activation energy obtained from the slope of the least squares fitted straight line is $2.84 \pm$
0.24 kcal/mole. Above 358 K, the spin-lattice relaxation time decreases with increasing temperature until it reaches the melting point. The activation energy obtained from the slope is $4.3 \pm 0.6$ kcal/mole. No attempt was made to resolve the $T_1$ data since, in phase I, there is no assurance that there are only two relaxation mechanisms involved. In addition, the range of $T_1^{-1}$ is so small in phase I that we do not know which is the predominant mechanism. The sample melts sharply at 391 K. The melting point cited in the literature was 391 - 394 K. The activation energy of $4.3 \pm 0.6$ kcal/mole might be assigned to the self-diffusion process of trimethylphosphine-trimethylborane. This value, however, is extremely low when compared with the activation energy for the self-diffusion process of other compounds studied [4.10, 4.15, 4.20]. The value is somewhat doubtful because we do not know the contribution to the relaxation rate from other mechanisms. The activation energy $2.84 \pm 0.24$ kcal/mole in the range of 324 - 358 K is not assigned.

Table 4.6 gives a summary of energy and rate parameters for trimethylphosphine-trimethylborane in the temperature range studied.
TABLE 4.6
Energy and Rate Parameters for Trimethylphosphine-trimethylborane

<table>
<thead>
<tr>
<th>Type of Motion</th>
<th>$E_A$ (kcal/mole)</th>
<th>$\tau_c^0$ (sec)</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation of methyl groups at Me$_3$P</td>
<td>1.47</td>
<td>$2.65 \times 10^{-12}$</td>
<td>77 - 200</td>
</tr>
<tr>
<td>Rotation of methyl groups at Me$_3$B</td>
<td>2.14</td>
<td>$5.45 \times 10^{-13}$</td>
<td>77 - 200</td>
</tr>
<tr>
<td>Rotation of the whole molecule</td>
<td>8.00 ± 0.08</td>
<td>$9.87 \times 10^{-16}$</td>
<td>200 - 310</td>
</tr>
<tr>
<td>?</td>
<td>1.00 ± 0.45</td>
<td>-</td>
<td>310 - 324</td>
</tr>
<tr>
<td>?</td>
<td>2.84 ± 0.24</td>
<td>-</td>
<td>324 - 358</td>
</tr>
<tr>
<td>Self-diffusion</td>
<td>4.3 ± 0.6</td>
<td>-</td>
<td>358 - m.p.</td>
</tr>
</tbody>
</table>
References

[4.2] N. Davidson and H.C. Brown, J.A.C.S., 64 (1942) 316
[4.3] S. Sujishi, Ph.D. Thesis, Purdue University, 1949
[4.5] Interatomic Distances, Chemical Society (London), Special Publications No. 11 (1958), and No. 18 (1965)
[4.7] S.H. Bauer and J.Y. Beach, J.A.C.S., 64 (1942) 1142
[4.21] H.D. Springall and L.O. Brockway, J.A.C.S., 60 (1938) 996
CHAPTER V

An NMR Study of Trimethylphosphine and Trimethylborane

A. Introduction

This chapter describes the details of an nmr study of trimethylphosphine and trimethylborane. The molecular structure of trimethylphosphine has been studied by electron diffraction [5.1, 5.2] and microwave spectroscopy [5.3], and the rotation barrier for the methyl groups was obtained in the gaseous phase from these studies. The molecular structure of trimethylborane has been studied by electron diffraction [5.4], but no energy or rate parameters were obtained for this compound. It is our purpose to study the activation energy and correlation time of the methyl group rotation and other possible molecular motions in these two compounds in the solid state.

B. Experimental

B.1 Materials

Trimethylphosphine was obtained from Pfaltz and Bauer, Inc., and was directly transferred in a dry box to a 10 mm O.D. sample tube for broadline work and to a 7.5 - 8.0 mm thin wall sample tube for pulsed nmr measurement. The dissolved oxygen was pumped off by the freeze-pump-thaw method. Trimethylborane was purchased from Alfa Inorganics and was trapped in the sample tubes at liquid nitrogen temperature with the aid of a vacuum line. Samples were sealed in the sample tube immediately after being trapped.
B.2 Measuring Procedures

These were the same as described in Chapter III. $T_1$ values for trimethylphosphine were obtained by using a $180^\circ - \tau - 90^\circ$ pulse sequence with a $180^\circ$ pulse length of 2-3 $\mu$sec. The same method was used to obtain $T_1$ values for trimethylborane when these were shorter than 5 sec. For $T_1$ values which were longer than 5 sec, a $90^\circ - \tau - 90^\circ$ pulse sequence was used. The $T_1$ values were calculated from the slope of a least squares fit straight line of $\frac{M_0 - M(\tau)}{2M_0}$ versus $\tau$. The standard deviation of the slope is less than 5% in all cases.

C. Trimethylphosphine

C.1 Experimental Line Widths and Second Moments

The experimental second moments and line widths of trimethylphosphine are plotted versus temperature in Figure 5.1. The second moment has a value of $29.0 \pm 1 \, \text{G}^2$ at 65 K. It decreases to a plateau value of $9.5 \pm 0.5 \, \text{G}^2$ at 105 K. At about 155 K the second moment decreases again from $8.5 \, \text{G}^2$ to a plateau value of $2.2 \pm 0.4 \, \text{G}^2$ at about 175 K. Superimposed solid and liquid lines appear between 186 and 189 K. Above 189 K no solid signal was observed. The melting cited in CRC handbook is 187.8 - 188.8 K. This agreed quite well with our observation. The shape of the line width versus temperature curve is similar to that of the second moment versus temperature curve.

C.2 Calculation of Second Moment and Discussion of Molecular Motion

Although the molecular structure of trimethylphosphine has been studied by electron diffraction [5.1, 5.2] and microwave spectroscopy [5.3], no crystal structure study has been made on the solid state. Thus the calculation
Fig. 5.1. Line width and second moment of trimethylphosphine as function of temperature.
of the intramolecular second moment is based on the structure parameters obtained from the microwave studies, which agree very well with the electron diffraction studies. For calculation of the intramolecular second moment, the following bond lengths and bond angles from the microwave study are used: \( r(C-H) = 1.09 \text{ \AA} \), \( r(C-P) = 1.84 \pm 0.003 \text{ \AA} \), \( \gamma_{HCH} = 107.0^0 \pm 1.0^0 \), \( \gamma_{CPC} = 99.1^0 \pm 0.2^0 \). The intermolecular second moment cannot be calculated without a knowledge of the crystal structure. It is, however, estimated that the intermolecular second moment of trimethylphosphine would be approximately the same as the intermolecular second moment of trimethylamine [5.5, 5.6]. Haigh et al. [5.5] estimated the intermolecular second moment for trimethylamine to be about 2.1 G$^2$ while Fyfe [5.6] estimates it to be 4.8 G$^2$. Both workers may have had saturation problems while recording the spectrum since a spin-lattice relaxation time study [5.7] shows the \( T_1 \) at liquid nitrogen temperature is extremely long. Our estimate of intermolecular second moment for trimethylphosphine is therefore 3.5 \( \pm 0.5 \text{ G}\). Table 5.1 shows the results of the calculation and estimation and their comparison with the experimental values.

The observed second moment at 65 K agrees quite well with the calculated rigid lattice second moment. We also found from our \( T_1 \) study (see later) that the correlation frequency of methyl group reorientation at this temperature is about 1 KHz, which is smaller than the line width of the rigid lattice spectrum expressed in frequency. Thus at 65 K, the trimethylphosphine can be regarded as a "rigid" molecule. The second moments between 105 - 145 K agree very well with the calculated values when all methyl groups are rotating. The decrease of second moment above 145 K shows that
TABLE 5.1

Comparison of theoretical and experimental second moments of trimethylphosphine (second moments in $G^2$)

<table>
<thead>
<tr>
<th>Kind of motion</th>
<th>Interaction</th>
<th>$\text{CH}_3$</th>
<th>$\text{CH}_3$-CH$_3$</th>
<th>Proton to phosphorus</th>
<th>Intermolecular</th>
<th>Total</th>
<th>Experimental Second Moment</th>
<th>Temperature $^\circ$K</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td></td>
<td>24.7 ± 0.9</td>
<td>1.5</td>
<td>0.2</td>
<td>3.5 ± 0.5</td>
<td>29.9 ± 1.4</td>
<td>29.1 ± 1</td>
<td>65</td>
</tr>
<tr>
<td>RS</td>
<td></td>
<td>6.2 ± 0.2</td>
<td>1.3</td>
<td>0.2</td>
<td>1.3 ± 0.4</td>
<td>9.0 ± 0.6</td>
<td>9.5 ± 0.5</td>
<td>105 - 145</td>
</tr>
<tr>
<td>RR</td>
<td></td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>1.2 ± 0.3</td>
<td>1.8 ± 0.3</td>
<td>3.2 ± 0.4</td>
<td>175 - 186</td>
</tr>
</tbody>
</table>

SS = stationary
RS = methyl groups rotating while the molecule is stationary.
RR = methyl groups as well as the whole molecule are rotating about their C$_3$ axis
there is an additional motion in the molecule. Comparison of the experimental second moment and calculated value suggests that the additional motion is the reorientation of the whole molecule about its molecular axis. The activation energy of the motion determined from the line width measurements was 7.5 ± 2 kcal/mole. The accuracy of activation energy obtained from line width measurement is not good because when the line width at transition temperature approaches the line width after transition, the uncertainty in correlation times or frequencies obtained becomes so large. In addition, the temperature range of the line width transition is small and hence the range of correlation times or frequencies which are obtained is fairly small.

C.3 Spin-Lattice Relaxation Time

Figure 5.2 is a plot of experimental values of $T_1$ for trimethylphosphine versus the inverse of temperature. For a relaxation process characterized by a single correlation time $\tau_c$, the $T_1$ can be expressed by the modified BPP equation [5.8, 5.9]

$$\frac{1}{T_1} = \frac{c}{\omega_0} \left[ \frac{\omega_0 \tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\omega_0 \tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]$$

(5.1)

where $c$ is a constant and $\omega_0 \tau_c$ are conventional symbols. $\tau_c$ is assumed to have an Arrhenius dependence on an activation energy $E_a$ and on temperature $T$.

$$\tau_c = \tau_c^0 \exp \left( \frac{E_a}{RT} \right)$$

which can be written as

$$\omega_0 \tau_c = \omega_0 \tau_c^0 \exp \left( \frac{E_a}{RT} \right)$$

(5.2)
Fig. 5.2. Spin-lattice relaxation time of trimethylphosphine as a function of inverse temperature.
Fig. 5.3. Plot of $\omega_0 \tau_c$ versus reciprocal of temperature of trimethylphosphine.
The constant \( c \) in Equation (5.1) can be calculated from the experimental \((T_1)_{\text{min}}\) and \( \omega_C^x \) can be obtained for each \( T_1 \) point from Equation (5.1). Figure 5.3 is a plot of \( \omega_C^x \) versus the inverse of temperature. A least squares fit of the straight line gave

\[
\ln(\omega_C^x) = (-7.95 \pm 0.17) + (2.08 \pm 0.4) \times 10^3 / RT
\]

The activation found for this relaxation process is thus \( 2.08 \pm 0.04 \) kcal/mole and it can be assigned unambiguously to the rotation of methyl groups in trimethylphosphine. The correlation time of the rotation of the whole molecule about its molecular axis is too long to affect \( T_1 \) below the melting point. Thus it is not possible to determine the activation energy from \( T_1 \) measurement. However, we found from the line widths an activation energy of \( 7.5 \pm 2 \) kcal/mole for this process. A more precise value might be obtained from \( T_1^P \) measurements, but this is beyond the capability of our equipment.

A microwave study [5.3] has shown that the rotational barrier for the methyl groups is \( 2.6 \pm 0.5 \) kcal/mole. An electron diffraction study [5.2] has shown that the barrier, which depends on the assumed skeletal amplitudes for gauche and trans C-H interactions, is greater than \( 1.5 \) kcal/mole. Our result, which is \( 2.08 \pm 0.04 \) kcal/mole, agrees quite well with these studies. The agreement with the microwave study suggests that the rotation barrier for methyl groups is predominantly an intramolecular interaction.
D. Trimethylborane

D.1 Experimental Second Moments and Line Widths

The experimental second moments and line widths are plotted as functions of temperature in Figure 5.4. The second moment has a plateau value of $12.5 \pm 0.5 \text{ G}^2$ from 65 K to 77 K. It then decreases to a plateau value of $2.5 \pm 0.2 \text{ G}^2$ at about 90 K. The plateau value remains constant up to the melting point of this compound.

D.2 Calculation of Second Moment and Discussion of Molecular Motion

The crystal structure of trimethylborane is unknown. The intramolecular second moment therefore was calculated from the structural parameters obtained from an electron diffraction study [5.4]. The electron diffraction study shows that trimethylborane is a planar molecule and the bond lengths and bond angles are $r(\text{B-C}) = 1.56 \text{ \AA}$, $r(\text{C-H}) = 1.05 \text{ \AA}$, $\angle \text{CBC} = 120^\circ$. The $r(\text{C-H})$ assumed by Lévy and Brockway seems somewhat short, and therefore another set of calculations using $r(\text{C-H}) = 1.10 \text{ \AA}$ was obtained for comparison. The intermolecular second moment cannot be obtained without knowledge of the crystal structure. We thus estimated it from the known intermolecular second moment of another planar molecule, hexamethylbenzene, whose intermolecular second moment is $5.6 \text{ G}^2$ [5.11]. However, the deviation of the intermolecular second moment of trimethylborane from $5.6 \text{ G}^2$ may be quite large. We therefore adopt a value of $5.6 \pm 2\text{ G}^2$. Smith [5.10] has summarized estimates made in the literature of reduction factors for second moment contributions from interactions between two rotating groups. These range from 0.42 to 0.25, and we choose a factor of $0.33 \pm 0.09$. Thus a value of $2.0 \pm 0.5 \text{ G}^2$ was obtained for the intermolecular second moment when all methyl groups are rotating.
Fig. 5.4. Line width and second moment of trimethylborane as function of temperature.
TABLE 5.2

Comparison of theoretical and experimental second moments of trimethylborane (second moment in G2)

<table>
<thead>
<tr>
<th>Type of Motion</th>
<th>Intra CH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Inter CH&lt;sub&gt;3&lt;/sub&gt; but intra-molecular</th>
<th>Proton to Boron</th>
<th>Inter-molecular</th>
<th>Total</th>
<th>Experimental Second Moment</th>
<th>Temperature T&lt;sub&gt;K&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>29.1</td>
<td>2.4</td>
<td>0.6</td>
<td>5.6 ± 2</td>
<td>38.1 ± 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RS</td>
<td>7.3</td>
<td>2.1</td>
<td>0.6</td>
<td>1.9 ± 1</td>
<td>11.1 ± 1</td>
<td>12.5 ± 0.5</td>
<td>65 - 77</td>
</tr>
<tr>
<td>RR</td>
<td>1.8</td>
<td>0.5</td>
<td>0.2</td>
<td>0.7 ± 0.6</td>
<td>3.2 ± 0.6</td>
<td>2.5 ± 0.2</td>
<td>90 - m.p.</td>
</tr>
<tr>
<td>SS</td>
<td>21.3</td>
<td>2.4</td>
<td>0.6</td>
<td>5.6 ± 2</td>
<td>29.9 ± 2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RS</td>
<td>5.3</td>
<td>2.1</td>
<td>0.6</td>
<td>1.9 ± 1</td>
<td>9.9 ± 1</td>
<td>12.5 ± 0.5</td>
<td>65 - 77</td>
</tr>
<tr>
<td>RR</td>
<td>1.3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.7 ± 0.6</td>
<td>2.7 ± 0.6</td>
<td>2.5 ± 0.2</td>
<td>90 - m.p.</td>
</tr>
</tbody>
</table>

SS = Methyl groups and the moiety are both stationary
RS = Methyl groups are rotating while the molecule is stationary
RR = Methyl groups and moiety are rotating
A = Calculation base on r(C-H) = 1.05 Å
B = Calculation base on r(C-H) = 1.10 Å
The reduction factor for the intermolecular contribution for methyl group rotation plus the rotation of the whole molecule about its molecular axis, which is perpendicular to the C$_3$ axis of the methyl groups, is unknown. If we assume the same factors also apply to the reduced second moment, then the intermolecular second moment for rotation of methyl groups plus rotation of whole molecule about its molecular axis becomes 0.7 ± 0.3 G$^2$. Table 5.2 shows the comparison of the calculated second moment and experimental second moment. Set A refers to the calculation on the assumption that r(C-H) = 1.05 Å and set B refers to the calculation on the assumption that r(C-H) = 1.10 Å.

Table 5.2 shows that even at the lowest temperature obtained, the trimethylborane is not rigid. The plateau value between 65 and 77 K corresponds to the rotation of the three methyl groups, and the plateau value between 90 K and the melting point corresponds to the rotation of methyl groups plus the rotation of whole molecule about the molecular axis. Comparison of the calculated value and experimental value for methyl group rotation shows the agreement of the experimental second moment with the calculation based on r(C-H) = 1.05 Å is better than the calculation based on r(C-H) = 1.10 Å. However, the agreement of set B is better than set A when the methyl groups and the whole molecule rotate. This may be due on the one hand to the inaccuracies in the various approximations we have assumed for calculation of the theoretical second moments, or on the other hand to inaccuracy in the experimental second moments because of saturation at low temperature. It should be noted that $T_1$ is about 20s at 77 K.
Fig. 5.5. Spin-lattice relaxation time of trimethylborane as a function of inverse of temperature.
D.3 Spin-lattice Relaxation Time

The spin-lattice relaxation time $T_1$ for trimethylborane is plotted versus inverse of temperature in Figure 5.4. The $T_1$ minimum is not reached before the sample melts. Therefore it is hopeless to try to obtain the correlation time for the motional process. However, the energy parameter can be obtained from Equation (5.1) if $\omega_0 \tau_C >> 1$, or $\omega_0 \tau_C << 1$. The $T_1$ values for trimethylborane between 90 K and melting point are on the lower temperature side of a minimum and therefore $\omega_0 \tau_C >> 1$. Equation (5.1) can be written as

$$\frac{1}{T_1} = \frac{C_1}{\omega_0 \tau_C}$$

where $C_1 = 2c/\omega_0$. Thus the activation energy can be obtained from a plot of $\ln T_1$ versus $T^{-1}$. The activation energy obtained in the range of 90 - 112 K is $2.87 \pm 0.18$ kcal/mole. This value is higher than the activation energy for reorientation of methyl groups attached to boron in trimethylamine-trimethylborane. Since reorientation of the methyl groups attached to boron which is bonded tetrahedrally has a lower activation energy than $2.87 \pm 0.18$ kcal/mole, we conclude that $2.87 \pm 0.18$ kcal/mole cannot be assigned to the rotation of methyl groups in trimethylborane in which the $\angle$CBC bond angle is 120°. The activation energy, $2.87 \pm 0.18$ kcal/mole can possibly be assigned to the rotation of the whole molecule about its molecular axis. The $T_1$ curve below 90 K is probably due to the contribution of methyl group rotation to the relaxation rate. But we have not attempted to extract the activation energy for this mechanism because the uncertainty will be quite large from the only results at this temperature range.
References

[5.1] H.D. Springall and L.O. Brockway, J.A.C.S., 60 (1938) 996
CHAPTER VI

An NMR Study of Dimethylamine Complexed with Trimethylaluminium or Trimethylborane

A. Introduction

This chapter describes the nmr study of the addition complex of dimethylamine with trimethylaluminium and trimethylborane. Broadline nmr studies of dimethylamine have been made by Haigh et al. [6.1], who found the methyl groups reorient more rapidly than the methyl groups in trimethylamine. Khanzada [6.2] has also studied the spin-lattice relaxation time of dimethylamine and the clathrate dimethylamine hydrate, and found the activation energy for the methyl group reorientation is less than that in trimethylamine. Our purpose is to study the dimethylamine when it forms addition complexes with trimethylaluminium and trimethylborane.

B. Experimental

B.1 Preparation of the Complexes

Dimethylamine (anhydrous) was obtained from Eastman Kodak Chemicals. Trimethylaluminium and trimethylborane were purchased from Alfa Inorganics. The dimethylamine-trimethylaluminium complex was prepared [6.3] by mixing the amine and trimethylaluminium at liquid nitrogen temperature and warming the mixture slowly to room temperature. The excess amine was pumped off and the complex was purified by vacuum sublimation. The same method was used for
preparation of the dimethylamine-trimethylborane complex [6.4]. The melting points agree very well with the melting points cited in the literature [6.3, 6.4]. Samples were transferred to 7.5 - 8.0 mm.O.D. thin wall sample tubes for spin-lattice relaxation time measurement and to 10 mm. O.D. sample tubes for broadline nmr measurement.

B.2 Procedure of measurement

The method of measurement has been described in Chapter III, except that in the case of the dimethylamine-trimethylborane complex the spin-lattice relaxation times were recorded with a Bruker B-KR 300 Z15 boxcar integrator with a gate time of 0.5 μsec. The output signal from the boxcar integrator was displayed on a digital voltmeter.

C. Dimethylamine-trimethylaluminium

C.1 Experimental Line Widths and Second Moments

The experimental second moments and line widths are plotted versus temperature in Figure 6.1. The second moment has a plateau value of 9.4 ± 0.5 G² between 77 K and 235 K. Then it decreases from 7.5 G² at 250 K to a plateau value of 3.8 ± 0.5 G² at 294 K. The change of line widths versus temperature is similar to that of the second moment versus temperature.

C.2 Calculation of Second Moments and Determination of Molecular Motion

Since no molecular parameters or crystal structure is known for the dimethylamine-trimethylaluminium complex, only an estimated second moment can be obtained. The calculation of second moment has been described in Chapter IV, and for calculation of second moment in the dimethylamine-trimethylaluminium
Fig. 6.1. Line width and second moment of dimethylamine-trimethylaluminium as a function of temperature.
complex, we have taken $r(\text{N-H}) = 1.00 \text{ Å}$, $r(\text{C-N}) = 1.47 \text{ Å}$, $r(\text{C-Al}) = 2.00 \text{ Å}$ and $r(\text{N-Al}) = 1.93$, $r(\text{C-H}) = 1.10 \text{ Å}$. The bond angles are assumed to be tetrahedral. The results of the calculation are shown in Table 6.1 and are compared with the experimental second moments.

From Table 6.1, it is clear that even at liquid nitrogen temperature, dimethylamine-trimethylaluminium, like trimethylamine-trimethylaluminium, cannot be considered to be rigid. Contrary to the situation in trimethylamine-trimethylaluminium, the methyl groups attached to nitrogen in dimethylamine-trimethylaluminium are not rigid, for the observed second moment agrees quite well with the value calculated on the assumption that all methyl groups in the molecule are rotating freely. This can be explained in terms of the steric hindrance of methyl groups in the trimethylamine moiety being larger than that in the dimethylamine moiety. The decrease of second moment about 235 K is due to some additional motion and this motion could be the reorientation of the whole molecule along its N-Al bond as in trimethylamine-trimethylaluminium or the reorientation of either the dimethylamine or the trimethylaluminium moiety. The rotation of the dimethylamine moiety while the trimethylaluminium is fixed seems less probable because the dimethylamine moiety is asymmetric and also for a rotating dimethylamine moiety the theoretical second moment is much higher than the observed second moment. The observed value of the second moment is higher than the value calculated on the assumption that the whole molecule is rotating about its N-Al bond, but is less than the value calculated on the assumption that the dimethylamine moiety is fixed. Comparing the experimental and theoretical values of the second moment for all the methyl groups rotating but the
### TABLE 6.1

Calculation of Second Moments for Dimethylamine-trimethylaluminium complex and Comparison with the Experimental Values

(Second moment in $G^2$)

<table>
<thead>
<tr>
<th>Group</th>
<th>Motion</th>
<th>$\text{Me}_2\text{NH}$</th>
<th>$\text{Me}_3\text{Al}$</th>
<th>CH$_3$ to CH$_3$</th>
<th>Proton at N to CH$_3$</th>
<th>Proton to N and Al</th>
<th>Intermolecular</th>
<th>Total</th>
<th>Experimental Second Moment</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>SS</td>
<td>20</td>
<td>1.6</td>
<td>2.0</td>
<td>0.4</td>
<td>6 ± 1</td>
<td>30.0 ± 1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RS</td>
<td>RS</td>
<td>5</td>
<td>1.4</td>
<td>1.8</td>
<td>0.2</td>
<td>2.2 ± 1</td>
<td>10.6 ± 1</td>
<td>9.4 ± 0.5</td>
<td>77 - 235</td>
<td></td>
</tr>
<tr>
<td>RR</td>
<td>RR</td>
<td>0.6</td>
<td>0.2</td>
<td>0.2</td>
<td>0.0</td>
<td>1.2</td>
<td>2.2</td>
<td>3.8 ± 0.5</td>
<td>294 - 320</td>
<td></td>
</tr>
<tr>
<td>RS</td>
<td>RR</td>
<td>2.3</td>
<td>0.7</td>
<td>0.7</td>
<td>0.0</td>
<td>1.6</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RR</td>
<td>RS</td>
<td>3.2</td>
<td>0.9</td>
<td>1.0</td>
<td>0.2</td>
<td>1.7</td>
<td>7.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**SS** = stationary  

**RS** = methyl groups are rotating but the moiety is stationary  

**RR** = methyl groups and the moiety are both rotating
moieties stationary, we find that the calculated value is higher than the experimental value, although the two values agree within the uncertainties of each. The higher value for the theoretical second moment could arise from an overestimate of intermolecular contribution, neglect of vibrational motions, or incorrect assumptions concerning bond angles. The carrying over of these possible errors to the calculated second moment for the case of rotating moieties could account for at least part of the disagreement between the observed second moment of $3.8 \pm 0.5 \text{ G}^2$ between 294 and 320 K and any of the theoretically calculated values. The most probable motion above 235 K, in addition to methyl group rotation, would seem to be rotation of the trimethylaluminium moiety, while the dimethylamine moiety remains "fixed". A second moment study of $(\text{CD}_3)_2\text{NDAC(CH}_3)_3$ and $(\text{CH}_3)_2\text{NHA}\text{CD}_3)_3$ would help to clear this uncertainty.

**C.3 Spin-lattice Relaxation Times**

Figure 6.2 shows the variation of the experimental spin-lattice relaxation times with the inverse of temperature. The curve was resolved into three parts and the resolution is illustrated by the broken line in the figure. The activation energy from the resolved straight line portion in the region 290 - 315 K, in which $T_1$ decreases as the temperature increases, is $9.68 \pm 0.3 \text{ kcal/mole}$. This value agrees very well with the activation energy for the rotation of the trimethylaluminium moiety in the trimethylphosphine-trimethylaluminium complex ($9.95 \pm 0.19 \text{ kcal/mole}$). It is higher than the activation energy for rotation of the whole molecule about its N-Az bond in the trimethylamine-trimethylaluminium complex ($5.42 \pm 0.18 \text{ kcal/mole}$). The
Fig. 6.2. Spin-lattice relaxation time of dimethylamine-trimethylaluminium as a function of inverse temperature. The broken lines indicate the resolution of observed $T_1$ into more than one mechanism.
Fig. 6.3. Plot of $\omega_\tau$ versus inverse of temperature for the rotation of the methyl groups attached to nitrogen in dimethylamine-trimethylaluminium.
second moment study also shows that above 235 K, the trimethylaluminium moiety rotates with a frequency greater than the narrowed line width. The activation energy, $9.68 \pm 0.3$ kcal/mole, obtained from the high temperature part of the curve can probably be assigned to the rotation of the trimethylaluminium moiety. The $T_1$ minimum which occurs at about 132 K is due to some other kind of molecular motion. Using $(T_1)_\text{min} = 52$ msec for this second motional process and the experimental $T_1$ values between 135 and 250 K, values of $\omega_0 T_c$ were obtained from the BPP [6.5, 6.6] equation and have been shown in Figure 6.3. A least squares fit of the straight line gave

$$\ln \omega_0 T_c = (-10.88 \pm 0.1) + (2.74 \pm 0.04) \times 10^3/RT \quad (6.1)$$

Thus the activation energy found is $2.74 \pm 0.04$ kcal/mole and it can be assigned to the methyl group rotation in the dimethylamine moiety. Equation (6.1) shows that if $\omega_0 T_c$ is of the order of $10^2 - 10^3$, $T$ should be between 89 and 77 K. Therefore according to the spin-lattice relaxation study, there should be a line width or second moment transition between 77 and 89 K. However, there is no such transition observed in the line width and second moment study. This contrariness was also observed in ammonia [6.7] and some polymethyl benzenes [6.8 - 6.10] and can be explained by the postulate that there is tunnelling motion of the methyl groups at low temperature [6.11]. The slope of the resolved straight line portion in the region 77 - 108 K corresponds to an apparent activation energy of $0.89 \pm 0.10$ kcal/mole. Although the decrease in $T_1$ with
decreasing temperature below 100 K is probably primarily due to motion of the methyl groups in the trimethylaluminium moiety, the probable existence of multiple minima in $T_1$ at low temperatures due to tunnelling motion of the methyl groups in the dimethylamine moiety may also contribute to the observable $T_1$ in this region.

D. Dimethylamine-trimethylborane

D.1 Experimental Line Widths and Second Moments

Figure 6.4 is a plot of second moments and line widths versus temperature. The second moment has a plateau value of $11.7 \pm 0.5 \text{ G}^2$ between 100 and 220 K. Below 100 K the second moment increases as the temperature decreases. The second moment decreases slowly from $11.3 \text{ G}^2$ at 227 K to a value of approximately $4 \text{ G}^2$ near the melting point. The change of line widths versus temperature is similar to that of second moment versus temperature.

D.2 Calculation of Second Moments and Determination of Molecular Motion

Since no molecular structure and crystal structure is known for the dimethylamine-trimethylborane complex, the theoretical second moment can only be estimated. The calculation of second moment has been described in Chapter IV, and for calculation of second moment in the dimethylamine-trimethylborane complex, we have taken $r(\text{N-H}) = 1.00 \text{ Å}$, $r(\text{C-N}) = 1.47 \text{ Å}$, $r(\text{C-B}) = 1.56 \text{ Å}$ and $r(\text{N-B}) = 1.60 \text{ Å}$, $r(\text{C-H}) = 1.10 \text{ Å}$. The bond angles are assumed to be tetrahedral. The results of the calculations are shown in Table 6.2, and are compared with the experimental second moments.
Fig. 6.4. Line width and second moment of dimethylamine-trimethylborane versus temperature.
TABLE 6.2
Calculation of Second Moments for Dimethylamine-trimethylborane Complex and Comparison with the Experimental Values (second moment in $G^2$)

<table>
<thead>
<tr>
<th>Group</th>
<th>Motion</th>
<th>$CH_3$- $CH_3$</th>
<th>Proton at $N$ to $CH_3$</th>
<th>Proton to $N$ and $B$</th>
<th>Intermolecular</th>
<th>Total</th>
<th>Experimental Second Moment</th>
<th>Temperature ToK</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>SS</td>
<td>20</td>
<td>3.3</td>
<td>2.2</td>
<td>0.6</td>
<td>6 ± 1</td>
<td>31.9 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>RS</td>
<td>RS</td>
<td>5</td>
<td>2.9</td>
<td>1.9</td>
<td>0.2</td>
<td>2.2 ± 1</td>
<td>12.4 ± 1</td>
<td>11.7 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0</td>
<td>1.3</td>
<td>2.6</td>
<td>4.0 ± 0.5</td>
</tr>
<tr>
<td>RR</td>
<td>RR</td>
<td>.6</td>
<td>0.4</td>
<td>0.3</td>
<td>0.0</td>
<td>1.3</td>
<td>2.6</td>
<td>4.0 ± 0.5</td>
</tr>
<tr>
<td>RS</td>
<td>RR</td>
<td>2.3</td>
<td>1.4</td>
<td>1.0</td>
<td>0.0</td>
<td>1.6</td>
<td>6.3</td>
<td>6.3</td>
</tr>
<tr>
<td>RR</td>
<td>RS</td>
<td>3.2</td>
<td>1.9</td>
<td>1.3</td>
<td>0.2</td>
<td>1.7</td>
<td>8.3</td>
<td>-</td>
</tr>
</tbody>
</table>

SS = stationary
RS = methyl groups are rotating but the moiety is stationary
RR = methyl groups and the moiety are both rotating
Table 6.2 shows that the experimental second moments between 100 and 220 K correspond to the rotation of all methyl groups in the dimethylamine-trimethylborane complex. The increase of second moments below 100 K is due to less mobility of the methyl groups. The rigid lattice second moment is not reached at temperatures down to 77 K. The decrease of second moment above 220 K is due to some additional motion in the molecule and this motion could be the rotation of the whole molecule along its N-B bond, or the rotation of either the dimethylamine moiety or the trimethylborane moiety. The rotation of the dimethylamine moiety while the trimethylborane moiety is fixed seems less probable, because the estimated second moment for this condition is much higher than the observed value, 4 G². The second moment near the melting point is higher than the estimated value for the whole molecule rotating about the N-B bond, but is less than the estimated value for the trimethylborane moiety rotating while the dimethylamine moiety is fixed. Like the dimethylamine-trimethylaluminium complex, the additional motion may be due to the reorientation of trimethylborane moiety. A second moment study on (CD₃)₂ND-B(CH₃)₃ and (CH₃)₂NH-B(CD₃)₃ would help to clear this argument.

D.3 Spin-lattice Relaxation Times

Figure 6.5 is a plot of the experimental spin-lattice relaxation times versus inverse of temperature. The T₁ minimum is broad, and the apparent activation energies obtained from the low and high temperature parts of the curve are 2.04 ± 0.07 kcal/mole and 2.68 ± 0.04 kcal/mole respectively. It is obvious that the motion cannot be described with a unique correlation
Fig. 6.5. Spin-lattice relaxation time of dimethylamine-trimethylborane versus inverse of temperature. The broken curve between 95 and 180 K shows the calculated $T_1$ curve as discussed in detail in the text. The broken lines at high temperature part show the resolution of $T_1$ into two mechanisms.
time. The broadening in the $T_1$ minimum may arise from two types of independent motions, which in our case are the rotations of methyl groups attached on the one hand to nitrogen and on the other to boron, at the same temperature but proceeding at different rates and each contributing towards the efficiency of the spin-lattice relaxation. An attempt was made to fit the $T_1$ curve by assuming there are two types of motion, each characterized by a correlation time, and that the ratio of the $T_1$ minima of the two motions is about 2:3. Reasonable values of activation energies, $T_1$ minima, and temperatures at which the $T_1$ minima occur for each of the two motional processes were put into a computer programme (Appendix C) which calculated $T_1$ values from these adjustable parameters and compared them with experimental $T_1$ values. The calculated values agree very well with the experimental $T_1$ values in both the low and the high temperature parts but deviate quite significantly in the region where the broad $T_1$ minimum occurs if we assume the activation energy for the reorientation of methyl groups attached to boron is 2.04 kcal/mole, that $(T_1)_{\text{min}} = 34$ msec at 110 K, that the activation energy for reorientation of methyl groups attached to nitrogen is 2.689 kcal/mole, and that $(T_1)_{\text{min}} = 50$ msec at 142 K. The broken line in Figure 6.5 shows the calculated values in the region where the broad $T_1$ minimum occurs. Another possibility may account for the presence of more than one correlation time in dimethylamine-trimethylborane. A distribution of correlation times may exist if, for a single type of motion which produces relaxation, there is a distribution of environments within the sample. The only known distribution function that describes an asymmetric $\ln T_1$ curve is
the Cole-Davidson distribution function [6.12, 6.13]. However, the minimum in $T_1$ calculated from the Cole-Davidson distribution is not as broad as the experimental minimum obtained here. As a result of the failure to obtain a completely satisfactory fit of experimental and calculated values by either two discrete relaxation processes or a Cole-Davidson distribution, activation energies obtained from the low and high temperature sides cannot be assigned without any ambiguity.

The activation energy obtained from the resolved $T_1$, where $T_1$ decreases with increase of temperature, in the temperature region of 280 - 308 K, is $14.03 \pm 1.51$ kcal/mole. This activation energy may be assigned to the reorientation of the trimethylborane moiety.
References


[6.3] N. Davidson and H.C. Brown, J.A.C.S., 64 (1942) 316


CHAPTER VII
Spin-lattice Relaxation Study of Trimethylamine-Boron Trihalides Complexes

A. Introduction

This chapter describes the study of proton spin-lattice relaxation times for trimethylamine-boron trichloride and trimethylamine-boron tribromide. The wide-line nuclear magnetic resonance study of molecular motion in complexes of trimethylamine with boron trihalides [7.1, 7.2] and borane [7.1] has already been made. These earlier investigators attributed line width and second moment transitions to methyl group reorientation in the temperature range below 110 K, followed by rotation of trimethylamine group about the B-N axis at higher temperatures. The temperature dependence of the $^{35}$Cl NQR spectrum in the trimethylamine-boron trichloride complex has also been studied [7.3]. We have not chosen trimethylamine-boron trifluoride in our study since the proton and fluorine resonance frequencies are very close and this fact will complicate the interpretation of the results [7.4].

B. Experimental

B.1 Materials and Preparation

Anhydrous trimethylamine was obtained from Eastman Kodak Chemicals. Boron trichloride was purchased from Matheson and boron tribromide was purchased from Alfa Inorganics. Complexes were prepared according to the methods described in the literature [7.5, 7.6]. Trimethylamine-boron trichloride complex was recrystallized three times from absolute alcohol. Trimethylamine-boron tribromide complex was recrystallized from benzene. Table 7 shows the
result of a combustion analysis for H, C, and N.

TABLE 7.1
Results of Combustion Analysis on Trimethylamine-boron trihalides Complexes

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$NBCl$_3$</td>
<td>20.44</td>
<td>20.48</td>
<td>5.15</td>
<td>5.09</td>
<td>7.94</td>
<td>8.07</td>
</tr>
<tr>
<td>Me$_3$NBBr$_3$</td>
<td>11.62</td>
<td>11.46</td>
<td>2.9</td>
<td>3.11</td>
<td>4.52</td>
<td>4.63</td>
</tr>
</tbody>
</table>

Samples were sealed in 7.5 - 8.0 mm O.D. thin wall tubes under vacuum.

B.2 Procedure

The method of measurement has been described in Chapter III. Values of $T_1$ were measured by a 180 - τ - 90° pulse sequence. The standard deviation of the slope of the straight line which $T_1$ is obtained is less than 5%.

C. Results and Discussion

C.1 Trimethylamine-boron tribromide Complex

Figure 7.1 shows a plot of proton $T_1$ values for trimethylamine-boron tribromide complex versus inverse of temperature. It exhibits two minima in the $T_1$ curve. The $T_1$ minimum at high temperature is sharp whereas the $T_1$ minimum at low temperature is very broad. No study was made beyond 450 K since we did not want to risk injury to the probe head.
Fig. 7.1. Spin-lattice relaxation time of trimethylamine boron tribromide complex as a function of inverse temperature. The broken lines show the resolution of observed $T_1$ into more than one mechanism as discussed in detail in the text.
The broad minimum in $T_1$ indicates the relaxation process cannot be described with only a single correlation time. The activation energy obtained from the slope of the low temperature part of the curve is $2.86 \pm 0.08$ kcal/mole, while the activation energy obtained from the slope of the high temperature part is $3.23 \pm 0.07$ kcal/mole. An attempt was made to fit the experimental $T_1$ data using a Cole-Davidson [7.7, 7.8] distribution function with the width of the distribution given by $\delta = 2.86/3.23$. The calculated values agreed very well on both sides of the $T_1$ minimum. However, the calculated $(T_1)_\text{min}$ was much lower than the experimental $(T_1)_\text{min}$ and the minimum in the calculated curve was not as broad as the experimental minimum. Within 10% error we get a very good fit with the experimental $T_1$ data, if we assume there are two correlation times, each having an Arrhenius temperature and activation energy dependence, and if the relaxation rate can be described by the BPP [7.9, 7.10] equation. The resolution of the experimental $T_1$ curve is shown by the two dotted BPP curves, one with $(T_1)_\text{min} = 60$ ms at about 162 K and with an activation energy of 2.86 kcal/mole, and the other with $(T_1)_\text{min} = 55$ ms at about 198 K and with an activation energy of 3.24 kcal/mole. The line width and second moment [7.1] study suggests that in this temperature range the probable mechanisms for spin-lattice relaxation is the reorientation of methyl groups. A simple picture to explain the results is to assume there are two types of crystallographic site for the trimethylamine-boron tribromide complexes. The methyl groups in each crystallographic site experience a different environment. Therefore there exist two correlation times and different activation energies for the methyl group reorientation. However, other explanations for the existence of two
relaxation mechanisms might possibly be found. The line width and second moment [7.1] study shows that the whole molecule is rotating at a frequency of the order of line width at about 260 K. The high temperature minimum in $T_1$ can therefore be attributed to the reorientation of the whole molecule about its B-N bond. The $T_1$ in the region of 300 - 400 K is affected by the reorientation of methyl groups as well as the reorientation of the whole molecule about its B-N bond. The resolution of the two contributions is shown in the Figure 7.1. The resolved $T_1$ for the reorientation of the whole molecule along its N-B bond can be characterized by a motion with a single correlation time

$$\tau_c = (4.24 \pm 0.49) \times 10^{-16} \exp (12.80 \pm 0.55) \times 10^3/RT$$

Thus the activation energy for the reorientation of the whole molecule along its N-B bond is 12.80 ± 0.55 kcal/mole. The activation energies found for methyl groups reorientation and the reorientation of the whole molecule about its N-B bond by our pulsed nmr study are both higher than the activation energies found from line width measurement [7.1]. Their values are 1.7 - 2.0 kcal/mole for methyl groups reorientation and 9.1 kcal/mole for the rotation of the whole molecule about the N-B bond.

**C.2 Trimethylamine-boron trichloride**

The temperature dependence of proton $T_1$ for trimethylamine-boron trichloride complex is shown in Figure 7.2. The $T_1$ minimum at low temperature is slightly broad, but it is not as broad as the minimum in the trimethylamine-boron tribromide complex. There is a sudden change in $T_1$ at 390 K and we
Fig. 7.2. Spin-lattice relaxation time of trimethylamine boron trichloride complex as a function of inverse temperature. The broken lines at about 300 K show the resolution of observed $T_1$ into two mechanisms.
attribute this to a phase transition. This phase transition is confirmed by our DSC study. Figure 7.3 is the DSC curve for trimethylamine-boron trichloride complex. Below 380 K, normal FID signals were observed for the trimethylamine-boron trichloride complex, but at higher temperatures there is a relatively strong high frequency noise superimposed on the FID signal. This phenomenon persisted and did not disappear at 430 K, the highest temperature of measurement. The high temperature phase may be piezoelectric [7.11] in nature and the noise generated by the rf pulse on the sample. This phenomenon was also observed in tetramethylammonium chloride [7.11]. There was no such phase transition observed in the line width and second moment measurement. Probably the molecular motions are the same in both phases and the correlation frequencies of the motions are higher than the line widths expressed in frequency.

The analysis of the $T_1$ data is straightforward. We attribute the $T_1$ minimum at low temperature to the methyl group reorientation. The solid curve is the fitted BPP curve with a single correlation time:

$$\tau_C = (1.35 \pm 0.16) \times 10^{-12} \exp (2.79 \pm 0.04) \times 10^3/RT$$

Thus the activation energy for methyl group reorientation was found to be $2.79 \pm 0.04$ kcal/mole.

Since both nmr [7.1] and nqr [7.3] studies have shown the reorientation of both amine and boron trichloride moieties, we assign the $T_1$ minimum which occurs at about 350 K to the reorientation of the whole molecule about its N-B bond. In the region of 290 - 340 K, the spin-lattice relaxation rate, $T_1^{-1}$,
Fig. 7.3. DSC curve of trimethylamine-boron trichloride.
is the sum of two relaxation rates, namely the spin-lattice relaxation rate due to the methyl group rotation and the spin-lattice relaxation rate due to the rotation of the whole molecule about its N-B bond. The two contributions to the experimental $T_1$ were resolved and are shown in Figure 7.2 by dotted lines. The resolved $T_1$ for the reorientation of the whole molecule about its N-B bond can be characterized by a single correlation time

$$\tau_c = (9.45 \pm 0.5) \times 10^{-18} \exp (13.79 \pm 0.91) \times 10^3/RT$$

The activation energy for the reorientation of the whole molecule about its N-B bond was therefore found to be $13.79 \pm 0.91$ kcal/mole. The activation energies obtained from the $T_1$ study for methyl group reorientation and the reorientation of the whole molecule about its N-B bond are higher than those obtained from line width measurement (1.6 - 1.9 kcal/mole and 9.3 kcal/mole [7.1]). The activation energy obtained from the $T_1$ points above 390 K is $3.72 \pm 0.39$ kcal/mole. This activation energy is not assigned and is possibly only an apparent value arising from more than one mechanism.
References


Additional Note

After the completion of this thesis, a report on crystal and molecular structures of three trimethylamine-boron halide adducts: Me₃NBCl₃, Me₃NBBBr₃ and Me₃NBI₃ which appeared in J. of Cryst. and Mol. Structure, 1 (1971) 363, came to our attention. In Me₃NBBBr₃ there is slight distortion from C₃ symmetry in the trimethylamine moiety. This might account for the two values of activation energy for the methyl group reorientations.
CHAPTER VII

Spin-lattice Relaxation Study of Trimethylamine-
halogens Complexes

A. Introduction

There has been considerable interest recently in the structure and
bonding in addition complexes in which trimethylamine acts as the electron
donor and halogen acts as an electron acceptor. X-ray measurement on tri-
methylamine-iodine and trimethylamine-iodine chloride [8.1, 8.2] have shown
that the nitrogen-halogen-halogen linkage is linear and the nitrogen-halogen
and halogen-halogen bond lengths are longer than their 'normal' covalent
bonds. Fyfe and Ripmeester [8.3] have measured the proton nmr line width
and second moment for these complexes. It is our purpose to study the spin-
lattice relaxation times of these compounds at various temperatures and to
extract the activation energies and rate parameters for the motions in the
solid state.

B. Experimental

Anhydrous trimethylamine was obtained from Eastman Kodak Chemicals,
iodine chloride from BDH, and bromine from Alfa Inorganics. The iodine used
was reagent grade. Complexes were prepared according to the method described
in the literature [8.1, 8.2]. Table 8.1 shows the results of the combustion
analysis for C, H, and N.
TABLE 8.1
Results of Combustion Analysis on Trimethylamine-halogen complexes

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>C</th>
<th></th>
<th>H</th>
<th></th>
<th>N</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
</tr>
<tr>
<td>(CH₃)₃N-I₂</td>
<td>11.52</td>
<td>11.20</td>
<td>2.90</td>
<td>2.76</td>
<td>4.48</td>
<td>4.32</td>
</tr>
<tr>
<td>(CH₃)₃N-ICₓ</td>
<td>16.27</td>
<td>16.16</td>
<td>4.10</td>
<td>4.17</td>
<td>6.32</td>
<td>6.29</td>
</tr>
<tr>
<td>(CH₃)₃N-Br₂</td>
<td>16.45</td>
<td>16.32</td>
<td>4.15</td>
<td>4.13</td>
<td>6.45</td>
<td>6.60</td>
</tr>
</tbody>
</table>

All samples were sealed in 7.5 - 8.0 mm O.D. thin wall tubes under vacuum and stored in liquid nitrogen in the dark when not in use. Spin-lattice relaxation times were measured by a π - π/2 pulse sequence and the procedure described in Chapter III.

C. Results and Discussion

C.1 Trimethylamine-iodine Complex

The experimental values of the proton T₁ for the trimethylamine-iodine complex are plotted versus inverse of temperature in Figure 8.1. The solid line has been calculated using the modified BPP equation [8.4, 8.5] and the relation

\[ \tau_c = (2.13 \pm 0.06) \times 10^{-12} \exp (3.57 \pm 0.11) \times 10^3/RT, \]

which was in turn obtained from the experimental points, \( (T_1)_{min} = 30 \, ms \) and the BPP equation. From the second moment and line width study [8.3]
Fig. 8.1. Spin-lattice relaxation times of trimethylamine-iodine complex as a function of inverse temperature.
Fig. 8.2. Spin-lattice relaxation times of trimethylamine-iodine chloride complex as a function of inverse temperature.
Fig. 8.3. Spin-lattice relaxation times of trimethylamine-bromine complex as a function of inverse temperature.
the relaxation mechanism can probably be assigned to methyl group reorientation. The activation energy, $3.57 \pm 0.11$ kcal/mole, obtained from our measurement is lower than the value obtained by Fyfe and Ripmeester [8.3]. They obtained $6.9 \pm 0.4$ kcal/mole from line width measurement.

C.2 Trimethylamine-iodine chloride Complex

The temperature dependence of proton $T_1$ for trimethylamine-iodine chloride complex is shown in Figure 8.2. The solid line is the fitted BPP curve with

$$\tau_c = (1.64 \pm 0.07) \times 10^{-12} \exp(4.25 \pm 0.17) \times 10^3/RT$$

From second moment and line width study, the relaxation mechanism can probably be assigned to methyl group reorientation. The activation energy obtained is $4.25 \pm 0.17$ kcal/mole. This value is again lower than the value, $6.2 \pm 0.5$ kcal/mole, obtained from line width measurement [8.3].

C.3 Trimethylamine-bromine Complex

The temperature dependence of proton $T_1$ for trimethylamine-bromine complex is shown in Figure 8.3. The solid line is the fitted BPP curve with

$$\tau_c = (4.38 \pm 0.07) \times 10^{-13} \exp(4.31 \pm 0.08) \times 10^3/RT$$

Second moment and line width study had shown that the reorientation of methyl groups as well as the reorientation of the trimethylamine moiety occur simultaneously. The relaxation mechanism in the temperature region studied can probably be assigned to the reorientation of both methyl groups and the trimethylamine moiety. In fact we cannot distinguish the rotation of the trimethylamine moiety or the rotation of the whole molecule along the molecular axis. The activation energy, $4.31 \pm 0.08$ kcal/mole, obtained from our pulsed
nmr study is lower than the value, 6.8 ± 0.5 kcal/mole, obtained from line width measurement.

D. **Summary**

Values of activation energy for methyl group reorientation were obtained by a pulsed nmr technique for trimethylamine-halogen complexes. They are systematically lower than the values obtained from line width measurement. The difference is particularly large for the iodine complex. This is probably because in the line width study of the iodine complex, the two regions of motional narrowing overlap more than for the bromine and iodine chloride complexes.
References

A. Conclusion of the Present Work

The activation energies and rate parameters for various types of motion for the compounds studied have been summarized in Table 9.1. Table 9.2 shows the values of the calculated and experimental $T_1$ minima for methyl group reorientation. In all cases, the experimental $T_1$ minimum for methyl group reorientation is higher than the predicted value even though we neglected the contribution for intermethyl group contributions and intermolecular interactions. Look and Lowe [9.1] and Blinc [9.2] have considered the effect of hindered molecular rotation between unequal potential wells for two spin systems upon nmr spin-lattice relaxation times. They showed that spin-lattice relaxation rate due to such hindered rotation is affected by any difference in the depths of the potential wells of the order of $kT$ (about 0.1 to 0.6 kcal/mole at 50 K to 300 K) and for such a case the spin-lattice relaxation rate should be multiplied by a factor of $\frac{4a}{(1+a)^2}$ where $a = \exp \left( \frac{E_\beta - E_\alpha}{kT} \right)$. Here $E_\beta - E_\alpha$ is the difference in depth of the unequal potential wells and is at the order of $kT$. It was thus shown that the effect of having $E_\beta \neq E_\alpha$ is a lengthening of spin-lattice relaxation time. The theory has been applied in an analysis of the spin-lattice relaxation
### TABLE 9.1

Activation energies (in kcal/mole) and rate parameters for various motions in addition complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Me₂⁺-Me₃</td>
<td>1.63</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
<td>1.70</td>
<td>1.90</td>
<td>1.60</td>
<td>1.80</td>
<td>1.30</td>
<td>1.40</td>
</tr>
</tbody>
</table>

1 cc = Calc. 1 cc
TABLE 9.2
Values of $T_1$ minimum for methyl group reorientation

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Methyl Group Attached to</th>
<th>$(T_1)_{min,\text{expt.}}$</th>
<th>$(T_1)_{min,\text{calc.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me}_3\text{N-BMe}_3$</td>
<td>Boron</td>
<td>36 ms</td>
<td>35.6 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{N-A&amp;Me}_3$</td>
<td>Nitrogen</td>
<td>36 ms</td>
<td>35.6 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{P-A&amp;Me}_3$</td>
<td>Phosphorus</td>
<td>50 ms</td>
<td>35.6 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{P-BMe}_3$</td>
<td>Phosphorus</td>
<td>50 ms</td>
<td>35.6 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{P-BMe}_3$</td>
<td>Boron</td>
<td>52 ms</td>
<td>35.6 ms</td>
</tr>
<tr>
<td>$\text{Me}_2\text{NH-A&amp;Me}_3$</td>
<td>Nitrogen</td>
<td>52 ms</td>
<td>47.5 ms</td>
</tr>
<tr>
<td>$\text{Me}_2\text{NH-BMe}_3$</td>
<td>Nitrogen</td>
<td>50 ms</td>
<td>47.5 ms</td>
</tr>
<tr>
<td>$\text{Me}_2\text{NH-BMe}_3$</td>
<td>Boron</td>
<td>34 ms</td>
<td>31.7 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{P}$</td>
<td>Phosphorus</td>
<td>26 ms</td>
<td>17.8 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{B}$</td>
<td>Boron</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$\text{Me}_3\text{N-BCl}_3$</td>
<td>Nitrogen</td>
<td>28 ms</td>
<td>17.8 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{N-BBr}_3$</td>
<td>Nitrogen</td>
<td>55 - 60 ms</td>
<td>17.8 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{N-I}_2$</td>
<td>Nitrogen</td>
<td>29 ms</td>
<td>17.8 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{N-ICl}_2$</td>
<td>Nitrogen</td>
<td>27 ms</td>
<td>17.8 ms</td>
</tr>
<tr>
<td>$\text{Me}_3\text{N-Br}_2$</td>
<td>Nitrogen</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
in the low temperature phase of solid hydrogen sulfide \([9.3]\).

Although the effect of hindered molecular rotation between unequal potential wells upon nmr spin-lattice relaxation times has not been worked out for a three spin system, the same effect, i.e. the lengthening of spin-lattice relaxation time, is expected.

A difference in potential wells for groups which undergo reorientation can arise if various positions of the group are non equivalent with respect to lattice symmetry. It is conceivable that in some cases the energies might differ by \(kT\) or more. This difference in energy barriers is small compared to the observed values of activation energy for methyl group reorientation and is not detected by spin-lattice relaxation study.

A number of expressions have been proposed for the pre-exponential factor \(\tau_c^0\) of the Arrhenius equation \(\tau_c = \tau_c^0 \exp (E_a/RT)\), the best known being that of Erying \([9.4]\). Recently, there has been renewed interest \([9.5, 9.6]\) in Bauer's \([9.7]\) purely classical treatment. A third approach expresses the pre-exponential factor in terms of frequency of libration of the molecule in its potential well \([9.8]\). Brot \([9.9]\) has demonstrated that the three approaches are, in the classical limit, strictly equivalent. We therefore calculate the \(\tau_c^0\) using the third approach. The librational frequency of the molecule in its potential well can be calculated \([9.10]\) by

\[
\nu_{\text{lib}} = \frac{3}{2\pi} \sqrt{\frac{\nu}{2I}}
\]
for a molecule or group which has a $C_3$ symmetry. Here $V$ is the depth of potential well and $I$ is the moment of inertia of the rotor. The correlation time for reorientation of the group should be given by $\tau_0 = 1/2\nu_1$. The calculated values are within one or two orders of magnitude of the experimental values for the reorientation of methyl groups and are always smaller, as one should expect, than the experimental values. For the reorientation of a moiety or a molecule about the central bond, however, the difference is, in some cases, very large, and the calculated value is often larger than the experimental value. This large deviation in an improbable direction may be due to lattice expansion and thus to temperature dependence of the activation energies [9.11]. A qualitative conclusion can be made that the activation energy for methyl group reorientation depends to a first approximation on the central atom to which the three methyl groups are attached. The longer the carbon-central atom bond is the lower the activation energy is. Thus the activation energies for the three methyl groups attached to various central atoms are in the order $N > C > B > Si > Al$ [9.12, 9.13, 9.14].

We may now turn to the activation energies of methyl groups in trimethylamine complexes. The activation energies for methyl group reorientation in the trimethylamine complexes follow the trend of stability of the complexes,* i.e. the activation energy decreases when the stability of the complex increases, if we assume that the intermolecular interactions for the methyl group reorientation

---

*Me$_3$N-Br$_2$, Me$_3$N-ICl decompose at about 25°C, $K_p = 0.47$ for Me$_3$N-BMe$_3$ at 100°C, Me$_3$N-I$_2$ decomposes at 66°C, $K_p$ for Me$_3$N-AlMe$_3$ is too small to measure at 150°C and Me$_3$NBCl$_3$, Me$_3$N-BBr$_3$ are stable at 240°C [9.21 - 9.23].
are small and have the same order. This trend is not surprising since the activation energy for methyl group reorientation in a trimethylamine moiety is affected predominantly by the CNC bond angle and C-N bond length. As the nitrogen forms a new $\sigma$ bond, the CNC bond angle will expand and the C-N bond will lengthen [9.15].

**B. Suggestion for Further Work**

The previous chapters have shown the results of spin-lattice relaxation time and second moment studies on some addition complexes of main group III and V elements between 77K and their melting points. The results can be explained quite satisfactorily in terms of various types of molecular motion in the solid state, and the activation energies and rate parameters of the molecular motions were extracted. However, there are some results which are uncertain, especially the activation energy of the diffusion process in some compounds. The spin-lattice relaxation times cannot be resolved without unambiguity immediately below the melting point because the frequency of the diffusion process is not high enough to give an overwhelming relaxation mechanism below the melting point. The activation energy for the diffusion process in trimethylphosphine-trimethylborane is abnormally low in comparison to that in hexamethyldisilane, hexamethylethane, or trimethylamine-trimethylaluminium, for all of which the molecular structures are very similar. To determine the activation energy accurately for diffusion process, a study of relaxation times in the rotating frame, $T_1^p$, is necessary. This technique
enables one to study the low frequency molecular motions [9.16, 9.17], and to exclude other high frequency molecular motions. Another technique, which is available in our laboratory, is to study the diffusion constant by the pulsed-gradient, spin-echo method [9.18 - 9.20].

More information on the nature of methyl group reorientation can be obtained for those attached to boron, phosphorus and aluminium if the study is pursued down to liquid helium temperature, where the tunnelling effect may become important.

Very little nmr study has been done in the solid state on the addition complexes of group III and group V, or group III and group VI elements. A detailed study of these complexes would lead to the activation energies and rate parameters for methyl groups attached to a wide range of central atoms, as well as to activation energies and rate parameters rotation about the bond formed by groups III and V, and by groups III and VI elements in the solid state.
References


[9.14] Present Studies


J.E. Tanner, J. Chem. Phys. 56 (1972) 3850


APPENDIX A

$COMPILE
DIMENSION X(30), Y(30), MZ(30), JT(30), F(30), RMZ(30)

READ(5, 20) M, N, TEMP, SCALE

WRITE(6, 43) TEMP

FORMAT(/41, 2X, F7.1, 'K')

RM0 = M0
RMZ = 2 * RM0
READ, (JT(I), I = 1, N)
WRITE(6, 40) (JT(I), I = 1, N)

FORMAT(2515)
READ, (MZ(I), I = 1, N)
WRITE(6, 41) (MZ(I), I = 1, N)

DO 30 I = 1, N
X(I) = JT(I)
RMZ(I) = MZ(I)
F(I) = (RM0 - RMZ(I)) / RM2
Y(I) = ALOG(F(I))

CONTINUE
WRITE(6, 42) (F(I), I = 1, N)

FORMAT(25F5.3)
SUMX = 0.
SUMY = 0.
DO 20 I = 1, N
SUMX = SUMX + X(I)
SUMY = SUMY + Y(I)
CONTINUE

AV = SUMX / N
AY = SUMY / N

DIFAY = 0.
DIFXAY = 0.
DO 300 I = 1, N
DIFXY = DIFXY + (X(I) - AV) * Y(I)
DIFX0 = DIFX0 + (X(I) - AV) ** 2
C = DIFXY / DIFX0
BD = YAV - C * XAV
DSG = 0.
YS = 0.
DO 301 I = 1, N
DSG = DSG + (RR + C * X(I) - Y(I)) ** 2
XSQ = XSQ + (X(I) ** 2
C = SQRT(DSG / (AM - P.))
DEL = AM * XSQ - (AM * XAV) ** 2
C = SQRT(C / SQRT(DEL))
STDPC = C * SQRT(XSQ)
STDPI = C * SQRT(XSQ)
ERR = -STDDEC/C*100.
T1 = -1./C
WRITE(6,50) T1, SCALE
FORMAT(/,2X,' T1 = ',F10.4,' IN ',A4)
WRITE(6,51) ERR
FORMAT(2X,'ERROR IN SLOPE IS ',F9.4)
GO TO 405
END
$DATA
APPENDIX B

1  SCOMPIL
2  C EXPERIMENTAL SECOND MOMENTS
3  DIMENSION I(52),A(2),B(2),S(2)
4  WRITE(C,27)
5  27 FORMAT(1X,'TRACE',2X,'TEMP',4X,'S(1),3X,'S(2),4X,'SECOND MOMENT','
6  1,4X,'LINE WIDTH',5X,'SCAN',5X,'MODULATION')
7  READ(5,20) K,L,J,X,Y,KTFNP,DELTA!,C(1),I=1,52)
8  20 FORMAT(A4,2F4.3,F7.3,15,FG.7/2613/2613)
9  ALINE=2.*X*DELTA!
10  DO 1 l=1,2
11  A(l)=0.
12  1  E(l)=0.
13  DO 21 I=1,L
14  A(l)=A(l)+FLOAT(I*I*I*:N(I))
15  21 E(l)+FLOAT(I*N(I))
16  CONTINUE
17  DO 22 I=1,2
18  A(2)=A(2)+ FLOAT(I*I*I*:N(1+2E))
19  22 E(2)=E(2)+ FLOAT(I*N(I+2E))
20  CONTINUE
21  DO 24 M=1,2
22  S(M)= 0.333*X*X*A(H)/B(H)-0.25*Y*Y
23  CONTINUE
24  SM=0.5*(S(1)+ S(2))
25  WRITE(5,28)K,KTEMP,S(1),S(2),SM,ALINE,X,Y
26  28 FORMAT(X,A5,16,1X,2F7.2,5X,F7.2,5X,F11.2,5X,F7.3,5X,F8.3)
27  DO TO 19
28  END
29  $DATA
30  $STOP