A STUDY OF INTRA- AND INTERAGGREGATE EXCHANGE PROCESSES OF ALKYLITHIUM COMPOUNDS USING ONE- AND TWO-DIMENSIONAL NMR SPECTROSCOPY

DISSERTATION

Presented to the Graduate Council of the University of North Texas in Partial Fulfillment of the Requirements For the Degree of

DOCTOR OF PHILOSOPHY

By

Daniel K. Pannell, B.S., M.S.
Denton, Texas
May, 1992
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One- and two-dimensional NMR spectroscopy, including \(^{13}\text{C}(^{6}\text{Li})^{1}\text{H}\) triple resonance techniques, were used to characterize a series of mixed alkyllithium aggregates and to study their exchange processes. Four systems were investigated: lithium tert-butoxide/tert-butyllithium, \(n\)-alkyllithium/tert-butyllithium, \(n\)-propyllithium/\(n\)-butyllithium, and racemic 2-methylbutyllithium.

Mixed lithium tert-butoxide/tert-butyllithium hexamers undergo a newly identified limited fluxionality which is much faster than random fluxionality. This limited fluxionality is an intraaggregate exchange, whereby groups which are opposite each other remain opposite while migrating over the entire hexamer. Hexamers of tert-butyllithium with either \(n\)-propyllithium or \(n\)-butyllithium undergo this limited fluxionality, as do hexamers of 2-methylbutyllithium. This process is thus proposed as a general process for alkyllithium hexamers.

\(^{6}\text{Li}\) two-dimensional exchange NMR spectroscopy was developed and used to study the intraaggregate exchange
processes of mixed tetramers. The resulting activation parameters from this study were as follows: $\Delta H^* = 17.9 \pm 1.5 \text{ kcal/mol}$ and $\Delta S^* = 14.4 \pm 6.4 \text{ eu}$ for $(n$-propyl$)(\text{tert}$-butyl)$, Li_4$, $\Delta H^* = 17.5 \pm 1.0 \text{ kcal/mol}$ and $\Delta S^* = 13.3 \pm 3.0 \text{ eu}$ for $(n$-butyl$)(\text{tert}$-butyl)$, Li_4$, and $\Delta H^* = 13.7 \pm 1 \text{ kcal/mol}$ and $\Delta S^* = -4.7 \pm 3.6 \text{ eu}$ for $(\text{tert}$-butoxide$)(\text{tert}$-butyl)$, Li_4$. These activation parameters are compared with previously determined values and mechanistic possibilities are examined.

Interaggregate exchange processes in the $n$-propyllithium/tert-butyllithium and the $n$-butyllithium/tert-butyllithium mixtures are examined qualitatively. Random fluxionality proceeds at approximately the same rate as interaggregate exchange for the hexamers in these systems.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vii</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylithium Compounds</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylithium Compounds and NMR</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Exchange Processes of Alkylithium Compounds</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>II. TWO-DIMENSIONAL EXCHANGE SPECTROSCOPY</td>
<td>23</td>
</tr>
<tr>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>III. LITHIUM tert-BUTOXIDE/tert-BUTYLLITHIUM MIXED HEXAMERS</td>
<td>70</td>
</tr>
<tr>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>IV. tert-BUTYLLITHIUM/n-ALKYLLITHIUM MIXED AGGREGATES</td>
<td>127</td>
</tr>
<tr>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td></td>
</tr>
<tr>
<td>V. n-PROPYLLITHIUM/n-BUTYLLITHIUM MIXED HEXAMERS AND RACEMIC 2-METHYLBUTYLLITHIUM MIXED HEXAMERS</td>
<td>225</td>
</tr>
<tr>
<td>Introduction</td>
<td></td>
</tr>
<tr>
<td>Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td></td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NMR Properties of Selected Nuclei</td>
<td>6</td>
</tr>
<tr>
<td>2. Rates of Fluxionality for (tert-Butyl),(tert-Butoxide)Li, using Absolute Value Spectra</td>
<td>43</td>
</tr>
<tr>
<td>3. Phase Cycling for Pure Absorption Spectroscopy</td>
<td>46</td>
</tr>
<tr>
<td>4. Fluxional Exchange Rates (tert-Butyl),(tert-Butoxide)Li, using Pure Absorption 2DEXSY</td>
<td>50</td>
</tr>
<tr>
<td>5. Data from $^{13}$C NMR Spectra in Figure 14</td>
<td>83</td>
</tr>
<tr>
<td>6. $^1$H, $^{13}$C, &amp; $^6$Li NMR Equivalencies Theoretical and Observed for the 5:1 Hexamer</td>
<td>97</td>
</tr>
<tr>
<td>7. $^1$H, $^{13}$C, &amp; $^6$Li NMR Equivalencies Theoretical and Observed for the Ortho/Meta Hexamer</td>
<td>103</td>
</tr>
<tr>
<td>8. $^1$H, $^{13}$C, &amp; $^6$Li NMR Equivalencies Theoretical and Observed for the Para Hexamer</td>
<td>104</td>
</tr>
<tr>
<td>9. Exchange Rates of the tert-Butyl Methyl Carbons of the Ortho/Meta Hexamer with the tert-Butyl Methyl Carbons of the Para Hexamer</td>
<td>113</td>
</tr>
<tr>
<td>10. Exchange Rates of the Two Types of tert-Butoxides in the 5:1 Hexamer</td>
<td>114</td>
</tr>
<tr>
<td>11. Coupling Constants and Chemical Shifts of the α-Carbons of the Alkyl groups of the n-Propyllithium/tert-Butyllithium Mixed Hexamers</td>
<td>150</td>
</tr>
<tr>
<td>12. $^6$Li Correlation and Intensity of the Unidentified α-Carbons which Showed a $^6$Li Correlation</td>
<td>156</td>
</tr>
</tbody>
</table>
13. Summary of the Assignments of the α-Carbons of the n-Propyllithium/tert-Butyllithium Mixture ...................... 179

14. Coupling Constants and Chemical Shifts of the α-Carbons of the Alkyl groups in the n-Butyllithium/tert-Butyllithium Mixture ......................... 186

15. $^{13}$C-$^6$Li Correlations in the n-Butyllithium/tert-Butyllithium Mixtures .................. 188

16. Summary of the Assignments of the α-Carbons of the n-Butyllithium/tert-Butyllithium Mixture ......................... 197

17. Rates of Fluxionality of the (n-Propyl) (tert-Butyl)$_3$Li$_4$ Tetramer .......................... 199

18. Rates of Fluxionality for the (n-Butyl) (tert-Butyl)$_3$Li$_4$ Tetramer ......................... 200

19. Activation Parameters for the Fluxionality of Alkyllithium Tetramers ...................... 203

20. Normalized Peak Intensities of Low Temperature $^6$Li Spectrum of 2-Methylbutyllithium ... 234


22. $^{13}$C Shifts of 2-Methylbutyllithium According to Reference 10 .............................. 238

23. $^{13}$C Shifts, Intensities, and $^6$Li Correlations of the α-Carbon Region of 2-Methylbutyllithium .......................... 243
LIST OF ILLUSTRATIONS

Figure                                                                 | Page
1. Alkyllithium Aggregates                                              | 4
2. $^1$C Spectra of the $\alpha$-Carbon of tert-Butyllithium           | 11
3. Tetramer Fluxional Exchange Mechanisms                                | 14
4. 2DEXSY Pulse Sequence                                                | 26
5. $^7$Li 2DEXSY of (tert-Butoxide)(tert-Butyl)$_3$Li$_4$                | 28
6. The tert-Butyllithium Tetramer and the (tert-Butoxide)(tert-Butyl)$_3$Li$_4$ Tetramer | 35
7. Variable Temperature $^7$Li Spectra of Lithium tert-Butoxide/tert-Butyllithium Mixture | 37
8. Eyring plot of the Rates of Fluxionality for the (tert-Butyl)$_3$(tert-Butoxide)Li$_4$ Tetramer Using Absolute value Spectra | 42
9. Comparison Between the Summation of Traces from the 2DEXSY and a Normal One-Dimensional $^7$Li Spectrum | 44
10. $^7$Li 2DEXSY, Pure Absorption Mode, of the (tert-Butoxide)(tert-Butyllithium)$_3$Li$_4$ Tetramer | 48
11. Comparison Between the Summation of Traces from the Pure Absorption 2DEXSY Spectrum and a Normal One-Dimensional $^7$Li Spectrum | 49
12. Eyring Plot of the Rates of Fluxionality for the (tert-Butyl)₃(tert-Butoxide)Li₄ Tetramer Using Pure Absorption Mode Spectroscopy ........................................ 51

13. Twelve-Membered Ring Proposed by Brown as a Possible Intermediate in Hexamer Fluxionality ........................................ 74

14. Variable Temperature ¹³C Spectra of the Methyl Region of a Lithium tert-Butoxide/ tert-Butyllithium Mixture .................. 80

15. ¹³C-2DEXSY Spectrum at +20.8 °C of the Methyl Region of the tert-Butyllithium /Lithium tert-Butoxide Mixture .................. 85

16. Hexamer of Composition (tert-Butoxide)₅(tert-Butyl)Li₆ .................. 89

17. The (tert-Butoxide)₅(tert-Butyl)Li₆ Hexamer Undergoing the Limited Fluxionality .................. 92

18. The Simplified Representation Displaying the Structural Possibilities of the (tert-Butoxide)₅(tert-Butyl)Li₆ Hexamer .................. 95

19. The (tert-Butoxide)₄(tert-Butyl)₂Li₆ Hexamers .................. 99

20. The Ortho Isomer of the 4:2 Hexamer Undergoing the Limited Fluxional Exchange .................. 100

21. The Ortho Isomer of C₇B₁₀H₁₂ Undergoing the Diamond-Square-Diamond Isomerization .................. 106

22. The Ortho Isomer of (tert-Butoxide)₄(tert-Butyl)₂Li₄ Hexamer Undergoing a Form of the Diamond-Square-Diamond Isomerization .................. 108

23. Eyring plots of Exchanges in Tables 5 and 6 .................. 115

24. Variable Temperature ⁶Li Spectra of n-Propyllithium/ tert-Butyllithium Mixture .................. 134
25. Variable Temperature $^{13}$C Spectra of α-Carbon Region of n-Propyllithium/tert-Butyllithium Mixture ........................................ 136

26. $^{13}$C Spectra of n-Propyllithium/tert-Butyllithium Mixture ........................................ 138

27. $^{13}$C Spectra of the α-Carbon Region of n-Propyllithium/tert-Butyllithium Mixture ........................................ 141

28. Variable Temperature $^6$Li Spectra of n-Propyllithium/tert-Butyllithium Mixture ........................................ 143

29. $^{13}$C{$^6$Li}-$^1$H HETCOR of n-Propyllithium/tert-Butyllithium Mixture ........................................ 144

30. $^{13}$C-$^6$Li HETCOR of n-Propyllithium/tert-Butyllithium Mixture ........................................ 146

31. The Tetramer of Composition: (n-Propyl) (tert-Butyl)$_4$Li$_4$ ........................................ 148

32. Vertical Projection of $^{13}$C-$^1$H HETCOR ........................................ 153

33. The Three Conformations Possible for the Hexamer of Composition: (tert-Butyl)$_2$ (n-Propyl)$_4$Li$_6$ ........................................ 160

34. The Three Possible Environments of the n-Propyl Groups in the Hexamers of Composition (tert-Butyl)$_2$ (n-Propyl)$_4$Li$_6$ ........................................ 164

35. Tetramer of Composition: (tert-Butyl)$_2$ (n-Propyl)$_4$Li$_4$ ........................................ 170

36. Variable Temperature $^{13}$C Spectra of the Hexameric α-Carbon Region of n-Propyllithium/tert-Butyllithium Mixture ........................................ 173

37. $^{13}$C 2DEXY of the α-Carbon Region of the n-Propyllithium/tert-Butyllithium Mixture ........................................ 175

38. Variable Temperature $^6$Li Spectra of n-Butyllithium/tert-Butyllithium Mixture ........................................ 181
39. $^{13}$C Spectra of the $\alpha$-Carbon Region of $n$-
Butyllithium/tert-Butyllithium
Mixture ........................................... 182

40. $^{13}$C Spectrum and Vertical Projection from
$^{13}$C-$^1$H HETCOR of $n$-Butyllithium/tert-
Butyllithium Mixture .......................... 185

41. $^{13}$C-$^6$Li HETCOR of $n$-Butyllithium/tert-
Butyllithium Mixture .......................... 187

42. $^6$Li 2DEXSY of $\{(n$-Propyl)$\{\text{tert-Butyl}\}$,$ \text{Li}_4$
Tetramer ........................................... 198

43. Eyring Plot of the (tert-Butyl)$_3$
$\{(n$-Propyl)$\text{Li}_4$ Tetramer Fluxionality .... 201

44. Eyring Plot for the (n-Butyl)
(tert-Butyl)$_3$, $\text{Li}_4$ Tetramer Fluxionality ... 202

45. Variable Temperature $^6$Li Spectra of
$n$-Propyllithium/ $n$-Butyllithium
Mixture ........................................... 229

46. $^{13}$C Spectra with and without $^6$Li Decoupling
of $n$-Propyllithium/$n$-Butyllithium
Mixture ........................................... 230

47. Variable Temperature $^6$Li Spectra of 2-
Methylbutyllithium ................................. 233

48. $^6$Li Spectrum at -42.7°C of 2-
Methylbutyllithium Using Resolution
Enhancement ........................................ 235

49. Variable Temperature $^{13}$C Spectra of 2-
Methylbutyllithium ................................. 237

50. $^{13}$C Spectra of 2-Methylbutyllithium .......... 240

51. $^{13}$C-$^6$Li HETCOR of 2-Methylbutyllithium .... 242

52. The $R_3S$ Hexamer Using the Simplified
Representation ................................... 246

53. The Three Possible Structures for the $R_3S_3$
Hexamers ........................................... 248

54. The Six Possible Structures for the $R_3S_3$
and $S_3R_3$ Hexamers ............................. 251
55. The Local Environments for the Three Types of R isomers in the R_4S_2 Hexamers . . . . . . . 257

56. Variable Temperature $^{13}$C Spectra of (R)-2-Methylbutyllithium . . . . . . . . . . . . . 259

57. The $\alpha$-Carbon Region of the $^{13}$C($^6$Li) Spectra of (R)-2-Methylbutyllithium and Racemic 2-Methylbutyllithium . . . . . . . . 261

58. $^6$Li Spectra of (R)-2-Methylbutyllithium and Racemic 2-Methylbutyllithium . . . . . . . 262
CHAPTER 1

INTRODUCTION

Introduction

Organolithium compounds are among the most widely used reagents in organic and organometallic syntheses (1)(2)(3). The emergence of these compounds as synthetically useful coincided with the perfection of their synthesis from alkyl halides (4). Currently, organolithium compounds are commercially available and are common laboratory reagents. Despite their widespread usage as synthetic reagents, much about their structure and exchange processes remain a mystery (5). The major focus of this present work is to provide information about the nature of organolithium compounds in solution.

Structure and Bonding of Alkyl lithium Compounds. Much of the early work on the structure of alkyl lithium compounds was done by Brown (6)(7)(8)(9)(10)(11)(12). This work centered around the structure and bonding in organolithium compounds and is summarized in several early reviews (13)(14)(15).

In hydrocarbon solution alkyl lithium compounds commonly exist as aggregates ranging from dimers, (RLi)₂, (16) (17) to nonamers, (RLi)₉, (18). The degree of association of
these alkyllithium compounds is dependent upon size of the alkyl group, concentration of the alkyllithium compound, temperature of the solution, and the solvent employed.

Generally, the more sterically bulky the alkyl group, the lower the aggregation state. This is exemplified in comparing n-propyllithium to tert-butyllithium. n-Propyllithium commonly exists in hydrocarbon solution as a mixture of hexamer, octamer, and nonamer (18)(19)(20). The more bulky tert-butyllithium exists in hydrocarbon solution as a tetramer (21) (22). This is a trend to which alkyllithium compounds conform (23).

Stronger coordinating solvents lead to a decrease in aggregation state (5). This is aptly exemplified in a recent study of the effect of the addition of ethyl ether to hydrocarbon solutions of tert-butyllithium (24). It was shown in this study that the addition of the coordinating solvent to the hydrocarbon solution resulted in a dynamic equilibrium between uncoordinated tetramers and tetracoordinated dimers. tert-Butyllithium has been shown to be monomeric in THF (25).

Concentration is also known to affect the degree of association of alkyllithium compounds with the more concentrated solutions tending to the higher aggregation states. In hydrocarbon solution, increasing the temperature of an alkyllithium solution has the effect of lowering the aggregation state.
Figure 1 depicts the structures of the dimer, tetramer, and hexamer alkyl lithium aggregates. The tetramer and hexamer structures were proposed by Brown (8) and later verified by X-ray crystal studies (26)(27)(28)(29). A related study has recently revealed the hexameric crystal structure of a lithium alkoxide (30). Crystal studies of organolithium compounds have been reviewed (31).

The alkyl lithium dimer is a planar four-membered ring with the alkyl group in a bridging position between the two lithium atoms. Dimers are more common in coordinating solvents in which the two lithiums are coordinated to two solvent molecules, as well as the two α-carbons from the alkyl groups.

The alkyl lithium tetramer is arranged with the lithiums in a tetrahedral structure creating four triangular faces. Over each triangular face is an α-carbon from the alkyl groups. The bonding in the alkyl lithium tetramers has been examined with both covalent and electrostatic models. Considering a covalently bonded model of the alkyl lithium compound, this α-carbon is bonded to the three lithiums composing the face through a four center, two electron bond. Likewise, each lithium is bonded to three α-carbons from the alkyl groups. The methyllithium tetramer has been successfully explained with a purely electrostatic model (32). This study indicated that alkyl lithium compounds may be held together by purely ionic bonds.
Figure 1 - Alkylithium aggregates. Dimer (top), tetramer (middle), and hexamer (bottom).
The alkyllithium hexamer is arranged with the lithiums in an octahedral geometry. This arrangement creates eight triangular faces, six of which are occupied by the α-carbons from the alkyl groups. The two open faces are opposite each other in the hexamer, leaving the hexamer in a distorted octahedral geometry possessing $D_{3d}$ symmetry.

There is some disagreement as to whether there is significant Li-Li bonding in these aggregates. The short Li-Li distances in these aggregates indicate appreciable Li-Li interaction could occur (33). Mass spectral evidence also supports Li-Li interaction (10), as does theoretical calculations (34)(35)(36)(37)(38)(39).

Lending support to the no Li-Li interaction theory, are EPR studies of tetrameric free radicals which indicate that the electron is between an α-carbon and three of the lithiums in a tetramer (40). Lack of observable $^6$Li-$^7$Li coupling in NMR studies (41), also indicates no Li-Li interaction as do past Raman studies (42).

**NMR Spectroscopy and Alkyllithium Compounds.**

Historically, NMR spectroscopy has been the tool of choice in the investigation of solution structures of organolithium compounds. The impact of NMR on the investigation of alkyllithium compounds has been detailed in recent reviews (43)(44). Even before the development of FTNMR, researchers made use of the easily observed $^1$H and $^7$Li nuclei found in
these systems (13) (14) (15) (45) (46). NMR spectroscopy of these nuclei proved to be very informative in the investigation of solution structures of these compounds. High natural abundance and large magnetogyric ratios, make these nuclei readily observable, even on the continuous wave spectrometers used in the earliest organolithium NMR studies. Investigation of these compounds using $^7$Li NMR techniques continues to be productive as evidenced by a recent report using $^7$Li two-dimensional exchange spectroscopy (2DEXSY) on a lithium/crown ether complex (47). The NMR properties of these nuclei and others of interest in these compounds are shown in Table 1.

**TABLE 1**

**NMR PROPERTIES OF SELECTED NUCLEI**

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Spin</th>
<th>Natural Abundance</th>
<th>NMR Frequency</th>
<th>Quadrupole Moment</th>
<th>Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1/2</td>
<td>99.98%</td>
<td>300.0 MHz</td>
<td>......</td>
<td>1.0</td>
</tr>
<tr>
<td>$^9$Li</td>
<td>1</td>
<td>7.42%</td>
<td>44.1 MHz</td>
<td>$-4.6 \times 10^{-4}$</td>
<td>$8.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^7$Li</td>
<td>3/2</td>
<td>92.58%</td>
<td>116.6 MHz</td>
<td>$-4.2 \times 10^{-4}$</td>
<td>$2.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1/2</td>
<td>1.11%</td>
<td>75.4 MHz</td>
<td>......</td>
<td>$1.6 \times 10^{2}$</td>
</tr>
</tbody>
</table>

A detriment to the information provided by $^7$Li NMR is the rapid relaxation of the $^7$Li nuclei. This problem becomes evident in observing both $^7$Li as well as $^{13}$C spectra.
of alkyllithium compounds. The rapid relaxation of quadrapolar nuclei (such as $^7$Li) often leads to broad featureless peaks in an NMR spectrum as peaks become increasingly broad with increasing relaxation rates of the observed nucleus. Thus many $^7$Li NMR spectra contained broad peaks, especially at low temperatures as quadrapolar relaxation rates increase. Due to the exchange processes alkyllithium compounds undergo, low temperature spectra are essential in the investigation of these compounds.

Wherli showed that the relaxation rates of $^6$Li nuclei are much slower than those of $^7$Li nuclei (48) (49) (50). Though both $^7$Li and $^6$Li are quadrapolar nuclei, as shown in Table 1, the quadrapole moment of $^7$Li is approximately 100 times that of $^6$Li resulting in slower relaxation for $^6$Li nuclei. Consequently, $^6$Li NMR spectra usually contain sharper and thus more resolvable peaks than corresponding $^7$Li spectra. This fact becomes very important in examining complicated alkyllithium systems.

As mentioned above, the relatively rapid relaxation of $^7$Li nuclei also affects the $^{13}$C spectra that may be obtained from alkyllithium compounds. Scalar coupling between $^{13}$C and $^7$Li has been observed in the past and used to characterize alkyllithium systems (46) (51). Coupling information in many alkyllithium systems is often lost; however, due to the rapid relaxation of $^7$Li.
Fraenkel reasoned that if the carbons in an alkyllithium compound were bonded to the more slowly relaxing $^6$Li nuclei, rather than $^7$Li nuclei, coupling information may be retained even at low temperatures (18) (19). He discovered he was able to observe $^{13}$C-$^6$Li coupling in $^6$Li-enriched alkyllithium systems. Other researchers have since made use of the multiplicity of the α-carbons that arises in these $^6$Li-enriched alkyllithium compounds to establish aggregation states. This is done by realizing that the number of peaks observed for the α-carbon is equal to $2mI+1$ where $m$ is the number of equivalently bonded $^6$Li nuclei and $I$ is equal to 1 (the spin of the $^6$Li nucleus). According to this formula the α-carbon of a non-fluxional tetramer would be a 7 line multiplet. The α-carbon of a fluxional tetramer would be a 9 line multiplet. For larger aggregation states however, a problem arises in using α-carbon multiplicity to determine aggregation state. Fluxional hexamer α-carbons would be 13 line multiplets, with the intensity of the outer peaks being only 0.7% the intensity of the center peak of the multiplet. Such peaks would be too small to observe using experiments of reasonable lengths. This problem increases with the increasing size of the aggregate, and thus the multiplet, such as the case with the octamer and the nonamer.

An alternative to using α-carbon multiplicity to
determine aggregation state, is to use the magnitude of the observed coupling. Schleyer has shown that, for many alkylolithium compounds, the observed $^{13}\text{C-}^6\text{Li}$ coupling is related to the aggregation state of the compound according to the formula

$$J_{ob} = (17 \pm 2 \text{ Hz})/m$$ [1]

where $m$ is the number of equivalently bonded lithiurns (25) (52). According to this formula the $\alpha$-carbon of a non-fluxional hexamer or tetramer would show a $J(^{13}\text{C-}^6\text{Li})$ equal to $5.67 \pm 0.7$ Hz. A fluxional tetramer would show a $J(^{13}\text{C-}^6\text{Li})$ equal to $4.25 \pm 0.5$ Hz and the $\alpha$-carbon of a fluxional hexamer would show a $J(^{13}\text{C-}^6\text{Li})$ equal to $2.83 \pm 0.3$ Hz. The coupling values predicted by this formula have proved fairly accurate for some alkylolithium tetramers and hexamers (23). However, this formula has been shown to be unreliable for many alkylolithium compounds, especially those which form aggregation states other than tetramers and hexamers (43).

With the success of the $^6\text{Li}$-enrichment technique, many research groups have used this technique with considerable success. Researchers have made use of $^{13}\text{C-}^6\text{Li}$ coupling values to establish aggregation states for several alkylolithium compounds in hydrocarbon solvent. This coupling has also been used in the determination of exchange
rates in some alkyllithium aggregates (22).

$^{13}$C-$^6$Li coupling has proven to be very useful and informative in the characterization of alkyllithium compounds in solution. The observation of this coupling prompted the investigation into the types of double resonance NMR experiments which might provide additional information in the study of these compounds. In order to perform such experiments the Varian VXr spectrometer used in this present study had been modified to allow $^6$Li decoupling. With this decoupling accessory, experiments can be run which more fully establish connectivity in these systems by making use of the $^{13}$C-$^6$Li coupling.

The use of $^6$Li decoupling has proven to be invaluable in the characterization of alkyllithium systems. Figure 2 shows $^{13}$C spectra of the $\alpha$-carbon of tert-butyllithium in cyclopentane at -70°C. At this temperature, tert-butyllithium exists in cyclopentane as a non-fluxional tetramer, therefore the $\alpha$-carbon should show coupling to three equivalent $^6$Li nuclei resulting in a seven line multiplet. This is what is observed in the $^{13}$C spectrum which uses only $^1$H decoupling (the lower $^{13}$C spectrum shown in Figure 2). The upper spectrum in this figure was acquired using $^6$Li decoupling. This decoupling causes the collapse of the multiplet into a single resonance greatly improving the signal-to-noise of the peak. As important as
Figure 2 - $^{13}$C spectra of the α-carbon of tert-butyl lithium with (top) and without (bottom) $^6$Li decoupling. Temperature = -70°C
the increase in the signal-to-noise ratio is the improved resolution using $^6$Li decoupling.

Aside from simply decoupling $^6$Li in one-dimensional $^{13}$C spectra, the use of $^6$Li decoupling provides for experiments essential in characterizing complicated alkyllithium systems. One such experiment is a one-dimensional experiment which makes use of spectral editing techniques to distinguish between different aggregation states \cite{53}. A two-dimensional experiment which makes use of $^6$Li decoupling in identifying aggregation states is the 2D-J resolved experiment. In a 2D-J-resolved spectrum, coupling information of the $^{13}$C $\alpha$-carbons is spread into the F1 dimension while chemical shift information of these carbons is retained in the F2 dimension \cite{43}(\cite{54}).

An NMR experiment of greater significance in this work is the $^{13}$C-$^6$Li Heteronuclear correlation experiment (HETCOR). Gunther first reported a $^{13}$C-$^6$Li HETCOR using a method based on double quantum coherence \cite{55}. More recently a $^{13}$C-$^6$Li HETCOR has been developed which makes use of $^6$Li decoupling. Such an experiment was developed by Thomas and Ellington and is used routinely in this research \cite{43}(\cite{54}). This HETCOR makes it possible to establish connectivities between the $\alpha$-carbons in a $^{13}$C spectrum and the different resonances in a $^6$Li spectrum. As will be explained in the following chapters this $^{13}$C-$^6$Li HETCOR was an essential experiment in
this work.

**Exchange Processes in Alkyl Lithium Aggregates.**

Alkyl lithium aggregates are known to undergo both intra and interaggregate exchange. The higher aggregation states tend to undergo both intra and interaggregate exchange more readily than do lower aggregation states (5).

The intraaggregate exchange of alkyl lithium tetramers has been the subject of considerable research \( (22)(38)(56)(59) \). Some suggested mechanisms stemming from this research are displayed in Figure 3 and discussed below.

One of these possible mechanisms for tetramer fluxionality is the dissociation of the tetramer into dimers. The activation parameters for dissociation of tert-butyllithium tetramers have been reported (9) and found to be very close to the activation parameters for the fluxionality of the tert-butyllithium tetramer (22). This suggests that fluxionality of the tert-butyllithium tetramers may proceed through dimers. However, as was stated in reference 22, it is difficult to account for the large difference in rates of intraaggregate and interaggregate exchange of these tert-butyllithium tetramers if the mechanism of fluxionality was dissociation into dimers.

Brown proposed a mechanism for tetramer fluxionality whereby the exchange proceeds through an eight-membered ring consisting of alternating carbon and lithium atoms as shown
Figure 3 - Tetramer fluxional exchange mechanisms: A) dissociation to dimers. B) dissociation to an eight-membered ring. C) concerted over-the-edge movement of three alkyl groups.
in Figure 3 (56). Such a mechanism is supported by the observation of eight-membered rings in some lithium/copper aggregates (58)(59). No such structures, however, have been observed in pure alkyl lithium solutions.

A third possible mechanism for tetramer fluxionality is an over-the-edge mechanism proposed by Schleyer (60). This mechanism involves the concerted migration of at least three of the alkyl groups over the edge of the tetrahedron. Schleyer proposed this process might occur by the $\alpha$-carbon converting from sp$^3$ to sp$^2$ hybridization as it migrates over the edge. Such a movement would be stabilized by the interaction of the $p$ orbital on the $\alpha$-carbon with the two lithiums composing the edge. Schleyer indicated this mechanism may be important for primary alkyl groups, but suggested that, in secondary and tertiary alkyl groups, the interaction between alkyl groups bonded to the $\alpha$-carbon with the lithium core would make this a high energy process.

Intraaggregate exchange of alkyl lithium hexamers is largely based on speculation (61). The lack of information on the nature of this fluxionality is due to the fact that this fluxionality does not lend itself readily to examination. The fluxionality of hexamers in solution is always fast (5), therefore, the study of this process is difficult.

Brown has proposed a twelve-membered ring to account
for hexamer fluxionality (8). This ring is composed of alternating carbon and lithium nuclei, similar to the eight-membered ring he proposed as an explanation for tetramer fluxionality. His suggested mechanism of fluxionality was a dissociation to the twelve-membered ring, then a reassociation to the hexamer in which the α-carbons may or may not be bonded to the same lithiums to which they were bonded before the dissociation.

Schleyer suggested his over-the-edge mechanism may play a part in hexamer fluxionality (63). This mechanism is explained above for tetramer fluxionality, but Schleyer suggested it may be more important in the fluxionality of hexamers. The importance of this process in hexamers is due to the presence of the open faces. These open faces may provide a lower energy path to fluxionality than an over-the-edge mechanism in tetramers.

Interaggregate exchange of alkyl lithium hexamers has proven more fruitful to study than intraaggregate exchange. This stems mainly from the ability to slow this process to below the NMR timescale in some alkyl lithium hexamers. Brown has suggested the possibility of hexamer dissociation into a dimer and a tetramer, thereby accomplishing interaggregate exchange (2).

Fraenkel’s studies of n-propyllithium (18)(19), and 2-methylbutyllithium (65) have led him to postulate the existence of a biaggregate. This biaggregate, of the
formula \((RLi)_2\), is formed by the combination of two hexamers. The alkyl groups are randomly distributed in the biaggregate which then decomposes to two hexamers, thus accomplishing interaggregate exchange. He suggested the presence of this biaggregate due to the large negative \(\Delta S^\circ\) he found upon quantitating the interaggregate exchanges of these hexamers.

The study reported here makes use of a method of studying exchange processes of alkyllithium aggregates which of late has been largely ignored. It is found that when a unique group is introduced into an alkyllithium aggregate, non-equivalencies in NMR spectra arise, which aid in the understanding of the exchange processes these aggregates undergo.

The current work is a study of the exchange processes these alkyllithium aggregates undergo. Mixed tetramers and hexamers are used throughout this study to distinguish the exchange processes which are occurring. The tool of choice for this study is NMR spectroscopy. Two-dimensional exchange spectroscopy is used routinely throughout this work, therefore it was imperative that this experiment be developed for routine use in these compounds. Chapter 2 is a description of the development of this experiment.

Chapter 3 is a report of lithium tert-butoxide/tert-butyllithium mixed hexamers. The observance of the non-
equivalencies discussed in this chapter led to the proposal of a previously unknown type of alkyllithium hexamer fluxionality. This unique exchange process might be supposed to be brought about by electronic factors of the tert-butoxide group. This is tested in chapter 4 on mixed alkyllithium systems to determine if this process is peculiar to alkoxide containing hexamers. Chapter 5 uses the optically active compound, 2-methylbutyllithium, to determine whether this unique fluxionality may be common to alkyllithium hexamers in general or peculiar to those which contain a tert-butyl group.
CHAPTER BIBLIOGRAPHY


CHAPTER 2

TWO-DIMENSIONAL EXCHANGE SPECTROSCOPY

Introduction

Nuclear magnetic resonance spectroscopy has developed into a valuable tool for the investigation of chemically exchanging systems. Line-shape analysis has been the technique used in the majority of these NMR studies. This method of studying exchange processes using NMR was pioneered by Gutowsky (1)(2). Line-shape analysis is based on the fact that exchange processes are manifested as changes in the shape of the peaks in an NMR spectrum. Simulated spectra may be used in either a visual comparison or in a least squares fitting process to determine exchange rates between exchanging sites. Line-shape analysis has proven to be very useful and has been used routinely in many different types of exchanging systems including some alkyl lithium compounds (3)(4)(5)(6)(7)(8). It is ideally suited to a two site exchange where the exchange rates are at, or near, the rate necessary to coalesce the two different NMR peaks.

A disadvantage of using line-shape analysis to examine exchanging systems is its non-deductive character. In a multi-site exchange it becomes necessary to examine all
potential exchange patterns to find the one that will produce the simulated spectrum that best fits the experimental spectrum. At exchange rates much slower than that of coalescence, the NMR line shapes become less sensitive to the exchange. Thus, exchanges which are slow on the NMR timescale are not well suited for line-shape analysis.

Saturation techniques have been developed to study exchange rates which are slow on the NMR timescale. This technique makes use of the fact that when non-equilibrium magnetization is created by multiple irradiation, the rate of return of the magnetization to equilibrium is governed by the exchange rates between exchanging sites. The rate of fluxional exchange of some lithium tetramers has recently been examined by this method. This method becomes difficult to use however, when the examined exchange is between more than two sites. In such cases all exchange sites must be irradiated and the other sites observed. The double irradiation method becomes useless as relaxation rates exceed exchange rates.

The use of two-dimensional exchange spectroscopy (2DEXSY) was first investigated by Ernst and coworkers. The 2DEXSY experiment makes use of the basic NOESY pulse sequence to produce a two-dimensional spectrum in which off-diagonal peaks are produced by magnetization being transferred from one site to another. Because of the
dynamic nature of alkyllithium compounds, and the large amount of mystery that remains concerning their exchange processes, a study of the advantages 2DEXSY might have in the investigation of alkyllithium compounds was undertaken.

The basic 2DEXSY pulse sequence is shown in Figure 4. This pulse sequence begins with the longitudinal magnetization at equilibrium along the main magnetic field $B_0$. The axis along which $B_0$ lies will be labeled $z$, for the purpose of explaining the pulse sequence. The first 90° pulse rotates the magnetization vector into the transverse (xy) plane. During the evolution period, $t_1$, each magnetization component is allowed to precess freely about the $z$ axis. Each component of magnetization from site $i$ precesses with its own Larmor frequency thus acquiring a frequency 'label' of its own resonance frequency $\omega_i$. The magnetization is then pulsed back onto the $z$ axis by the second 90° pulse, with the residual magnetization being subtracted out by phase cycling. During the mixing time, $t_m$, the magnetization components may undergo exchange with magnetization possessing another resonance frequency $\omega_j$, resulting in a new resonance frequency being acquired by the exchanging components. A third 90° pulse then rotates the magnetization into the xy plane for detection. Each component now has a post-exchange resonance frequency which may be different from its pre-exchange resonance frequency.
For an NMR spectrum to be two-dimensional, the pulse sequence must contain two time variables. The normal time variable for a one-dimensional experiment is the time in which the FID is measured. As shown in Figure 4, this time of FID measurement in the 2DEXSY experiment is called $t_2$. The other incremented time variable is the time variable $t_1$ which is incremented after every 'set' of FID's is collected. The number of FID's needed to make up a 'set' corresponds to the amount necessary to achieve the desired signal-to-noise ratio. The two-dimensional Fourier-transform results in the conversion from the two time dimensions, $t_1$ and $t_2$, to two frequency dimensions, $F_1$ and $F_2$.

In the two-dimensional spectrum which results from the pulse sequence described above there are two types of peaks. The peaks along the diagonal are simply a contour of a one-dimensional spectrum. The off-diagonal peaks are created by magnetization that has exchanged from the corresponding diagonal peak in the $F_1$ dimension to the corresponding diagonal peak in the $F_2$ dimension. An example of this type
of two-dimensional exchange spectrum is shown in Figure 5. This 2D EXSY spectrum is of a lithium aggregate which is explained later in this chapter. The explanation here is simply to explain a 2D EXSY spectrum.

In this spectrum, cross-peak 'ij' is caused by magnetization which has exchanged from diagonal peak 'i' to diagonal peak 'j'. Likewise, cross-peak 'ji' is caused by magnetization moving in the reverse direction from diagonal peak 'j' to diagonal peak 'i'. In such a way, chemical exchanges may be mapped through a single 2D EXSY experiment. The use of 2D EXSY NMR to map exchanges in organolithium compounds has been demonstrated recently with both $^6$Li (11) and $^7$Li (16) NMR.

Several methods for obtaining exchange rates from 2D EXSY spectra have been developed. These methods have been reviewed in depth elsewhere (17)(18)(19)(20). The quantification methods pertaining to this work are discussed below.

For a system involving exchange between two sites, the intensity of the diagonal peaks, $I_i$, may be expressed in exponential form as (21) shown in equation 2.

$$I_i = \frac{1}{2} \exp(-R_{t_m})\{1 + \exp(-2k_{t_m})\}$$  \[2\]

The intensity of the cross-peaks may be expressed as shown
Figure 5 - $^7$Li 2DEXSY of (tert-butoxide)(tert-buty1)$_4$Li$_4$. Sample is 1.3 F in lithium tert-butoxide/tert-butyl lithium. O/Li = 1/7. Temperature = +9.9°C
In equation 3 \((21)\).

\[
I_{ij} = \frac{1}{2} \exp(-Rt_m)\{1 - \exp(-2kt_m)\} \quad [3]
\]

In equations 2 and 3 above, \(t_m\) is the mix time in seconds and \(R\) is the spin-lattice relaxation rate of the nuclei at the exchanging sites.

In a simple two-site exchange with equal populations and equal relaxation rates at the exchanging sites, the rate constant may be calculated directly from the ratio of cross-peak \((I_{ii})\) and diagonal peak \((I_{ij})\) intensities according to equation 4 \((21)\).

\[
\frac{I_{ii}}{I_{ij}} = \frac{1 + \exp(-2kt_m)}{1 - \exp(-2kt_m)} \quad [4]
\]

In a more complicated exchange such as a multi-site exchange between sites of unequal population, it is more convenient to analyze the exchange data in matrix form \((14)(21)\). The intensities of both the diagonal peaks and the off-diagonal peaks are governed by a kinetic matrix and a relaxation matrix \((22)\). The kinetic matrix, \(K\), of a two site exchange is as shown in equation 5 where \(k_{ij}\) is the exchange rate constant for \(i \rightarrow j\). Assuming no cross-relaxation, the relaxation matrix, \(W\), would be as shown in equation 6 where \(R_i\) and \(R_j\) are the relaxation rates of the
nuclei at site i and those at site j respectively.

\[
K = \begin{bmatrix}
-k_{ij} & k_{ji} \\
k_{ij} & -k_{ji}
\end{bmatrix}
\]  \[5\]

\[
W = \begin{bmatrix}
-R_i & 0 \\
0 & -R_j
\end{bmatrix}
\]  \[6\]

These matrices lead to the combination matrix \( L \) (shown in equation 7 below) which governs peak intensities according to \( \exp(Lt_m) \) (22).

\[
L = \begin{bmatrix}
-R_i-k_{ij} & k_j \\
k_{ji} & -R_j-k_{ji}
\end{bmatrix}
\]  \[7\]

The rate constants are related to site population by

\[
p_i k_{ij} = p_j k_{ji}
\]  \[8\]

where \( p_i \) is the relative population at site i and \( p_j \) is the relative population at site j. The matrix \( L \) is thus related to the two-dimensional spectral intensities by the expression
\[ I = P \exp(L_{t_m}) \]  \[9\]

where \( P \) is the population array of the exchanging sites and \( t_m \) is the mix time.

The intensity matrix, \( I \), can be evaluated by diagonalizing \( L \) and generating an array composed of the eigenvalues of \( L \) as shown below.

\[ L = XA X^1 \]  \[10\]

\[ \exp(L_{t_m}) = X \exp(At_m) X^1 = J \]  \[11\]

\[ I = P \cdot J \]  \[12\]

The matrix \( L \) may be computed by assuming starting values of \( R_i \) and \( k_i \) for given values of \( t_m \) and comparing the matrix with spectral intensities (22).

A more efficient method of obtaining the matrix \( L \) has been reported by Perrin and Gipe (23) and detailed specifically by Abel et al (24). Matrix \( J \) above, can be calculated from \( I \) and \( P \) according to equation 13.

\[ J = I \cdot P^1 \]  \[13\]

Matrix \( J \) may then be used to regenerate the array \( \exp(At_m) \) and the matrices \( X \) and \( X^1 \) according equations 14, 15, and 16.
\[ J = X \exp(At_m) X' \]  
\[ (\ln J/t_m) = X \{ \ln \exp(At_m)/t_m \} X' \]  
\[ (\ln J/t_m) = X\Lambda X' = L \]

In this manner the matrix \( L \) can be generated from the intensities of cross peaks and the corresponding diagonal peaks in a single two-dimensional exchange experiment. Since only relative intensities are known the relaxation rates are not obtainable from such an experiment, but the off diagonal elements are the exchange rates as shown in matrix \( L \). This method of quantifying the exchange eliminates the need to run multiple experiments with different \( t_m \) times thus reducing the spectrometer time necessary.

Abel has used this method extensively for evaluating rate constants in platinum complexes using \(^{195}\)Pt 2DEXSY spectra (25) (26) (27) (28) (29), as well as using proton 2DEXSY spectra to quantitate exchange processes in molybdenum (30) and tungsten (31) complexes. Other researchers have routinely used this method to evaluate rate constants using \(^1\)H and \(^{13}\)C 2DEXSY spectra (32) (33) (34) (35) (36) (37) (38) (39) (40). 2DEXSY spectra observing \(^{51}\)V (41) and \(^{113}\)Cd (42) have also been quantitated in this manner. A recent study has shown this quantification method to be reliable on \(^{11}\)B 2DEXSY spectra.
A computer program titled D2DNMR, was designed by David Stephenson (24) for the purpose of converting 2DEXSY spectral intensities into exchange rates in the manner discussed above. This program was modified to be used with Microsoft FORTRAN (44), thus allowing it to be run on a PC. A copy of the modified program is listed in the appendix.

Results and Discussion

**Fluxionality of \((t\text{-butyl})_4(t\text{-butoxide})\text{Li}_4**. As a test case for the 2DEXSY experiment and the quantification by the D2DNMR computer program, the mixed tetramer \((t\text{-butyl})_3(t\text{-butoxide})\text{Li}_4\) was chosen. In order to discuss the exchange process examined, a brief explanation of the compound itself is necessary.

tert-Butyllithium commonly exists as a tetramer in hydrocarbon solution. This tetramer is composed of four lithiums in a tetrahedral arrangement with each \(\alpha\)-carbon of the tert-butyl group bonded to three lithiums and each lithium bonded to three \(\alpha\)-carbons from the tert-butyl groups. The result of this bonding is that the \(\alpha\)-carbons are centered symmetrically over each of the four triangular faces formed by the lithiums as depicted in Figure 6a.

The addition of a sufficient amount of tert-butanol to
tert-butyllithium to make a 1 to 1 mol ratio between lithium and oxygen results in the conversion of tert-butyllithium to lithium tert-butoxide (3). The reaction written for the monomer is as shown in equation 17.

\[(\text{CH}_3)_3\text{ClLi} + (\text{CH}_3)_3\text{COH} \rightarrow (\text{CH}_3)_3\text{COLi} + (\text{CH}_3)_3\text{CH}\quad [17]\]

If less than a 1 to 1 oxygen to lithium mole ratio is used, mixed aggregates, containing some tert-butyl groups and some tert-butoxide groups are formed. Some of these mixed aggregates are hexamers and will be discussed in chapter 3. Upon addition of small amounts of tert-butanol, the primary species formed is a mixed tetramer containing three tert-butyl groups and one tert-butoxide group. This tetramer is depicted in Figure 6b and will be referred to in this chapter as the 1:3 tetramer.

When viewing Figure 6b, it becomes apparent that if this tetramer is rigid, there are two types of lithium. The lithium labeled with a '*' in the figure, is bonded to the \(\alpha\)-carbons from three tert-butyl groups and will be referred to as the unique lithium. The unlabeled lithiuns in the figure are all bonded to two \(\alpha\)-carbons from the tert-butyl groups and the oxygen from the tert-butoxide group. \(^7\text{Li}\) spectra of this tetramer in a non-fluxional state would show two peaks in a ratio of 3 to 1.
Figure 6 - a) The tert-butyllithium tetramer. b) The (tert-butoxide)(tert-butyl),\textsubscript{4}Li, tetramer.
Variable temperature $^7$Li spectra of a lithium tert-butoxide/tert-butyllithium mixture are shown in Figure 7. The oxygen to lithium ratio of this tube is 1 to 7. In the low temperature spectrum there are three peaks, the peak referenced to 0 Hz are the lithiums from the tert-butyllithium tetramer as shown in Figure 6a. At the oxygen to lithium ratio of 1 to 7, there is an abundance of this tetramer in this solution.

The other two peaks in the low temperature spectrum of Figure 7 result from the two types of lithiums in the 1:3 tetramer. At this temperature, the 1:3 tetramer is non-fluxional and thus the two types of lithiums in the expected ratio of 1 to 3 are made apparent in the spectrum. As the solution is warmed, the 1:3 tetramer becomes fluxional and the 2 lithium peaks stemming from this tetramer coalesce to 1 very broad peak as is shown in the top spectrum of Figure 7.

Near the coalescence temperature, line-shape analysis is the method of choice for the determination of exchange rates. As will be shown below, a 2DEXSY experiment demands resolution of peaks for accurate exchange rate determination and thus is not useful at coalescence. However, at exchange rates much slower than the rate at coalescence, 2DEXSY is the NMR method more suited to examining these exchanges. The fluxionality of this tetramer had been previously
Figure 7 - Variable temperature \(^7\)Li spectra of 1.3 F lithium tert-butoxide/tert-butyllithium mixture. \(\text{O/Li} = 1/7\).
examined by line-shape analysis of the $^6$Li spectra (45). 2DEXSY had also previously been used to study the fluxionality of this tetramer (46). The method of quantification employed for the 2DEXSY study was the method developed by Hawkes (22) of running multiple spectra using different mix times and fitting the data to the appropriate line equations.

The possibility of migration of the tert-butyl groups about three faces while maintaining the position of the tert-butoxide groups has been previously investigated (45). It was concluded from the study in reference 45 that migration of the tert-butoxide group occurred at least as fast as migration of the tert-butyl groups. Previous investigation makes this tetramer an ideal test case for the 2DEXSY experiment using the D2DNMR computer program for quantification.

The 2DEXSY pulse sequence had previously been written into the software of the Varian VXR-300 spectrometer. This was the basic NOESY pulse sequence used by Ernst (13) and shown in Figure 4, but had been modified to accept $^6$Li decoupling. Two-dimensional exchange spectra at various temperatures were run on this sample to monitor the rate of exchange between the two types of lithium in the 1:3 tetramer, thus monitoring its rate of fluxionality.

The 2DEXSY spectrum at +9.9°C is shown in Figure 5.
The one-dimensional spectrum is displayed along each axis to clarify which species are exchanging. In this figure, diagonal peak $i$ was produced by the unique lithium composing the 1:3 tetramer (labeled with an asterisk in Figure 6b). The diagonal peak $j$ was produced by the other three lithiums in the 1:3 tetramer (unlabeled in Figure 6b). The large diagonal peak at 0 Hz, is produced by the pure tert-butyl lithium tetramer as shown in Figure 6a. The crosspeaks between $i$ and $j$ in this spectrum indicate exchange between the two types of lithiums in Figure 6b, thus indicating a slow fluxionality of the 1:3 tetramer.

Appropriate mix times for the 2DEXSY study were chosen according to equation 18

$$t_m = \frac{1}{k} \ln \frac{R + k}{R}$$  \[18\]

in which $t_m$ is the appropriate mix time, $k$ is the rate of exchange, and $R$ is the relaxation rate of the observed nucleus. This equation has been shown to provide mix times which result in accurate 2DEXSY spectra (47). Initially a trial and error process was used to predict the appropriate $t_m$ using previously determined exchange rates as a first approximation. The spectrum was then analyzed using D2DNMR to compute the exchange rates from the 2DEXSY spectrum. These rates were then used to arrive at more appropriate $t_m$. 
times using equation 18. This process was repeated until the rates computed from the 2D EXSY spectrum, when inserted into equation 18, yielded the $t_m$ time used to obtain the 2D EXSY spectrum.

In order to make use of the D2DNMR program, peak intensities must be determined. In a two-dimensional spectrum the peaks possess a volume, as opposed to an area, as the peaks in a one-dimensional spectrum. The integrated volume of a two-dimensional peak is most accurately determined by summing the signals along the F2 axis at a given frequency in the F1 dimension within the interval in which the signal at F1 is non-zero (17)(48). This was accomplished in this study by summing all the cross-sections along the F2 axis in which the peak of interest at the F1 frequency had a non-zero intensity. The result of this intensity determination for the spectrum in Figure 5 are shown in equation 19 which is the intensity matrix corresponding to this spectrum. In order to use this data in D2DNMR, this matrix must be symmetrized by adjusting the cross-peaks to equal intensities as required for a system at equilibrium. This results in the intensity matrix

\[
I = \begin{bmatrix}
.926 & .074 \\
.492 & .509 \\
\end{bmatrix}
\]
shown in equation 20. The matrix manipulation discussed above resulted in the exchange matrix shown in equation 21.

\[
I = \begin{bmatrix}
.926 & .074 \\
.074 & .077 \\
\end{bmatrix}
\]  

[20]

\[
K = \begin{bmatrix}
.239 & .758 \\
2.27 & -6.88 \\
\end{bmatrix}
\]  

[21]

As explained above, the off-diagonals of this matrix contain the exchange rates of \( k_y \) and \( k_j \). Which in this spectrum is the rate of exchange between the two types of lithiums in the 1:3 tetramer. The data obtained at various temperatures using this experiment is shown in Table 2.

An Eyring plot of this data is shown in Figure 8. The resulting activation parameters are \( \Delta H^* = 13.9 \pm 1.3 \) kcal/mol and \( \Delta S^* = -3.0 \pm 5 \) eu. The error bounds quoted reflect only the fitting of the plot to a straight line and are at one standard deviation. There is a considerable amount of scatter in the plot resulting in large error bounds in the activation parameters. This is a result of the inability to integrate the peaks accurately due to poor
Figure 8 - Eyring plot of the rates of fluxionality for the (tert-butyl)$_3$(tert-butoxide)Li$_4$ tetramer using absolute value spectra. Sample is 1.3 F lithium tert-butoxide/tert-butyl lithium. O/Li = 1/7.

$\Delta H^* = 14.2 \pm 1.3 \text{ kcal/mol}$  $\Delta S^* = -3.0 \pm 5 \text{ eu}$
resolution in the one-dimensional traces used to obtain the volumes of the peaks from the two-dimensional spectra.

An example of the spectrum resulting from the summation of the traces which display the i to j exchange is shown in Figure 9. Also displayed in this figure is the corresponding

Table 2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature(C)</th>
<th>t_m(s)</th>
<th>Rate(s⁻¹)</th>
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</thead>
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<tr>
<td>DP253L</td>
<td>-12.5</td>
<td>0.80</td>
<td>0.34</td>
</tr>
<tr>
<td>DP233L</td>
<td>0.1</td>
<td>0.40</td>
<td>1.64</td>
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<td>DP239L</td>
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<td>2.40</td>
</tr>
<tr>
<td>DP244L</td>
<td>9.9</td>
<td>0.20</td>
<td>3.03</td>
</tr>
<tr>
<td>DP241L</td>
<td>12.6</td>
<td>0.20</td>
<td>4.41</td>
</tr>
<tr>
<td>DP246L</td>
<td>15.0</td>
<td>0.20</td>
<td>5.53</td>
</tr>
</tbody>
</table>

AH* = 14.2 ± 1.3 kcal/mol
AS* = -3.0 ± 5 eu

Concentration of NMR sample is 1.3 F based on lithium. O:Li ≈ 1:7.

one-dimensional spectrum at this temperature. The traces used in the summation were taken along the F2 axis centered at approximately ≈-10 Hz on the F1 axis. The peak at approximately ≈-10 Hz (labeled with an i in the Figure 9) is thus the diagonal peak from the unique lithium in the 1:3
Figure 9 - A comparison between the summation of traces from the 2DEXY in Figure 5 (top), and a normal one-dimensional $^7$Li at the same temperature (bottom). Temperature = +9.9°C.
tetramer (labeled with an asterisk in Figure 6b). Peaks which appear in the trace, other than the diagonal peak, must either be crosspeaks or tails from large peaks. The peak at 0 Hz in the trace spectrum appears to indicate exchange between the unique lithium of the 1:3 tetramer and the lithiums of the pure tert-butyllithium tetramer. Upon closer examination of the entire spectrum, this peak proves to be a tail from the large tert-butyllithium tetramer peak. The peak in the trace spectrum at -90 Hz (labeled ji in Figure 9) is an exchange crosspeak and indicates exchange between the unique lithium in the 1:3 tetramer and the other three lithiums in this tetramer.

It is obvious from these spectra that the resolution from the one-dimensional experiment is lost in using the traces of a two-dimensional spectrum obtained with the conventional method of acquiring two-dimensional spectra in a magnitude or absolute-value mode. Also apparent from the spectra in Figure 9 is the fact that tails from large peaks obscure the information available from 2DEXSY spectra.

**Pure absorption mode spectroscopy.** Conventional methods of displaying two-dimensional NMR spectra make use of either the absolute value mode or the power mode to obtain suitable line shapes. Both of these methods combine the imaginary and the real FID’s, resulting in peaks with broad bases and long tails. Various methods exist for obtaining pure absorption spectra in four quadrants
(49)(50)(51). For the purpose of this work, the 16-step phase cycling developed by States (49) was incorporated into the existing 2DEXSY pulse sequence. This method requires acquiring two separate signals which are 90° out of phase with each other. The 16 cycle phase-cycling routine required in this method is given in Table 3 and the entire pulse sequence is listed in the appendix.

Table 3

Phase cycling for pure absorption spectroscopy

<table>
<thead>
<tr>
<th>Pulse phase</th>
<th>Receiver phase</th>
</tr>
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<tbody>
<tr>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Y</td>
<td>X</td>
</tr>
<tr>
<td>-X</td>
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<td>-Y</td>
<td>-Y</td>
</tr>
</tbody>
</table>

The spectra obtained using pure-absorption mode 2DEXSY were better resolved than those obtained using absolute
value mode. As a comparison, the sample that produced the 2DEXSY spectrum in Figure 5 was used to produce the 2DEXSY spectrum in Figure 10 with the difference between the two spectra being that the spectrum in Figure 10 was obtained using the phase cycling for pure absorption spectroscopy.

The improved resolution becomes even more apparent when viewing the traces extracted from this 2DEXSY spectrum. Figure 11 contains a summation of traces from the 2DEXSY spectrum shown in Figure 10 along with the normal one-dimensional $^7$Li spectrum shown previously in Figure 9. The traces used in the summation are from the same region of the spectrum as those used to provide the summation of the traces in Figure 9 and thus represent the same exchange. As can be observed, the broad tail from the large diagonal tert-butyllithium peak is now diminished to a very small out-of-phase peak. It is obvious in comparing Figure 9 to Figure 11 that the pure-absorption 2DEXSY spectrum will provide for more accurate integrations than the normal absolute value mode spectrum from Figure 5.

A temperature study of the fluxionality of the 1:3 tetramer was done using pure absorption mode spectroscopy and the results are tabulated in Table 4. The Eyring plot of this data is shown in Figure 12. This plot shows less scatter than the plot in Figure 8 which made use of absolute value mode spectroscopy. Indeed, the correlation
Figure 10 - $^7\text{Li}$ 2D{\textit{EXSY}}, pure absorption mode, of the \((\text{tert-butoxide})(\text{tert-butyllithium})\),\(\text{Li}_4\) tetramer. Sample is 1.3F in lithium tert-butoxide/tert-butyllithium. \(O/\text{Li} = 1/7\). Temperature = \(+9.9^\circ\text{C}\).
Figure 11 - A comparison between the summation of traces from the pure absorption 2DEXSY spectrum in Figure 10 (top), and a normal one-dimensional $^7$Li spectrum (bottom) at the same temperature. Temperature = +9.9°C.
coefficient for the plot in Figure 8 is .9891 while the correlation coefficient of the plot in Figure 12 is .9941. The activation parameters are $\Delta H^\ddagger = 13.7 \pm 1.0 \text{ kcal/mol}$ and $\Delta S^\ddagger = -4.7 \pm 4 \text{ eu}$.

These rates are on the order of the rate of $1.49 \text{ s}^{-1}$ obtained in a 2DEXSY study on this tetramer at $-2^\circ \text{C}$ (46). The rate of fluxionality of this tetramer has also been investigated by line shape analysis (45). The line shape analysis made use of $^6\text{Li}$ spectra to determine rates of exchange between the two types of lithiums in this tetramer. The resulting Eyring plot and activation parameters of $\Delta H^\ddagger = 14.8 \pm 0.8 \text{ kcal/mol}$ and $\Delta S^\ddagger = -0.9 \pm 3.0 \text{ eu}$ are in good agreement with the 2DEXSY experiments reported here, however the actual rates differ somewhat. The $^6\text{Li}$ line shape study yielded a rate of $2.0 \text{ s}^{-1}$ at $-2^\circ \text{C}$ (45) as compared to the

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature(C)</th>
<th>$t_m$(s)</th>
<th>Rate($\text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td>0.47</td>
<td>0.84</td>
</tr>
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<td>DP545X</td>
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<td>14.1</td>
<td>0.14</td>
<td>5.39</td>
</tr>
</tbody>
</table>

$\Delta H^\ddagger = 13.7 \pm 1 \text{ kcal/mol}$ $\Delta S^\ddagger = -4.7 \pm 4 \text{ eu}$
Figure 12 - Eyring plot of the rates of fluxionality for the \((\text{tert-butyl})_3(\text{tert-butoxide})\text{Li}_4\) tetramer using pure absorption mode spectroscopy. Sample is 1.3 F lithium tert-butoxide/tert-butyllithium. O/Li = 1/7. \(\Delta H^* = 13.7 \pm 1\) kcal/mol \(\Delta S^* = -4.7 \pm 4\) eu
computed rate of 1.2 s\(^{-1}\) for the 2D EXSY experiments using the quantification method discussed above. The exchange rates obtained at other temperatures by the line-shape-analysis study referred to (45) are consistently slightly more that would be predicted by this study. Based on the excellent agreement in the Eyring plots, this would seem to be a temperature measurement discrepancy.

The study done in reference 45 was performed by Matt Clarke. Clarke’s study yielded exchange rates consistent with a temperature approximately 2.2 °C warmer than the study reported here. This temperature measurement discrepancy may be attributable to decoupler heating. Clarke’s work made use of a 10 millimeter probe on both a JEOL-90 and a Varian VXR-300. In Clarke’s experimental description, it is mentioned that when using the Varian VXR-300 with the 10 mm probe, the temperature increase when using the proton decoupling was less than 1°C. The effect of proton decoupling using the 10 mm probe in the Varian VXR-300 has since been found to increase the temperature of the probe between 2 and 3°C depending on the VT temperature.

The study reported here made use of the VXR-300 5mm probe. The temperature measurement was done using a methanol chemical shift thermometer. This type of temperature measurement makes use of the fact that the peak
separation in the proton spectrum of neat methanol is
temperature dependent. The Varian VXR-300 software has a
macro called TEMCAL(M) which determines the temperature of
the sample using the chemical shift difference in the two
methanol \(^1\text{H}\) peaks. This has been shown to be a reliable
measurement of temperature (52). Proton decoupling cannot
be used during the proton acquisition, therefore one is
unable to reproduce the exact conditions under which the
exchange spectra are acquired. However, for the purpose of
temperature measurement, the neat methanol sample was
subjected to a 15 minute \(^{13}\text{C}\) experiment using normal \(^1\text{H}\)
decoupling. This experiment was immediately followed by a 1
transient proton spectrum. The proton spectra consistently
revealed a temperature variation of less than 0.5 °C. The 5
mm probe used in this study requires lower power \(^1\text{H}\)
decoupling than the 10 mm probe, thus the temperature is not
raised as much as when using the 10 mm probe. This data
implies that Clarke's temperature measurements were off by
approximately 2.2 °C.

The 2DEXSY experiment, employing pure absorption phase
cycling, is a reliable and convenient method for studying
exchanges in complicated systems. It provides for accurate
determination of exchange rates, and elucidates all the
exchanges occurring in a multiple site exchange system. The
absolute value mode 2DEXSY spectra have much poorer
resolution, thus providing less reliable integration, resulting in less accurate quantification of the exchange rates.

The development of the 2DEXSY experiment, as described above, was necessary for this reported study of exchange processes in alkyllithium compounds. Throughout this study 2DEXSY has proved invaluable in two ways. 1) Quantification of exchange rates which are too slow to be monitored by line-shape analysis, and 2) the definitive elucidation of complex exchange patterns by a single experiment.

**Experimental**

**Sample preparation.** All of the NMR spectra discussed above were produced by a single sample contained in a sealed 5 mm NMR tube. The preparation of this tube is explained below.

Due to the reactive nature of alkyllithium compounds, all manipulations of the solutions discussed below were performed in an argon filled drybox. This drybox was equipped with a purification system through which the atmosphere of the box was continuously circulated. This purification system consisted of a copper column filled with alternating layers of molecular sieves (Fisher Scientific, type 5A) and Alpha De-Ox oxygen removal catalyst. The oxygen removal catalyst was regenerated as needed by passing
a stream of 7% hydrogen and 93% argon through it. The water was removed from the molecular sieves during each catalyst regeneration by heating the purification system to 230°C under vacuum.

The synthesis of tert-butyllithium proceeded according to equations 22 through 25 shown below:

\[
\begin{align*}
\text{ROH} + \text{HCl} & \rightarrow \text{RCl} + \text{H}_2\text{O} & \text{[22]} \\
\text{RCl} + \text{Mg} & \rightarrow \text{RMgCl} & \text{[23]} \\
2\text{RMgBr} + \text{HgCl}_2 & \rightarrow \text{R}_2\text{Hg} + \text{BrMgCl} & \text{[24]} \\
\text{R}_2\text{Hg} + 2\text{Li} & \rightarrow 2\text{RLi} + \text{Hg} & \text{[25]}
\end{align*}
\]

In these four reactions the \( \text{R} \) is the tert-butyl group. The procedures used in each of these reactions are discussed below.

The tert-butyl group was provided by tert-butanol (Aldrich 99.9%) and the first step in the synthetic process was a halogenation reaction. In this reaction 105.6 grams of tert-butanol (1.43 mols) was mixed with an 173.8 grams (1.43 mols) of a 30% HCl solution. This mixture was shaken in a separatory funnel for 10 minutes and allowed to stand until two distinct layers were apparent. The bottom layer, containing the tert-butyl chloride, was collected and washed with two 50 ml portions of deionized water. After washing, the crude product was distilled at atmospheric pressure with
the fraction boiling at 50°C being collected and dried over anhydrous magnesium sulfate. The yield of product was 108.3 grams (1.17 mols), which translates to a 82 % yield. A $^{13}$C NMR spectrum revealed two resonances at 59.4 ppm and 32.1 ppm. These chemical shifts are in agreement with previously reported values (53).

The second step in the synthetic process proceeds according to equation 23 above. For this synthesis a 3000 ml 3-necked flask was fitted with a Friedrichs condenser, an addition funnel, and a mechanical stirrer. This glassware had been previously heated in an oven to 200°C and then assembled hot, under an argon flow. After the glassware had cooled under the argon flow, 24.3 grams of magnesium turnings were placed in the flask. The magnesium turnings had previously been washed with a 30% HCl solution, followed by two washings with deionized water, decanting the water off each time. The magnesium was rinsed last with acetone and blown dry with argon gas. This washing process removed any oxidized surface on the magnesium allowing the reaction between the tert-butyl chloride and the magnesium turnings to proceed. A small amount of iodine crystals was added to the magnesium and vaporized with a heat gun. To the flask was then added 1500 ml of anhydrous ether, which had been previously distilled from LiAlH$_4$. A solution composed of 80 grams (0.81 mols) of tert-butyl chloride and 100 ml of the
dry ether was then placed in the addition funnel. The reaction flask was heated slightly with a heating mantel and 10 ml of the tert-butanol/ether solution was added to the flask to initiate the reaction. A reaction was evident by a change in color and the boiling of the reaction mixture. Knowing that the reaction had begun, the remaining tert-butanol/ether solution was then added dropwise through the addition funnel with the total addition requiring 50 minutes. The reaction mixture was refluxed an additional 85 minutes after which the mixture was observed to be a dirty gray color with some unreacted magnesium in the bottom of the flask. The flask was sealed with glass plugs and parafilm and allowed to settle overnight. The next morning the reaction mixture was transferred to a second 3000 ml 3-necked flask using argon pressure and a double ended canula to avoid exposing the Grignard reagent to the atmosphere. A 65% yield of Grignard was assumed.

Bis(tert-butyl)mercury was synthesized according to equation 24 above. Due to the toxicity of bis(alkyl)mercury compounds, the synthesis and manipulation of these compounds was done in a fume hood and all glassware exposed to these compounds was rinsed in concentrated nitric acid before being removed from the hood. The procedure followed for the synthesis of bis(tert-butyl)mercury is the general procedure for bis(alkyl)mercury compound synthesis outlined by Nesmeyanov (54). Gould pioneered the use of Grignards in
bis(alkyl)mercury compounds but his yields were low due to the formation of alkyl mercury halides (55). Excess Grignard reagent, slow addition of HgCl₂, prolonged reaction times, and dilute solutions have been shown to favor the formation of the bis(alkyl)mercury compound over the alkylmercury halide, thus improving yields and purity of the product (56).

The reaction apparatus consisted of a 3000 ml 3-necked flask to which was attached a soxhlet extractor and a mechanical stirrer. A Freidrichs condenser with an argon gas inlet was attached above the soxhlet extractor. As in the previous reactions, all glassware was heated in an oven to 200°C and assembled under an argon flow. A 62 grams (0.23 mols) portion of HgCl₂ was placed in the thimble of the soxhlet extractor. In the flask was the Grignard/ether solution from the previous reaction containing approximately 1800 ml of dry ethyl ether and 0.53 mols of the tert-butyl Grignard (assuming a 65% yield from the previous reaction). The mercuric chloride was extracted into the flask over a 44 hour period. After this time period the reaction mixture appeared as a milky white solution. To the reaction mixture was then added approximately 1000 ml of saturated ammonium chloride solution for the purpose of quenching the excess Grignard reagent. A visible reaction occurred verifying that the Grignard was in excess. The reaction mixture was
transferred to a separatory funnel and allowed to stand until two distinct layers were apparent. These two layers were collected in separate flasks. The aqueous portion was washed 3 times with ethyl ether and the ether added to the organic layer previously collected from the separatory funnel. The organic layer was then washed 3 times with 150 ml portions of deionized water, with this water being added to the previously collected aqueous layer. The aqueous portion was placed in aqueous mercury waste bottles for waste collection. The organic portion was stored overnight over magnesium sulfate in a 3000 ml 1-necked flask which was wrapped in aluminum foil and placed in a refrigerator. The following day the ether was removed by roto-evaporation, with the mercury compound remaining in the flask.

The mercury compound itself was a white crystalline material. A $^{13}$C NMR spectrum of this white crystalline substance in CDCl$_3$ showed $^{13}$C resonances at 60.3 ppm and 31.2 ppm, which is in agreement with reported values (57). Both of these carbons showed $^{199}$Hg satellites with the carbon alpha to the mercury having $J(^{13}$C-$^{199}$Hg) equal to 732 Hz. This coupling value confirms the product to be bis(tert-butyl)mercury as opposed to the tert-butylmercuric chloride whose alpha carbon coupling would be around 1500 Hz (57). The bis(tert-butyl)mercury was purified by sublimation at 40°C and 1 µtorr. The sublimations yielded 25.3 grams of
bis(tert-butyl) mercury.

The final synthetic step was the lithiation reaction shown in equation 25 above. A reaction mixture to bring about this reaction was prepared in the following manner: 9.8 grams (0.031 mols) of the bis(tert-butyl)mercury was placed in a 100 ml Erlenmeyer flask equipped with a vacuum stopcock assembly. On the vacuum line, 50 mls of cyclopentane (Aldrich 99%, which had recently been distilled from LiAlH₄) was cryopumped into the Erlenmeyer flask containing the bis(tert-butyl)mercury. This solution was degassed on the vacuum line using the freeze-pump-thaw method, and then carried into the argon filled dry box. Inside the glove box, 1.0 gram (0.17 mols) of the lithium metal was prepared for the reaction by pounding it into flat sheets and then cutting these sheets into squares whose sides were approximately 2mm in length. This was done in order to expose as much surface area as possible of the lithium metal. The lithiation reaction, in this case, made use of natural abundance lithium which had previously been determined to be 95.5% ⁷Li and 4.5% ⁶Li (58). These squares of lithium were placed into a reaction vessel which had previously been prepared. This reaction vessel was a cylindrically shaped glass container with a 14/20 male ground glass joint to which a vacuum stopcock may be attached. After the lithium was placed in the reaction
vessel, the bis(tert-butyl)mercury/cyclopentane solution was added via pipette to the reaction vessel. The reaction vessel was then removed from the drybox and placed on the vacuum line where it was again degassed by the freeze-pump-thaw method. This vessel was then flame sealed and shaken on the shaker table for eleven days. After this time period the vessel still contained approximately 30% of the unreacted bis(tert-butyl)mercury. The presence of unreacted bis(tert-butyl)mercury led to the addition of 0.75 grams (0.125 mols) of lithium to the solution and another eight days on the shaker table. At the completion of this time period there remained no more unreacted mercury compound in the vessel.

Removal of the cyclopentane left a yellowish solid. This solid was sublimed at 1 \( \mu \)torr and 70°C on the vacuum line resulting in 1.13 grams (0.18 mols) of a white crystalline material. The \(^{13}\)C NMR spectrum of this material in cyclopentane solution showed \(^{13}\)C resonances at 10.7 ppm and 32.6 ppm, in agreement with the reported values for tert-butyllithium (23). No shifts corresponding to bis(tert-butyl)mercury or tert-butoxide were observed. The 1.13 grams of tert-butyllithium translates to a post-sublimation yield of 29% based on the amount of mercury compound used. The solid tert-butyllithium was stored in an Erlenmeyer flask, fitted with a glass plug, and placed in
the glove box. This was the tert-butyllithium source from which the NMR tube used in this study was prepared.

The solution used in the NMR tube was prepared by reacting tert-butyllithium with tert-butanol to bring about the reaction shown in equation 17. This reaction was accomplished as described below.

In the drybox, a tert-butyllithium solution was prepared in a 5mm NMR tube by dissolving 0.071 grams (1.1 mmols) of tert-butyllithium in 0.35 ml of cyclopentane. A second solution containing tert-butanol was prepared by mixing 0.012 grams (0.16 mmols) of tert-butanol in 0.35 ml of cyclopentane. The tert-butanol solution was then added slowly, via syringe, to the NMR tube containing the tert-butyllithium. A reaction was evident by a small amount of heat being generated upon addition of the tert-butanol. The mixing of these two solutions resulted in a 5 mm NMR tube which contained, based on the monomer, 0.94 millimols of tert-butyllithium and 0.16 millimols of tert-butoxide lithium. The resulting solution was 1.3 F based on the tert-butyl groups and the lithium. In this study, sample tubes are often referred to by their oxygen to lithium ratio, which in this case would be 1 to 7. The NMR tube was then fitted with a stopcock assembly, removed from the drybox, and placed on the vacuum line. After degassing the tube with three freeze-pump-thaw cycles, the tube was flame sealed and allowed to warm to room temperature.
The cyclopentane solvent used for the NMR sample was a mixture of 92 % cyclopentane (Wiley Organics 99.9%) and 8 % $d^{10}$ cyclopentane (MSD Isotopes 98.8% D). The $d^{10}$ cyclopentane was incorporated into the solvent for the purpose of locking and shimming the NMR magnet.

NMR spectra. All of the NMR spectra discussed above were obtained on a Varian VXR 300 FT-NMR spectrometer. The $^7$Li resonance frequency at this magnetic field strength is 116.6 MHz. The one-dimensional $^7$Li-$^1$H spectra shown, were typically acquired using the following parameters. A 90° pulse of 7.4 μs was used along with an acquisition time of 6.8 seconds. The number of data points collected was 3000, resulting in a data point density of 0.15 Hz/data point over a 500 Hz spectral width. Sufficient signal could be obtained in 4 scans. No resolution enhancement was used in the Fourier transform of the FID.

As discussed above two different types of 2D EXSY spectra were obtained. The absolute value mode 2D EXSY were run with 4 scans for each of 128 increments. A 90° pulse of 7.4 μs was used for each of the three pulses. The spectrum was obtained over 230 Hz in both dimensions with a 1024 data point acquisition time of 2.2 seconds. A relaxation delay was used, the value of which was dependent upon the $T_1$'s of the $^7$Li's, making it different for each temperature used. Typically a delay of three times the $T_1$ was used. Prior to
Fourier transform, the F1 dimension was zeroed filled to 256 points and the F2 dimension was zeroed filled to 2K. No resolution enhancement was used. Mixed times were different for each 2DEXSY as shown in Table 2.

The pure absorption 2DEXSY were obtained using 16 scans for each increment as required by the phase cycling employed. Pulse widths, spectra widths, relaxation delays, and mix times were typically the same as used for the absolute value spectra. Data processing was somewhat different from the absolute value 2DEXSY spectra as increments were obtained in two different sets as described by States (49). These two sets on the pulse sequence EXSY2D are P1 and P2 and are Fourier transformed separately. These two sets of data are then combined in the second Fourier transform. The macro used to carry out the process of Fourier-transformation of the two phases and then combine them for the second transform was WFT2DA.

Temperature Measurement. The temperature of the NMR 5 mm probe was measured using a methanol chemical shift thermometer (52). The process involved setting the variable temperature controller to the desired temperature with the methanol sample in the probe. After the controller reached the desired temperature a proton spectrum was obtained and the macro TEMCAL(M) used to obtain temperature. This routine makes use of the fact that the peak separation of the proton shifts in methanol is temperature dependent.
Cursors are placed on the two peaks and the difference between the two cursors is used by the computer to relate that difference to the temperature required to bring about that peak separation. The temperature of the methanol was allowed to equilibrate over a minimum of 15 minutes until no further change in temperature was detected by the methanol chemical shift thermometer. This temperature measuring process was repeated before each experiment and often upon concluding the experiment. The temperatures upon experiment conclusion typically differed by no more than 0.1 °C from the temperature upon beginning the experiment.

D2DNMR. Over the course of this research two different computers were used in the running of the D2DNMR program. Initially the University of North Texas' VAX main-frame computer was utilized. The program was later modified for Microsoft FORTRAN (44) and run on the group PC, a Gateway 2000 80386/25.
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66


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45. Thomas, R. D.; Clarke, M., unpublished results.
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CHAPTER 3

LITHIUM tert-BUTOXIDE/tert-BUTYLLITHIUM MIXED HEXAMERS

Introduction

Alkyllithium compounds have proven to be very useful in organic and organometallic syntheses (1). Fraenkel stated in a recent review that they, "form the largest single group of synthetically useful organometallic compounds" (2). Despite their widespread use in synthesis, the nature of alkyllithium compounds in solution is not well understood (3). Although some monomeric alkyllithium compounds can be prepared (4) (5), they most commonly exist in a variety of aggregation states, \((\text{RLi})_n\), where \(n = 2, 3, 4, 6, 8, \text{ or } 9\) (6). In hydrocarbon solutions, aggregation states ranging from dimer, \((\text{RLi})_2\), (7) (8) to nonamer, \((\text{RLi})_9\), (9) have been reported.

Historically, much work has centered around the study of aggregation states and the effect that the aggregation state may have on reactivity. Before widespread usage of FT-NMR spectroscopy, the aggregation states of these compounds were routinely determined using colligative measurements (10) (11) (12) (13). A difficulty arises in using colligative properties to determine aggregation
states when two or more different aggregation states are present in solution. The development of FT-NMR gave rise to experiments which not only are able to determine aggregation states, but provide information concerning the exchange processes these compounds undergo.

The use of $^6$Li-enriched lithium in the preparation of alkyllithium compounds has enabled researchers to make use of $^{13}$C-$^6$Li coupling to determine aggregation state (9) (14). This has been done by observing the multiplicity of the $\alpha$-carbon and using the equation $p = 2mI + 1$ to determine the number of $^6$Li's to which the $\alpha$-carbon is bonded (15). In this equation $m$ = the number of coupled $^6$Li nuclei, $I$ = the spin of the nuclei causing the observed coupling (in this case $^6$Li, which has a spin of 1), and $p$ = the number of peaks in the multiplet. The value of the observed coupling has been used to determine aggregation state of some alkyllithium compounds, according to the formula

$$J_{\text{obs}} = \frac{(17 \pm 2 \text{ Hz})}{m}$$

[26]

where $m$ is the number of equivalently bonded $^6$Li nuclei (16) (17). This equation, however, has been shown to be unreliable for many alkyllithium compounds, especially those which form aggregation states other than hexamers and tetramers (15).
Alkyllithium aggregates are known to undergo a variety of exchange processes such as intraaggregate exchange, interaggregate exchange, and inversion at the α-carbon. These exchange processes have been the subject of a considerable amount of research and much information has come from these studies. However, much remains to be learned about the nature of these exchange processes (3). The importance of alkyllithium compounds, coupled with the large amount of mystery associated with them, led to this study of the exchange processes in alkyllithium compounds.

Exchange Processes. Intraaggregate exchange, or fluxionality, of alkyllithium aggregates has been the subject of much research. As will be discussed in chapter 4, the fluxionality of various alkyllithium tetramers has been studied (18) (19) (20) (21) (22) (23). The nature of the fluxionality of hexamers in solution, however, remains largely speculation (3).

Hexamers are known to be fluxional down to very low temperatures with no non-fluxional hexamers yet reported (3). As discussed in chapter 1, hexamers differ from tetramers in that they possess two open faces. The role of these open faces in fluxionality has been questioned and presumed to be the cause of the more rapid fluxionality of hexamers over tetramers. It has been suggested that the alkyl groups may alternately move into the open faces, each time creating a new open face, and in such a fashion chase
each other around the lithium core \( \text{(3).} \)

Brown has proposed a mechanism of hexamer fluxionality that proceeds through an intermediate in which each lithium is bonded to two \( \alpha \)-carbons and each \( \alpha \)-carbon is bonded to two lithiums creating a 12-membered ring with alternating carbon and lithium nuclei as shown in Figure 13 \( \text{(24).} \) This intermediate is similar to the planar 8-membered ring considered to be a possible intermediate in the fluxionality of tetramers \( \text{(18).} \)

Schleyer has proposed a mechanism of fluxionality based upon a molecular orbital argument in which he proposes an over-the-edge type mechanism. He suggests this to be a low-energy process available to primary alkyllithium hexamers \( \text{(22).} \)

Interaggregate exchange involving hexamers has been examined to a larger degree than hexamer intraaggregate exchange and has yielded more solid results. Brown's early work led him to postulate that hexamer dissociation may play a role in tetramer interaggregate exchange according to equation 27 \( \text{(25).} \)

\[
R_6\text{Li}_6 \rightarrow R_2\text{Li}_2 + R_4\text{Li}_4 \quad \text{[27]}
\]

Fraenkel has examined \( n \)-propyllithium hexamers and used NMR line-shape analysis to model the interaggregate exchange
Figure 13 - Twelve-membered ring proposed by Brown as a possible intermediate in hexamer fluxionality.
of these hexamers (2)(14). His studies yielded a $\Delta H^* = 4.3$ kcal and $\Delta S^* = -36$ eu. No error bounds were reported. He has also used line-shape analysis to study what he interpreted to be interaggregate exchange in 2-methylbutyllithium hexamers. The exchange rates arrived at in his line-shape analysis led to the activation parameters $\Delta H^* = 3.3 \pm 0.5$ kcal/mol and $\Delta S^* = -39 \pm 7$ eu (26).

This data led him to propose an interaggregate exchange among hexamers involving a biaggregate in which the R's are randomized in the biaggregate. This is shown in equation 28 below.

$$2R_6Li_6 \longrightarrow R_{12}Li_{12} \longrightarrow 2R_6Li_6 \quad [28]$$

**Mixed alkylolithium systems.** The use of mixed alkylolithium systems has been shown to be valuable in the study of exchange processes in alkylolithium compounds. The first report of mixed hexamers came with the mixture of ethyllithium and tert-butyllithium (27). Brown examined mixtures of trimethylsilylmethyllithium and tert-butyllithium (25) (28). His studies on this system initially supposed trimethylsilylmethyllithium to be a tetramer in hydrocarbon solution. A later follow-up report corrected this oversight to include the fact that trimethylsilylmethyllithium was actually a hexamer in
hydrocarbon solvent. His conclusions remained largely unaffected; however, the importance of this correction was established in his statement, "certainly, no more than one tert-butyl group could exist on a hexamer (25)". This statement was related to the steric bulk necessary to force alkyllithium compounds to lower aggregation states. The study reported here also relates steric bulk to the aggregation states of mixed aggregates.

Recently, mixed tetramers composed of lithium 3,5-dimethylphenolate and either lithium iodide or lithium perchlorate were studied and their fluxionalities were examined using double irradiation techniques (29). The study reported in reference 30 made use of these techniques on the $^6$Li nuclei in the slowly fluxional tetramers. Such experiments would have been useless, were it not for the non-equivalent sites brought about by the presence of the lithium iodide or the lithium perchlorate group. The reactivities of mixed tetramers containing lithium diisopropylamide have also been studied of late (30). Both of these studies indicate the usefulness of the non-equivalent sites within organolithium aggregates.

**Lithium alkoxides.** Lithium alkoxides are present in many alkyllithium systems due to their reaction with atmospheric oxygen (6) or with ether, when it is used as a solvent (31) (32). McGarrity noticed the existence of
lithium butoxides in the n-butyllithium he used as a reactant, and verified its existence by increasing the lithium butoxide concentration upon the addition of n-butanol (33). He further established the existence of other mixed aggregates on reacting the n-butyllithium with other alcohols. Thomas has investigated the existence of tert-butyllithium/lithium tert-butoxide mixed aggregates (21) and the fluxionality of the (tert-butoxide)(tert-butyl)$_3$Li$_4$ tetramer has been studied with NMR line-shape-analysis (34).

George DeLong has recently examined alkyllithium/lithium alkoxide systems and identified the mixed hexamers formed in tert-butyllithium/lithium tert-butoxide mixtures (35). These mixtures were prepared by the reaction of tert-butyllithium with tert-butanol. This reaction based on the monomer is shown in equation 29 below.

\[
(CH_3)_3Cl + (CH_3)_3COH \rightarrow (CH_3)_3COLi + (CH_3)_3CH \quad [29]
\]

Lithium tert-butoxide has recently been shown to exist as a hexamer (35) in hydrocarbon solvent when as many as five tert-butoxide groups compose a hexamer with one tert-butyl group. Mass spectrometry has revealed that pure lithium tert-butoxide exists as a hexamer in the gas phase (36). A recent X-ray crystal study of the similar compound C$_6$H$_5(CH_3)_2COLi$ has revealed it to be hexameric (37).
Recent NMR studies by George DeLong (35) indicated that the addition of sufficient tert-butanol to tert-butyllithium to produce an oxygen to lithium ratio of from 0.7/1 to 0.9/1, resulted in the formation of three types of mixed hexamers. Through various NMR experiments the composition of these mixed hexamers were determined (35). It was found that one of the three hexamers was composed of five tert-butoxide groups and one tert-butyl group. Of the five tert-butoxide groups, one was unique from the other four. This hexamer will be referred to in this chapter as the (1:4):1 hexamer.

There were two hexamers composed of four tert-butoxide groups and two tert-butyl groups. One of these two hexamers had two types of tert-butoxide groups in a ratio of 2:2. This hexamer will be referred to in this chapter as the (2:2):2 hexamer. In the third hexamer all the tert-butoxide groups were equivalent, this hexamer will be referred to in this chapter as the 4:2 hexamer.

These hexamers were studied at a range of temperatures including as low as -85°C. At all temperatures studied the α-carbons of the tert-butyl groups showed $^1\text{C}-^6\text{Li}$ coupling consistent with fluxional hexamers. This fluxionality, combined with the knowledge of the hexamer composition gave rise to some interesting questions. These questions and the answers proposed are discussed below.

This study of mixed tert-butyllithium/lithium tert-
butoxide hexamers was prompted by the information that can be gained in mixed systems as well as the importance of alkoxides in alkyllithium compounds. Mixed systems have certain non-equivalencies which can provide valuable information about the exchange processes the aggregates undergo.

Results and Discussion

In order to investigate the exchange processes which might bring about the non-equivalencies observed by DeLong (35), a sample of tert-butyllithium/lithium tert-butoxide was prepared. This sample was 2 M based on the monomer of tert-butyllithium, and was reacted with sufficient tert-butanol to produce an oxygen to lithium ratio of 0.78 to 1.

This sample tube was examined to determine if the spectra it produced were consistent with previously observed spectra in which the three hexamers discussed above were known to exist. All regions of the $^{13}$C, $^1$H, and $^6$Li spectra were consistent with a system containing the three types of hexamers observed previously (35). Variable temperature $^{13}$C spectra of the tert-butyl and tert-butoxide methyl regions are displayed in Figure 14. This region of the spectra provides a convenient monitor of the perplexing non-equivalencies observed previously. Due to the temperature
Figure 14 - Variable temperature $^{13}\text{C}$ spectra of the methyl carbon region of a lithium tert-butoxide/tert-butyllithium mixture. Concentration of the lithium species is 2 F. The oxygen to lithium ratio is 0.7 to 1.
dependent chemical shifts of some of the methyl carbons, both the high and low temperature spectra shown in Figure 14 are labeled.

There are two prominent peaks in Figure 14 which are labeled with asterisks. These peaks have been shown to be produced by aggregates whose lithiums show $^6\text{Li}-^1\text{H}$ coupling (35). The exact nature of these aggregates remains a subject of study. The peaks labeled F and L are caused by the $(\text{tert-butoxide})(\text{tert-butyl})_4\text{Li}_4$ tetramer, with the F stemming from the methyl carbons of the tert-butoxide group and the L from the methyl carbons of the tert-butyl groups. Peak B results from the methyl carbons of the tert-butoxide groups from the hexamer of composition, $(\text{tert-butoxide})_6\text{Li}_6$. Peak K is caused by the methyl carbons in the pure tert-butyllithium tetramer.

Previous work on the lithium tert-butoxide/tert-butyllithium mixture, had established which methyl groups were part of which hexamers (35). Peaks A, E, and J were identified by chemical shift comparison to the previous assignments (35), to be the methyl groups which compose the $(1:4):1$ hexamer. The intensities of these methyl peaks were found to be 1 to 4 to 1, consistent with the $(1:4):1$ hexamer formed in the earlier work.

Peaks C, G, and H had chemical shifts consistent with the three types of methyl groups which compose the $(2:2):2$
hexamer. Peak intensities showed these peaks to be in a 1 to 1 to 1 ratio. These peak intensities are consistent with the intensities expected for the (2:2):2 hexamer if relaxation rates and NOE effects for the three different types of methyl carbons are similar.

The chemical shifts of peaks E and H verify the existence of the third type of hexamer, referred to as the 4:2 hexamer. The intensity of these peaks are in a 4 to 2 ratio for C and G respectively. The $^{13}$C data thus verified the existence of all three types of hexamers observed in the earlier study. The composition data for all three hexamers are summarized in Table 5.

It is of interest to note that the $^{13}$C spectra produced peak intensities consistent with the $^1$H intensities from which the hexamer compositions were determined (35). This is indicative of the fact that the relaxation rates and NOE effects of the methyl carbons on the different groups are very similar. This fact provides evidence that the bonding within the aggregates is very similar and that the rotations of all of the methyl groups within an aggregate are similar.

The variable temperature $^{13}$C spectra shown in Figure 14 reveal that the two types of tert-butoxide groups in the (2:2):2 hexamer undergo an exchange process which brings equivalence to them. This is made evident by the fact that
Table 5

Data from $^{13}$C NMR spectra in Figure 14
tert-butyllithium/lithium tert-butoxide system*
Displaying only the methyl groups from the mixed hexamers.

<table>
<thead>
<tr>
<th>peak</th>
<th>ppm</th>
<th>intensity**</th>
<th>hexamer***</th>
</tr>
</thead>
<tbody>
<tr>
<td>tert-butoxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>35.29</td>
<td>1.4</td>
<td>(1:4):1</td>
</tr>
<tr>
<td>C</td>
<td>34.92</td>
<td>1.0</td>
<td>(2:2):2</td>
</tr>
<tr>
<td>D</td>
<td>34.75</td>
<td>2.2</td>
<td>4:2</td>
</tr>
<tr>
<td>E</td>
<td>34.72</td>
<td>5.6</td>
<td>(1:4):1</td>
</tr>
<tr>
<td>G</td>
<td>34.69</td>
<td>1.0</td>
<td>(2:2):2</td>
</tr>
<tr>
<td>tert-butyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>33.52</td>
<td>1.0</td>
<td>(2:2):2</td>
</tr>
<tr>
<td>I</td>
<td>33.08</td>
<td>1.1</td>
<td>4:2</td>
</tr>
<tr>
<td>J</td>
<td>32.48</td>
<td>1.4</td>
<td>(1:4):1</td>
</tr>
</tbody>
</table>

* Sample was prepared to be 2 F in tert-butyllithium and reacted with sufficient tert-butanol to make an oxygen to lithium ratio of .78 to 1.

** The $^{13}$C spectrum from which the integrations and chemical shifts were taken was -4.6°C

*** The assignment to a particular hexamer was done by chemical shift comparison to the work in reference 36

with increasing temperature the $^{13}$C peaks C and G broaden and disappear into the baseline. One would expect, that in a randomly fluxional hexamer all the tert-butoxide groups would be equivalent. For this reason, the high temperature equivalency observed for peaks C and G is not surprising. However, these hexamers are fluxional at all temperatures
studied, therefore, the low temperature fluxionality must not be random. The observation of this exchange led to the speculation that perhaps other exchanges indicative of random fluxionality were occurring slow enough to not be apparent from viewing the line shapes.

In order to investigate slow exchanges which might be occurring, a $^{13}$C 2DEXSY experiment was run on this sample at +20.8°C. This spectrum is shown in Figure 15. Several exchanges are revealed in this spectrum. It is revealed that the tert-butyl methyl carbons of the (2:2):2 (peak H) hexamer are exchanging with the tert-butyl methyl carbons of the 4:2 hexamer (peak I). Careful observation of traces in the tert-butoxide methyl region also reveals that the tert-butoxide methyl carbons of the (2:2):2 hexamer (peaks C and G) are exchanging with the tert-butoxide methyl carbons of the 4:2 hexamer (peak D). This exchange is difficult to observe in the contour plot, due to the line-broadening occurring at the C and G peaks. These two exchanges indicate that a slow intraaggregate exchange is occurring which, if fast, would bring equivalence to these two hexamers of identical composition. This equivalence is what would be predicted from a randomly fluxional hexamer.

A third exchange revealed in the 2DEXSY spectrum shown in Figure 15 is the exchange between the two types of tert-butoxide methyl carbons in the (1:4):1 hexamer (peaks A and
Figure 15 - $^{13}$C-2DESY spectrum at +20.8 °C of the methyl region of the tert-butyllithium/lithium tert-butoxide mixture. Oxygen to lithium ratio is 0.78 to 1. Total concentration of lithium species is 2 F.
E). This exchange, if fast, would bring about equivalence between the tert-butoxide groups in this hexamer. As stated above, for the hexamers composed of four tert-butoxide groups and two tert-butyl groups, this exchange is what would be expected of randomly fluxional hexamers. These hexamers were shown to be fluxional down to −85 °C, whereas all of the non-equivalencies of similar groups within the same hexamer discussed above remained non-equivalent up to 0°C. And all but the non-equivalence between the two types of tert-butoxide groups in the (2:2):2 hexamer existed up to +40°C.

All of this data points to two types of fluxionality occurring in these hexamers. The fluxionality that continues to −85 °C is a 'limited' fluxionality. The term 'limited' meaning that groups are not randomly distributed about the hexamer. The fluxionality which is occurring slowly in these hexamers is a random fluxionality which does distribute the tert-butoxide and tert-butyl groups randomly throughout the hexamer. This exchange is revealed by the 2D EXSY spectrum. The 2D EXSY spectrum did not reveal any type of interaggregate exchange occurring in these hexamers. Another exchange not revealed in the 2D EXSY experiment is an exchange between tert-butoxide groups and tert-butyl groups. This fact eliminates the unlikely exchange in which dissociation between carbon and oxygen occurs in the
fluxionality process.

Questions that arise from this data are: 1) since these hexamers remain fluxional at low temperatures, why are there two different types of hexamers composed of four tert-butoxide groups and two tert-butyl groups? and 2) why are there two different types of tert-butoxide groups in the fluxional (2:2):2 hexamer and (1:4):1 hexamer. The answers to these questions were the beginning of a break-through in the understanding of hexamer fluxionality.

The information provided by this mixed hexamer system provides the first clues about the nature of hexamer fluxionality. A heretofore unknown limited fluxionality to account for the hexamers observed is discussed below.

Random fluxionality is the term used in this study to refer to a random scrambling of the tert-butyl and tert-butoxide groups about the hexamer. Although fast random fluxionality did not occur in these hexamers, this system does provide valuable information about the nature of this process.

Limited Fluxional Exchange. The data discussed above is interesting due to certain NMR non-equivalencies observed. These non-equivalencies are revealed through $^{13}$C spectra of both the $\alpha$-carbon and the methyl carbon regions. Proton spectra of the methyl proton region also reveal these same non-equivalencies.
Any fluxionality process proposed to account for the limited fluxionality must take into account all of the evidence observed. Not only must the non-equivalencies discussed above be accounted for, but the process must be such that all lithiums in a given hexamer must be equivalent. This is shown by the fact that there is only one $^6$Li resonance for each hexamer. Likewise the process must allow for each $\alpha$-carbon in a hexamer to migrate over the hexamer in a way in which it becomes bonded to each lithium over a period of time. This migration allows for the coupling consistent with fluxional hexamers, as is observed for the $\alpha$-carbons of the tert-butyl groups.

**Limited Fluxionality of the (tert-Butoxide)$_2$(tert-butyli)Li$_6$ Hexamer.** The (1:4):1 hexamer is depicted in Figure 16. In this figure, and the others in this chapter, the 'C' represents the tert-butyl groups and the 'O' represents the tert-butoxide groups. This hexamer is composed of one tert-butyl group and five tert-butoxide groups centered around the six lithium core. Crystal studies of several organolithium hexamers have revealed that in the solid state, the open faces are opposite each other (38) (39), therefore Figure 16a depicts the hexamer in such an arrangement.

A simpler representation of this hexamer is shown in Figure 16b. In this representation the tert-butyl groups
Figure 16 - Hexamer of composition (tert-butoxide)$_5$ (tert-butyl)Li$_6$. 16a displays the hexamer in the octahedral structure. 16b displays the hexamer in a simplified hexagonal structure.
and the tert-butoxide groups (represented by C's and O's respectively) are arranged in a hexagon. Such an arrangement is roughly a projection of the tert-butoxide and tert-butyl groups. The lines connecting them are not meant to signify bonds, but simply make the figure more easily understood. This type of figure is used below to diagram the limited fluxionality.

Figure 16a clearly reveals that in a non-fluxional hexamer there would be three types of tert-butoxide groups. In Figure 16a these three types are labeled x, y, and z. The tert-butoxide groups labeled x are bonded to two lithiums which are bonded to the tert-butyl group, the tert-butoxide groups labeled y are bonded to one lithium which is bonded to the tert-butyl group and the tert-butoxide group labeled z shares no lithiums with the tert-butyl group.

In Figure 16b the tert-butoxides are labeled according to their orientation relative to the tert-butyl group. Thus the tert-butoxide labeled x is referred to as ortho to the tert-butyl group, while the tert-butoxide groups labeled y and z are referred to as meta and para, respectively.

A fast randomly fluxional hexamer would render all tert-butoxide groups in a hexamer equivalent. NMR spectra of this hexamer undergoing fast random fluxionality would show only one $^{13}$C resonance for the tert-butoxide methyls and only one resonance for the tert-butoxide $\alpha$-carbons. As
shown in Figure 14 this is not consistent with what is observed.

The observed data suggests a non-random fluxionality must be occurring to bring about the equivalence that is seen in the NMR spectra. Fluxionality is known to be occurring in this hexamer by the fact that the α-carbon on the tert-butyl group shows coupling to six equivalent lithiums. Therefore this non-random or limited fluxionality must be a process that allows each group to migrate over the entire hexamer.

Since the most stable geometric arrangement of alkyl lithium compounds in the solid state is with the open faces opposite each other, a reasonable assumption might be that the lowest energy exchange would maintain this geometry. This restriction upon the fluxionality demands that as a group migrates into the open face, the group opposite the migrating face must simultaneously migrate to the other open face. This type of exchange is depicted in Figure 17. In this figure, the five tert-butoxide positions are numbered 1 through 5. Before the exchange occurs, the tert-butoxide groups labeled 1 and 5 occupy sites ortho to the tert-butyl group. The tert-butoxide groups labeled 2 and 4 occupy sites meta to the tert-butyl group and the tert-butoxide group labeled 3 occupies the site para to the tert-butyl group.

The structure on the right represents the arrangement
Figure 17 - The \((\text{tert-butoxide})_5(\text{tert-butyl})\text{Li}_6\) hexamer undergoing the limited fluxionality.
of the groups after the exchange has occurred. The post-exchange environments of the tert-butoxide groups labeled 1 and 5 are meta the tert-butyl group and the tert-butoxide groups 2 and 4 are now ortho to the tert-butyl group. Thus, this exchange brings equivalence between the ortho and meta positions in this hexamer. The tert-butoxide group labeled 3, however, remains para to the tert-butyl group throughout the exchange.

As this limited fluxionality continues, it will bring about equivalence between all the lithiums in a given hexamer, and cause the α-carbon on the tert-butyl group to be bonded to all six lithiums thus showing fluxional hexamer coupling values and multiplicities. However, the tert-butyl group and the tert-butoxide groups are not randomly dispersed over the hexamer by this process. While allowing the tert-butyl and tert-butoxide groups to migrate over the entire hexamer, this limited fluxionality maintains groups opposite each other.

To examine all structural possibilities of such an exchange process, one need only consider those structures which maintain opposite groups. This may most easily be done using the simplified representations as shown in Figure 18. The exchanging of groups opposite to each other is not the limited fluxionality process itself, but simply allows for the viewing of all possible structures from the limited fluxionality process.
Figure 18 uses the simplified representations to examine the permutations arising from the limited fluxional exchange process. In process A of Figure 18, the tert-butoxide which is para the tert-butyl group (labeled 3) exchanges positions with the tert-butyl group. This exchange leaves the environment of 3 unchanged but converts the tert-butoxide groups, labeled 1 and 5, from an ortho position to a meta position. Likewise the 2 and 4 groups are converted from the meta to the ortho positions. Process B in Figure 18 exchanges the tert-butoxide position 1 with the tert-butoxide position 4. The environments of 2, 3, and 5 are left unchanged by this exchange, but the tert-butoxide group labeled 1 exchanges from an ortho position to a meta position while the tert-butoxide group labeled 4 exchanges from a meta position to an ortho position. Process C has similar results with group 5 exchanging from an ortho to a meta position and group 2 exchanging from a meta to an ortho position. The environment of the tert-butoxide group labeled 3 does not change throughout any of the exchanges, but remains para the tert-butyl group.

Using this type of approach it becomes apparent that this limited fluxional exchange brings about equivalence between the tert-butoxide groups which are ortho the tert-butyl group and those which are meta the tert-butyl group. This is made evident by the fact that this limited fluxionality causes the tert-butoxide groups 1, 2, 4, and 5
Figure 18 - The simplified representation displaying the structural possibilities of the \((\text{tert-butoxide})_3(\text{tert-butyl})\text{Li}_6\) hexamer undergoing the limited fluxionality.
to interconvert between the ortho and meta positions.

In a $^{13}$C NMR spectrum, the chemical shifts of the methyl carbons of the tert-butoxide groups 1, 2, 4, and 5 would be the weighted average between the chemical shifts they would possess in a rigid structure at ortho and meta positions respectively. Likewise the chemical shifts of the quaternary carbons of these groups would be at a weighted average between the quaternary carbon of the group in the ortho position and the quaternary carbon of the group in the meta position.

The tert-butoxide group which is para the tert-butyl group (labeled 3 in the figure) is, in every structure, unique from the other two types. The chemical shift of the methyl carbons of the tert-butoxide group labeled 3 is thus different from the methyl carbons of the tert-butoxide groups at the 1, 2, 4, and 5 positions. Likewise, the chemical shift of the quaternary carbon of the tert-butoxide groups labeled 3, is different from the chemical shift of the quaternary carbons of the tert-butoxide groups at the 1, 2, 4, and 5 positions. The $^{13}$C spectrum of the methyl groups in the tert-butoxide region would thus be consistent with the observed spectrum, which is, as shown in Table 5, two types in a ratio of 4 to 1.

Although reference has been made to the $^{13}$C spectra of the methyl carbon region and the $\alpha$-carbon region, $^1$H and $^6$Li
spectra are also consistent with this limited fluxional exchange as shown in Table 6. This table summarizes the

Table 6

\[ {}^1\text{H}, \, {}^{13}\text{C}, \, \& \, {}^6\text{Li} \]
NMR Equivalencies
Theoretical and Observed*
For the 5:1 Hexamer

<table>
<thead>
<tr>
<th></th>
<th>Fluxionality</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rigid</td>
</tr>
<tr>
<td>tert-butoxide</td>
<td></td>
</tr>
<tr>
<td>( \alpha-{}^{13}\text{C} )</td>
<td>3(2:2:1)</td>
</tr>
<tr>
<td>methyl ( {}^{13}\text{C} )</td>
<td>3(2:2:1)</td>
</tr>
<tr>
<td>methyl ( {}^1\text{H} )</td>
<td>3(2:2:1)</td>
</tr>
<tr>
<td>tert-butyl</td>
<td></td>
</tr>
<tr>
<td>( \alpha-{}^{13}\text{C} )</td>
<td>1</td>
</tr>
<tr>
<td>methyl ( {}^{13}\text{C} )</td>
<td>1</td>
</tr>
<tr>
<td>methyl ( {}^1\text{H} )</td>
<td>1</td>
</tr>
<tr>
<td>( {}^6\text{Li} )</td>
<td>2(3:3)</td>
</tr>
</tbody>
</table>

*The numbers outside the parentheses are the numbers of non-equivalent sites. The numbers inside the parentheses are the mathematical ratio of the non-equivalent sites.

equivalencies expected for this hexamer if it were rigid, randomly fluxional, or undergoing the limited fluxionality and compares these three situations with the spectra that are observed.

Limited Fluxionality of the (tert-butoxide),(tert-
**butyl_Li Hexamer.** The hexamers with the composition \((\text{tert-butoxide})_4 (\text{tert-butyl})_2 \text{Li}_6\) may occur in three forms, these are shown in Figure 19. Figure 19 contains both the hexameric structure and the simplified structure used previously in Figure 18. In this study, these three forms of this hexamer will be referred to as ortho, meta, and para as shown in Figure 19.

Figure 20 uses the simplified structures to depict the permutations that arise upon the ortho hexamer undergoing the limited fluxional exchange. Since the two tert-butyl groups in these hexamers will be equivalent to each other in every structure, the concern will be focused on the tert-butoxide groups. The positions the tert-butoxide groups may occupy are labeled in the initial structure as 1, 2, 3, and 4. As in Figure 18, to examine the possible structures that may arise from the limited fluxionality, opposite groups may be exchanged. This process does not represent the limited fluxional exchange, but simply reveals the structures which may result from this exchange. There are two types of tert-butoxide groups in the initial structure. One type occupies the positions 1 and 4, the other 2 and 3. Upon undergoing the process A, a new hexamer arises. This hexamer is the meta hexamer. In this hexamer the tert-butoxide groups labeled 1 and 4 are no longer equivalent. Process B converts the environment of position 1 to that of position 4.
Figure 19 - The (tert-butoxide)$_4$(tert-butyl)$_2$Li$_6$ hexamers represented in both the octahedral and hexagonal structures.
Figure 20 - The ortho isomer of the 4:2 hexamer undergoing the limited fluxional exchange.
and vice versa. Process C returns the hexamer to the ortho structure. Other exchanges may be examined but the results are the same. The limited fluxional exchange as applied to this hexamer will always result in the ortho or meta structure.

The tert-butoxide groups labeled 2 and 3 always occupy equivalent positions under the application of the limited fluxional exchange. The tert-butoxide groups labeled 1 and 4 are non-equivalent in the meta hexamer, with both groups, over a time period, occupying either of the two non-equivalent positions, thus resulting in the same environment for positions 1 and 4.

The tert-butoxide groups labeled 2 and 3 are equivalent with each other in every structure, thus there methyl carbons possess the same chemical shifts. Likewise the methyl protons and the quaternary carbons of 2 and 3 occupy identical environments and have the same chemical shift.

The tert-butoxide groups labeled 1 and 4 occupy the same three environments, one from the ortho hexamer and two environments which they share in the meta hexamer. Thus the chemical shifts for their methyl carbons is an average between the methyl carbons in these three sites. The quaternary carbons are likewise an average between the quaternary carbons at these three sites. Proton spectra of the methyl groups will also be averaged in a similar manner for both the 1 and 4 tert-butoxide groups. If this exchange
is fast on the NMR time scale, NMR will be unable to
distinguish between the ortho and meta hexamers; therefore,
in this study, they are referred to collectively as the
ortho/meta hexamer.

This is consistent with the NMR spectra for the (2:2):2
hexamer in that there is only one $^{13}$C resonance in the tert-
butyl methyl region that is produced by these hexamers, as
well as one resonance produced by their tert-butyl $\alpha$-
carbons. These hexamers do produce two $^{13}$C resonances for
the methyl carbons of the tert-butoxide groups, these being
the positions 1 and 4 and positions 2 and 3 as predicted by
Figure 19. It is important to note that no matter how fast
this limited fluxionality occurs, the para hexamer does not
become equivalent with the ortho/meta hexamer. Nor do
positions 2 and 3 become equivalent with positions 1 and 4.

Table 7 summarizes the expected and the observed NMR
data for the ortho/meta hexamer. The expected equivalencies
for a rigid system are not listed in Table 7 because
specifying an ortho/meta hexamer makes the data for a rigid
system non-applicable.

In viewing Figure 19, it may be observed that the para
hexamer would be unaffected by the permutations as shown in
Figure 20. In the only structure that may arise for this
hexamer undergoing the limited fluxional exchange, all tert-
butoxide groups are equivalent, as are both tert-butyl
Table 7

$^1$H, $^{13}$C, & $^6$Li
NMR Equivalencies
Theoretical and Observed*
For the ortho/meta hexamer

<table>
<thead>
<tr>
<th></th>
<th>Fluxionality</th>
<th>Random</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Limited</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tert-butoxide</td>
<td>2(2:2)</td>
<td>1</td>
<td>2(2:2)</td>
</tr>
<tr>
<td>$\alpha^{-13}$C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>methyl $^{13}$C</td>
<td>2(2:2)</td>
<td>1</td>
<td>2(2:2)</td>
</tr>
<tr>
<td>methyl $^1$H</td>
<td>2(2:2)</td>
<td>1</td>
<td>2(2:2)</td>
</tr>
<tr>
<td>Tert-butyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha^{-13}$C</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>methyl $^{13}$C</td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>methyl $^1$H</td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$^6$Li</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*The numbers outside the parentheses are the numbers of non-equivalent sites. The numbers inside the parentheses is the mathematical ratio of the non-equivalent sites.

groups. This is consistent with the observed spectra resulting from the 4:2 hexamer. The expected and observed NMR data for the para hexamer is summarized in Table 8.

The Limited Fluxional Exchange Process. The study of this system is not consistent with Brown's twelve-membered ring intermediate as shown in Figure 13 (18). This intermediate would indeed allow migration of the tert-butyl and tert-butoxide groups over the entire hexamer, thus
Table 8

$^1H$, $^13C$, & $^6Li$
NMR Equivalencies
Theoretical and Observed*
For the Para Hexamer

<table>
<thead>
<tr>
<th>Fluxionality</th>
<th>Limited</th>
<th>Random</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tert-butoxide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha-^{13}C$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>methyl $^{13}C$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>methyl $^1H$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Tert-butyl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha-^{13}C$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>methyl $^{13}C$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>methyl $^1H$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$^6Li$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

*The numbers are the numbers of non-equivalent sites.

resulting in hexameric coupling of the $\alpha$-carbons and bringing about the equivalence of all the lithiums in a given hexamer. However, fluxionality which proceeded through this intermediate would allow scrambling of the tert-butyls and tert-butoxides. Therefore, the 1:5 hexamer would show only 1 type of tert-butoxide group as shown in Table 7 under the random fluxionality column.

If fluxionality occurred through Brown’s intermediate there would only be one type of hexamer composed of four
tert-butoxide groups and two tert-butyl groups. Although fluxionality through the twelve-membered ring may occur slowly in this system, this study reveals there must also be another fluxionality, such as the limited fluxionality, occurring fast on the NMR time scale.

Lipscomb in his work on carboranes has examined the intramolecular exchange processes of icosahedral complexes (40) (41). In his work he proposed a mechanism whereby an ortho carborane could be isomerized to a meta carborane but not to the para carborane via a cuboctahedral intermediate. He referred to this mechanism as the "diamond-square-diamond" mechanism. This mechanism was later tested on ortho-\( \text{C}_2\text{B}_{10}\text{H}_{12} \). It was found that when this compound was heated to 465 °C that rearrangement occurred only to the meta isomer (42). In a separate work the para isomer was later found to be formed in a small yield upon heating the ortho isomer to 615 °C (43). Lipscomb’s proposal of this mechanism was based in part on the small distances which atoms would be required to move to convert one isomer to another. This exchange process is shown in Figure 21 for the for \( \text{C}_2\text{B}_{10}\text{H}_{12} \). In Figure 21 the vertices which do not contain a 'C' are BH groups and the vertices containing a 'C' represent CH\(_2\) groups. In this figure the ortho compound isomerizes to the meta compound via the 'diamond-square-diamond' mechanism.
Figure 21 - The ortho isomer of \( \text{C}_7\text{B}_{10}\text{H}_{12} \) undergoing the diamond-square-diamond isomerization.
When comparing the icosahedral carborane complex to a lithium hexamer certain similarities become apparent. The alkyl lithium hexamer when considering lithiums and the quaternary carbons takes the geometry of a distorted icosahedron. The \((\text{tert-butoxide})_4 \text{ortho (tert-butyl)}_2\text{Li}_6\) hexamer discussed above, is shown undergoing this type of rearrangement in Figure 22. The geometric structure is similar to the boranes but the bonding is somewhat different; therefore, Figure 22 is different from Figure 21 in that lines which might indicate bonding between the quaternary carbons and/or the oxygens have not been drawn. Some lines are drawn between lithiums to simplify the diagram but not to indicate lithium-lithium bonding.

In this rearrangement, a carbon (or an oxygen) detaches from a lithium and moves across the open face to bond to the opposite lithium. While this occurs, a similar process must occur at the other open face. If the two processes did not occur simultaneously, one lithium would be left bonded to only two carbons while another would become bonded to 4 carbons. This rearrangement of the \((\text{tert-butoxide})_4 \text{ortho (tert-butyl)}_2\text{Li}_6\) hexamer yields only the meta hexamer and not the para hexamer.

The bonding is different from the carborane icosahedral complex, but the geometric shape is similar. Certainly Lipscomb’s proposal of small atom movements causing
Figure 22 - The ortho isomer of \((\text{tert-butoxide})_4(\text{tert-butyl})_2\text{Li}_4\) hexamer undergoing a form of the diamond-square-diamond isomerization.
isomerization would seem to be a possibility in this alkyllithium hexamer.

Such an exchange mechanism may be consistent with Schleyer’s over-the-edge mechanism (22). However, he suggested this exchange mechanism would be a low energy process only for those alkyllithium compounds in which the α-carbons were bonded to at least two protons. To undergo this exchange mechanism, two of the groups bonded to the α-carbons must point along the face of the hexamer. If these groups were large, this process would be difficult due to steric hindrance between these two groups and the lithium core. In the mixed hexamers composed of tert-butyl and tert-butoxide groups, the oxygens from the tert-butoxide groups possess only one group of steric bulk and thus would accommodate this exchange process. However, for fluxionality to occur by this process, the tert-butyl groups must also migrate over-the edge. This would seem to contradict Schleyer’s reasoning behind this exchange process. If this mechanism is active in these hexamers, then the steric problems Schleyer discussed for secondary and tertiary alkyllithium compounds are not as important as he perceived. A possible explanation of this discrepancy is the ioniticity of the alkyllithium compounds. If these compounds involve an exchange process in which the compounds are largely ionic, the steric interaction upon moving over-the-edge may not occur.
If this mechanism is occurring in this system, then the new data presented here puts the stipulation on the process that groups must move over-the-edge in pairs. A group would migrate into the open face while simultaneously the group opposite the migrating group would move into the other open face. This requirement is necessary in order to maintain the non-equivalencies observed in the $^{13}$C spectra. Schleyer's over-the-edge mechanism is based on molecular orbital arguments and would not be valid in a system which is primarily ionic. If alkylolithium systems are primarily ionic, it is unclear how this ioniticity would affect an over-the-edge movement.

The possibility of migration of only the tert-butoxide groups while holding the tert-butyl groups meta to each other would not allow the $\alpha$-carbons on the tert-butyl groups to migrate over the entire hexamer and would also maintain the tert-butoxide groups opposite them in their respective positions. These restrictions are not consistent with the observations discussed above.

The limited fluxionality as described above is the fluxionality most consistent with the observed NMR spectra. A mechanism such as Lipscomb's icosahedral "diamond-square-diamond" mechanism (40)(41) would account for such an exchange process. This mechanism may proceed by an over-the-edge migration in which the exchange intermediate is
largely ionic. Brown’s twelve-membered ring intermediate would not account for the NMR spectra observed (24). This limited fluxionality will be discussed further in chapters 4 and 5.

Random Fluxionality. Past work that has been done on the investigation of the nature of fluxionality in alkyl lithium hexamers has assumed that the fluxionality is random (3). As shown above, a fast random fluxionality is not consistent with the hexamers observed in this mixed alkyl lithium/ lithium alkoxide system. Further studies on this system have yielded the elucidation of a random exchange process occurring slowly on the NMR time scale.

As discussed in chapter 2, 2D EXSY is ideally suited to examine multi-site exchange processes which are slow on the NMR time scale. The random fluxionality of the hexamers discussed above was examined using $^{13}C$ 2D EXSY spectroscopy. In order to achieve the best possible resolution in a two-dimensional spectrum, a small spectral width is chosen. To examine the entire $^{13}C$ spectrum of this system at 75 MHz would require a spectral width of approximately 4000 Hz. Achieving a reasonable resolution over such a wide spectral width would require an extremely large amount of time. For this reason, a relatively small region of the spectrum was examined using 2D EXSY.

Several regions of the spectra could be examined, such
as the α-carbon region of the tert-butyl groups or the quaternary carbon region of the tert-butoxide groups. The region that will give the strongest signal for a given amount of transients, as well as the most information in the smallest spectral width, is a region that includes the methyl carbons of both the tert-butyl groups and the tert-butoxide groups. A $^{13}$C 2D EXSY spectrum of this region is shown in Figure 15.

The exchanges revealed by the 2D EXSY spectrum show a slow exchange bringing equivalence to all sites in hexamers of the same composition. Exchange is not observed between any tert-butoxide methyls with tert-butyl methyls, revealing the tert-butoxide moieties move over the faces intact, with no dissociation between the α-carbons and the oxygen of these groups.

Two-dimensional exchange spectroscopy provided an ideal method for studying these exchange processes using the D2DNMR computer program for quantification, as described in chapter 2. A temperature study of exchange was performed on this system using 2D EXSY. The results of this study on the exchange between the ortho/meta tert-butyl methyl carbons and the para tert-butyl methyl carbons is shown in Table 9. This exchange is the exchange between the two types of hexamers which possess the composition (tert-butoxide)$_4$ (tert-butyl)$_2$Li$_6$. 
Table 9

Exchange rates of the tert-butyl methyl carbons of the ortho/meta hexamer with the tert-butyl methyl carbons of the para hexamer*

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$t_m$ (s)</th>
<th>Temperature (°C)</th>
<th>Rate ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP317C</td>
<td>0.40</td>
<td>38.3</td>
<td>1.76</td>
</tr>
<tr>
<td>DP315C</td>
<td>0.50</td>
<td>33.4</td>
<td>1.28</td>
</tr>
<tr>
<td>DP312C</td>
<td>0.75</td>
<td>29.5</td>
<td>0.92</td>
</tr>
<tr>
<td>DP309C</td>
<td>1.00</td>
<td>25.3</td>
<td>0.57</td>
</tr>
<tr>
<td>DP307C</td>
<td>1.00</td>
<td>20.8</td>
<td>0.38</td>
</tr>
<tr>
<td>DP303C</td>
<td>1.30</td>
<td>14.9</td>
<td>0.14</td>
</tr>
</tbody>
</table>

* This sample was 2F in the tert-butyl group and the lithium. It possessed an oxygen to lithium ratio of 0.78 to 1

$\Delta H^\ddagger = 18.6 \pm 1.5$ kcal/mol

$\Delta S^\ddagger = 5 \pm 5$ eu

Shown in Table 10 are the exchange rates for the two types of tert-butoxide methyl carbons in the (tert-butoxide)$_5$(tert-butyl)Li$_6$ hexamer as revealed by the $^{13}C$ 2DEXSY experiments. This exchange is the exchange which, if fast, would make all the tert-butoxide sites in this hexamer equivalent. This exchange, as the exchange in the (tert-butoxide)$_4$(tert-butyl)$_2$Li$_6$ described above, is a random fluxionality.

The temperature range at which these exchanges can be monitored is limited at the high temperature end by vapor pressure of the solvent in the sealed NMR tube. The lowest temperature at which exchanges may be monitored is limited
Table 10

Exchange rates of the
two types of tert-butoxides
in the 5:1 hexamer*

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$t_m$ (s)</th>
<th>Temperature (C)</th>
<th>rate ($s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP317C</td>
<td>0.40</td>
<td>38.3</td>
<td>0.76</td>
</tr>
<tr>
<td>DP315C</td>
<td>0.50</td>
<td>33.4</td>
<td>0.53</td>
</tr>
<tr>
<td>DP312C</td>
<td>0.75</td>
<td>29.5</td>
<td>0.29</td>
</tr>
<tr>
<td>DP309C</td>
<td>1.00</td>
<td>25.3</td>
<td>0.21</td>
</tr>
</tbody>
</table>

* This sample was $2F$ in the tert-butyl group and the lithium. It possessed an oxygen to lithium ratio of 0.78 to 1.

$ΔH^* = 18.3 \pm 1.3$ kcal/mol

$ΔS^* = 3 \pm 3$ eu

by decreasing exchange rate. The exchange between the two types of tert-butoxide groups in the $(\text{tert-butoxide})_5(\text{tert-butyl})\text{Li}_6$ hexamer could not be quantitated as low in temperature as the exchange between the two types of tert-butyl groups in the hexamers with the composition $(\text{tert-butoxide})_4(\text{tert-butyl})_2\text{Li}_5$, due to the slightly slower exchange in the 5:1 hexamer.

The Eyring plots of the data from Tables 6 and 7 are shown in Figure 23. The error bounds quoted for the activation parameter reflect only the deviation from the line using a least-squares fitting routine and are at one standard deviation. The error bounds probably underestimate the actual error due to the small temperature range over
Figure 23 - Eyring plots of exchanges in Tables 5 and 6. NMR sample is 2 F based on the lithium species and the oxygen to lithium ratio is 0.78 to 1.
which the data was acquired.

An important point to consider in this random fluxionality is the fact that the tert-butoxide groups of the ortho/meta hexamer exchange more quickly with each other than the ortho/meta hexamer exchanges with the para hexamer. This is borne out in two observations. The first observation is qualitative and comes from examining the variable temperature $^{13}$C shown in Figure 14. It is apparent from viewing these spectra that the peaks corresponding to the two types of tert-butoxide groups in the ortho/meta hexamer (peaks B and E in Figure 14) broaden with increasing temperature and actually disappear into the baseline by $+40^\circ$C. The tert-butoxide group from the para hexamer does not appear to broaden at all. Chemical shift differences cannot account for this difference in broadening, as the chemical shift of the tert-butoxide methyl carbons from the para hexamer, is closer to the shifts from the ortho/meta hexamer tert-butoxide methyl carbons than the ortho/meta tert-butoxide methyl carbons are to each other. Thus the line-broadening effect should be greater on the peak from the para hexamer than on either of the peaks from the ortho/meta hexamer if the exchanges between them are the same.

This qualitative approach may not be valid however, due to the fact that the coalescence peak from the ortho/meta
peaks should have a chemical shift of 34.91 ppm. This shift is very close to the shift of the tert-butoxide group from the para hexamer. If the exchange between the two types of tert-butoxide groups was only slightly faster than their exchange with the para tert-butoxide group the normal broadening effect might be altered.

Quantitatively, the exchange rate necessary to coalesce the peaks from the two types of tert-butoxide groups in the ortho/meta hexamer should correspond to their difference in chemical shift according to equation 30 shown below (44).

\[
k_c = \pi (v_a - v_b)/2^{1/2}
\]

This formula computes an exchange rate of 43 s\(^{-1}\) necessary to coalesce these two peaks, using the difference in their chemical shifts at -15°C as their non-exchange shifts. From the spectra shown in Figure 14, one observes these peaks are definitely lost in the baseline at +40°C, indicating their exchange rate at this temperature is slightly below the coalescence rate. The exchange rate between the two types of tert-butyl groups for the hexamers composed of four tert-butoxides and two tert-butyls at this temperature however, is less than 2 s\(^{-1}\) according to the 2DEXSY spectra. This indicates the exchange between the two types of tert-
butoxide groups in the ortho/meta hexamer is indeed faster than their exchange with the one type of tert-butoxide group in the para hexamer.

The findings of this study provide much information about the nature of random fluxionality. In describing random fluxionality, one must consider several facts brought forth by this study. The first fact to be considered is the preference of the tert-butoxide groups over the tert-butyl groups for random distribution in the hexamers composed of four tert-butoxide groups and two tert-butyl groups. This may be a result of the less steric hindrance at the oxygen of the tert-butoxide groups over the carbon at the tert-butyl groups.

Another important consideration is the fact that the random distribution of the tert-butoxides in the hexamer composed of five tert-butoxide groups and one tert-butyl group is slower than both the randomizing of the four tert-butoxide groups in the ortho/meta hexamer, and the randomizing of all six groups in the hexamers composed of composed of four tert-butoxide groups and two tert-butyl groups.

The activation parameters reported here are the first for the random fluxional exchange process. Fraenkel in his study of 2-methylbutyllithium reported activation parameters for inversion at the α-carbon of $\Delta H^* = 15.6 \pm 1.1 \text{ kcal/mol}$
and $\Delta S^* = -0.6 \pm 3$ eu for (R)-2-methylbutyllithium and $\Delta H^* = 14.8 \pm 1$ kcal/mol and $\Delta S^* = -3 \pm 3$ eu for a racemic mixture of 2-methylbutyllithium (26).

The similarities of Fraenkel's activation parameters for inversion at the $\alpha$-carbon of 2-methylbutyllithium, with those for random fluxionality of the hexamers in this study, indicate that perhaps the process bringing about inversion at the $\alpha$-carbon of 2-methylbutyllithium is the same as the process that causes this random fluxionality in these hexamers. Fraenkel's assumption that 2-methylbutyllithium underwent interaggregate exchange down to $-60$ °C (26) was in error. In fact, as will be discussed in chapter 5, interaggregate exchange of 2-methylbutyllithium decreases to the slow limit at approximately the temperature where he saw inversion at the $\alpha$-carbon decrease to the slow limit. Therefore, his data on 2-methylbutyllithium may not be valid.

The type of process which best fits with this data on random fluxionality is a concerted over the edge movement of the tert-butoxide and the tert-butyl groups with the preference being toward the tert-butoxide groups due to less steric hindrance. This process need not involve all six groups of a hexamer but may involve as many as four. Although the tert-butoxide groups are randomly distributed more readily than the tert-butyl groups, having five tert-
butoxides on the hexamer, as opposed to four, actually slightly decreases the rate of random fluxionality.

Experimental

Sample Preparation. The tert-butyllithium used in this study was prepared via the bis(tert-butyl)mercury compound as explained in chapter two. The lithium metal used in the lithiation reaction for the samples discussed in this chapter was "Li-enriched lithium. The isotopic abundances were "Li 95.5% and "Li 4.5% (U.S. Services). The tert-butyllithium/lithium tert-butoxide mixtures were prepared by reacting tert-butyllithium with tert-butanol in the manner described below. The solvent used in the NMR samples was 93% cyclopentane (Wiley Organics 99.9%) and 8% d\textsuperscript{10} cyclopentane (MSD Isotopes 98.8% D). Use of the deuterated solvent was for the purpose of locking and shimming the magnet.

In the argon-filled drybox, as described in chapter two, a tert-butyllithium/lithium tert-butoxide mixture was prepared by reacting 1.4 mmols of tert-butyllithium with 1.1 mmols of tert-butanol. Before mixing the tert-butyllithium with the tert-butanol, each was dissolved in 0.35 ml of the cyclopentane solvent. This solution was placed in a 5 mm NMR tube and fitted with a stopcock assembly which was then
removed from the box. The tube and stopcock assembly was then placed on a vacuum line and degassed using the freeze-pump-thaw method. After the degassing process was complete, the tube was flame sealed.

In this study of tert-butyllithium/lithium tert-butoxide mixtures, tubes are often referred to by their oxygen to lithium ratio. This tube possessed an oxygen to lithium ratio of 0.78 to 1 and was 2F based on the lithiuns and the tert-butyl groups.

**NMR Spectra.** All of the $^{13}$C spectra displayed and discussed in this chapter were acquired on the Varian VXR 300 FT-NMR and made use of the 5 mm probe. The one dimensional $^{13}$C spectra were typically acquired around the tert-butyl/tert-butoxide methyl regions, this being a region contained from approximately 32 ppm to 35.5 ppm. The chemical shifts are assigned relative to tetramethylsilane by setting the cyclopentane $^{13}$C shift to 25.8 ppm.

Typical parameters for these experiments were 256 scans, a 75° pulse of 6.4 µsec, an acquisition time of 2.4 seconds, a sweep width of 430 Hz, 4096 data points collected, and a spin rate of 15 Hz. The data point density was typically, approximately 0.42 Hz/data point. The number of data points was zero filled to twice the number of data points before Fourier transformation. No line broadening was used in these spectra.
The 2D EXSY spectra acquired were run on the same region of the spectra, thus the spectral width is also approximately 430 Hz. A 90° pulse of 8.5 \( \mu \)seconds was used for all three pulses in the 2D EXSY pulse sequence. The 16 scans required by the phase cycling were sufficient to obtain a satisfactory signal-to-noise ratio. The number of increments used in these experiments was 128. Prior to Fourier transformation, the \( F_1 \) dimension was zero-filled to 256 points and the \( F_2 \) dimension was zero-filled to 2K data points.

A relaxation delay was used to insure relaxation of the observed nucleus after each scan. This delay is dependent upon the \( T_1 \) of the nucleus which in turn is dependent upon the temperature, therefore this delay was different for each experiment. A delay of twice the \( T_1 \) was used to insure relaxation of most of the nuclei. Typical values for the relaxation delay ranged from five to ten seconds. The unrelaxed magnetization was subtracted by the phase cycling used. For a discussion of the \( t_{mix} \) times used in the 2D EXSY experiments, see text.

Although 2D EXSY spectra are symmetric about the diagonal, for accurate quantification unfolded spectra must be used to obtain relative intensities (45). Therefore the spectra were examined without folding.

Temperature Measurement. The temperature of the NMR 5
mm probe was measured using a methanol chemical shift thermometer as described in chapter 2.
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CHAPTER 4

tert-BUTYLLITHIUM/n-ALKYLLITHIUM MIXTURES

Introduction

With the success of the study of lithium tert-butoxide/tert-butyllithium mixtures in chapter 3, it became apparent that the non-equivalencies observed within mixed hexamers provides an excellent monitor for the exchange processes these hexamers undergo. The advantage of mixed systems in the investigation of alkyllithium compounds stems from certain non-equivalencies observed. Introducing one unique group into an alkyllithium aggregate, introduces non-equivalence which is valuable in the elucidation of structures of the aggregates and, exchange processes which may occur in these aggregates.

The observance of the limited fluxional exchange in the mixed hexamers in chapter 3 provides much information about the nature of hexameric intraaggregate exchange processes. The hexamers in chapter 3, however, may not be representative of alkyllithium hexamers in general, due to the presence of the tert-butoxide groups within these hexamers. It might be suggested that the limited fluxional exchange is a process peculiar to alkoxide containing hexamers. If such is the case, the role of the open faces
in alkyllithium hexamer fluxionality is left unexplained (1). The reason for hexamer fluxionality being much faster than tetramer fluxionality would also remain a mystery.

In order to investigate the possibility of the limited fluxional exchange being an exchange process available to alkyllithium hexamers composed of only alkyl groups or a process peculiar to tert-butyllithium/lithium tert-butoxide mixed hexamers, a study of mixed alkyllithium compounds was undertaken. This chapter makes use of the straight chain alkyl groups, n-propyl and n-butyl, to determine whether hexamers similar to the lithium tert-butoxide/tert-butyllithium mixed hexamers will form. The steric requirements of these straight chain alkyllithium compounds should provide for the formation of hexamers, much like the tert-butoxide group, but the electronic factors of the alkyl groups differ greatly from those of the tert-butoxide group. This comparison will provide evidence for whether this exchange is available to tert-butyllithium mixed hexamers in which the hexamer contains at least four non-bulky groups, or whether the electronic factors of the oxygen play a part in promoting this exchange. The results of this study are contained in this chapter.

The value of using mixed alkyllithium systems to investigate the structure and exchange properties of organolithium compounds was first recognized by Weiner and West (2). This study was followed by Brown’s investigation
of tert-butyllithium/trimethylsilylmethyllithium mixtures (3)(4). Mixed aggregates were observed in Brown's study including possibly a mixed hexamer. More recently mixtures of lithium 3,5-dimethylphenolate with either lithium iodide or lithium perchlorate were used to characterize exchanges in tetramers (5). The importance of mixed aggregates in reactions of lithium alkylamides has also been examined of late (6)(7)(8).

**tert-Butyllithium.** tert-Butyllithium has long been known to exist as a tetramer in hydrocarbon solvent (9)(10). Upon the addition of tert-butanol to tert-butyllithium, lithium tert-butoxide is produced (11). If less than a one to one mol ratio of tert-butanol to tert-butyllithium is reacted, mixed aggregates, containing both tert-butyl and tert-butoxide groups are formed. These aggregates range from a tetramer of composition \((\text{tert-butoxide})\text{tert-butyl})_3\text{Li}_4 (11)\) to hexamers composed of \((\text{tert-butoxide})_4 (\text{tert-butyl})_2\text{Li}_6\) and \((\text{tert-butoxide})_5(\text{tert-butyl})\text{Li}_6 (12)\). This indicates that the presence of at least four tert-butoxide groups are necessary to allow the incorporation of tert-butyl groups into a lithium tert-butoxide/tert-butyllithium mixed hexamer.

The relieving of steric hindrance by the tert-butoxide group should not be peculiar to alkoxides. It is known that many alkyl lithium compounds exist as hexamers in hydrocarbon
The formation of hexamers is indicative of relief of steric hindrances in these compounds. Such alkylolithium compounds would thus be worthy of investigation in mixtures with tert-butyllithium to determine the structures of the mixed alkylolithium hexamers formed. Such systems might prove fruitful in the study of exchange processes in these alkylolithium aggregates.

\textit{n-Propyllithium} is known to exist as a mixture of hexamers, octamers, and nonamers in hydrocarbon solution \((17)(18)(19)\). This is shown by both the \(^6\text{Li}\) spectra and the \(^{13}\text{C}\) spectra. Variable temperature \(^{13}\text{C}\) spectra of \textit{n-propyllithium} in hydrocarbon solvent reveal one \(\alpha\)-carbon at room temperature which splits into five different peaks as the temperature is lowered. Variable temperature \(^6\text{Li}\) spectra are likewise one sharp resonance at high temperature which splits into five peaks at low temperature. This splitting has been attributed to the existence of \textit{n-propyllithium} as a hexamer, octamer, and three types of nonamers \((18)\). All of these aggregates are interaggregately exchanging at room temperature. This exchange slows until, at the slow limit, there is a different \(\alpha\)-carbon peak and a different \(^6\text{Li}\) peak for each type of aggregate.

Fraenkel has studied this exchange using line-shape-analysis to quantitate the interaggregate exchange among these aggregates and determined activation parameters for
this exchange to be \( \Delta H^\circ = 4.3 \text{ kcal/mol} \) and \( \Delta S^\circ = -36 \text{ eu} \) \((18)\). These activation parameters along with interaggregate exchange parameters for other alkyllithium hexamers \((20)\) led Fraenkel to propose the existence of a biaggregate of composition, \( R_{12} Li_{12} \), as an intermediate in the interaggregate exchange of alkyllithium hexamers.

An alkyl group, such as \( n \)-propyl, which provides for the formation of these higher aggregates certainly seems conducive to the formation of tert-butyllithium/\( n \)-propyllithium mixed hexamers. A study of such a mixed system has the advantage over the (tert-butoxide/tert-butyll)lithium system in that one is able to observe \( ^{13}C \)-\( ^6Li \) coupling for the \( \alpha \)-carbon of the \( n \)-propyl group, whereas the \( \alpha \)-carbon of the tert-butoxide group is bonded to oxygen and thus has no observable \( ^{13}C \)-\( ^6Li \) coupling.

*\( n \)-Butyllithium.\* \( n \)-Butyllithium is a widely used chemical reagent \((15)\). However, in comparison with other alkyllithium systems, very little has been deduced about the nature of \( n \)-butyllithium in solution. Colligative properties have been used to establish \( n \)-butyllithium as primarily hexameric in hydrocarbon solution \((21)\). More recent NMR studies have shown that at low temperature it exists as an equilibrium of hexamer, octamer, and nonamer, much like \( n \)-propyllithium \((19)\).

\( n \)-Butyllithium produces a single \( ^6Li \) resonance at room
temperature, which splits into at least three peaks at low
temperature. The $\alpha$-carbon in the $^{13}$C spectra is likewise a
single peak at high temperature which splits into at least
three peaks at low temperature (19).

By comparison with $n$-propyllithium, the three peaks are
assumed to be the lithiums from the hexamer, octamer, and at
least one kind of nonamer (19). $^{13}$C-$^6$Li coupling has not
been observed at any temperature for this compound in
hydrocarbon solvent due to its fast interaggregate exchange
(13). For this reason unambiguous assignment of the
aggregation state is not possible. However, it may be
assumed that these three peaks are the three different $n$-
butyllithium aggregation states of composition $(RLi)_6$, $(RLi)_8$, $(RLi)_9$.

The $n$-butyllithium dimer has been observed in THF
solution and the $^{13}$C-$^6$Li coupling observed to be 7.8 Hz (22).
In THF solution it was found that the tetramer existed in
equilibrium with the dimer, but $^{13}$C-$^6$Li coupling of the $\alpha$-
carbons of the tetramer was not observable, presumably due
to fast interaggregate exchange.

$^{13}$C spectra of $n$-butyllithium/tert-butyllithium mixed
systems may prove more difficult to characterize than the $n$-
propyllithium/tert-butyllithium mixed system due to the
possibility of non-observable coupling and the presence of
another $^{13}$C resonance crowding the spectra. For this reason,
in the study of these systems, \textit{n-propyllithium/tert-butyllithium} mixtures were examined first, in order to aid in the characterization of the \textit{n-butyllithium/tert-butyllithium} mixed systems.

Results and Discussion

\textit{n-Propyllithium/tert-Butyllithium Mixtures.} Shown in Figure 24 are variable temperature $^6$Li spectra of a mixture of \textit{n-propyllithium} and \textit{tert-butyllithium}. This mixture was composed of an \textit{n-propyl} to \textit{tert-butyl} ratio of 1:24 and will be referred to as the 1:24 mixture. The sample that produced these spectra was contained in a sealed 5 mm NMR tube and was 1F \textit{tert-butyllithium} in cyclopentane based on the monomer.

The spectrum in Figure 24 acquired at +23.1$^\circ$C shows one sharp peak and one broad peak. By comparison with the chemical shift of pure \textit{tert-butyllithium} in cyclopentane, the sharp peak (labeled II in the low temperature spectrum) was determined to be the \textit{tert-butyllithium} tetramer. Therefore, this peak was assigned the chemical shift of 0.2 ppm. $^6$Li chemical shifts of \textit{alkyllithium} compounds has been shown to be magnet dependent. On the VXR-300 used in this work, 0.2 ppm is the reported chemical shift of the \textit{tert-butyllithium} tetramer based upon the chemical shift of
Figure 24 - Variable temperature $^6\text{Li}$ spectra of $n$-propyllithium/tert-butyllithium mixture. Total alkyl lithium concentration = 1 F. $n$-propyl:tert-butyl = 1:24
LiClO₄ in acetone-d₆ (14). The $^{13}$C satellites of this peak at +23.1°C show $^6$Li-$^{13}$C coupling of 4.1 Hz, a value also consistent with reported data for the tert-butyllithium fluxional tetramer (11).

As temperature decreases, the broad peak at 0.40 ppm splits into two peaks whose chemical shifts are 0.50 ppm and 0.15 ppm and whose intensity ratio is 3 to 1 (these are labeled I and III respectively in the low temperature spectrum). This data is reminiscent of the $^6$Li spectra observed for the (tert-butoxide)(tert-butyl)$_3$Li$_4$ mixed tetramer as it slows from fluxional to non-fluxional (11).

This mixture was also examined using variable temperature $^{13}$C spectroscopy. These variable temperature $^{13}$C spectra, displaying only the α-carbon region, are shown in Figure 25. These spectra reveal the presence of three different α-carbons. In the figure, these are labeled A, B, and C. The α-carbon at 10.7 ppm (labeled A in the figure) has a $^{13}$C-$^6$Li coupling value of 4.1 Hz at +15°C which changes to 5.4 Hz by 0°C. Based on chemical shift and coupling values, peak A may be assigned to the α-carbons of the tert-butyllithium tetramers.

The α-carbon at 10.0 ppm (labeled B in the figure) has a $^{13}$C-$^6$Li coupling value of 5.2 Hz at +15°C which converts to 6.9 Hz by -30°C. The α-carbon at 9.8 ppm (labeled C in the figure) has a $^{13}$C-$^6$Li coupling value of 4.0 Hz at +15°C which
Figure 25 - Variable temperature $^{13}$C spectra of $\alpha$-carbon region of $n$-propyllithium/tert-butyllithium mixture. Total alkyl lithium concentration = 1 F. $n$-propyl:tert-butyl = 1:24.
changes to 5.4 Hz by -30°C. The changing in coupling values of these α-carbons in each case is indicative of an α-carbon converting from one which is bonded to four $^6$Li’s to one which is bonded to three $^6$Li’s. This effect may be produced by the fluxionality of a tetramer slowing from the fast limit to the slow limit.

Figure 26 shows the entire $^{13}$C spectrum from which the expansions of Figure 25 at 0°C were obtained. In Figure 26 the $^{13}$C resonance at 32.6 ppm is identified by its chemical shift to be the methyl carbons of the tert-butyl groups comprising the tert-butyllithium tetramer (13).

The chemical shift of the peak at 32.0 ppm suggests this peak to also be produced by methyl carbons of the tert-butyl groups. However, the fact that the shift is slightly different from the shift of the methyl carbons of the pure tert-butyllithium tetramer implies these tert-butyl groups compose a different type of aggregate than the pure tert-butyllithium tetramer.

At approximately 23.8 ppm are two resonances which are very close together in chemical shift. The chemical shifts of these peaks indicate them to be the β carbon and the methyl carbon of the n-propyl group. The fact that there is only one of each of these peaks, necessitates that there is only one type of n-propyl group. The reported chemical shift at 30 °C of these two carbons in pure n-propyllithium
Figure 26 - $^1$H spectra of n-propyllithium/tert-butyllithium mixture at $0^\circ$C displaying all chemical shifts of the compound. Mixture of 1F tert-butyllithium and 0.042F n-propyllithium. n-propyl:tert-butyl = 1:24.
in cyclopentane is 22.4 ppm and 22.3 ppm (13). The
difference between the reported shifts and the shifts of
these carbons in this tert-butyllithium/n-propyllithium
mixture suggest that, although these peaks are from carbons
comprising the n-propyl group, they are not part of a pure
n-propyllithium aggregate. Peaks in the 24 to 26 ppm region
are impurities from the cyclopentane solvent.

In sum, this data points to two types of tetramers in
solution. One of these tetramers is the tert-butyllithium
tetramer. The formation of this tetramer would be expected
with an n-propyllithium to tert-butyllithium mole ratio of 1
to 24. The other tetramer is a mixed tetramer composed of
both n-propyl and tert-butyl groups.

The assignment of the unknown tetramer as a tetramer
composed of \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) is a temptation, and
seems to be the most plausible explanation; however, all
peaks in the \(^{13}\text{C}\) and \(^6\text{Li}\) spectra cannot unambiguously be
assigned based on this data. In order to fully elucidate
the structure of the tetramers formed in the 1:24 mixture, a
second sample was prepared in a 10 mm NMR tube. As
described in chapter one, the Varian VXR-300 NMR being used
in this study has a 10 mm probe which has been modified to
allow \(^6\text{Li}\) decoupling. This modification allows numerous
experiments to be run which are essential in the elucidation
of these alkyllithium structures.
The new sample, contained in a sealed 10 mm NMR tube, was prepared to be a 1 to 2 mole ratio of \(n\)-propyllithium to tert-butyllithium and will be referred to as the 1:2 mixture. The total concentration of alkyllithium compound in the sample tube was 2.9 F. The increased amount of \(n\)-propyl relative to tert-butyl was for the purpose of increasing the amount of the unknown tetramer in solution, as well as the possible preparation of other mixed aggregates along with this tetramer.

A portion of \(^{13}\text{C}\) spectra of this sample acquired at -72.6\(^{\circ}\)C, are shown in Figure 27. The top spectrum in this figure makes use of \(^6\text{Li}\) decoupling while the bottom spectrum reveals this coupling. As can be observed in this figure, the three \(\alpha\)-carbons found in the 1:24 sample are prominent in this tube (again labeled A, B, and C), along with several other \(^{13}\text{C}\) signals showing \(^6\text{Li}\) coupling. The new aggregates will be discussed below, after the species present in the 1:24 sample have been fully explained.

The effect of decoupling the \(^6\text{Li}\) nuclei is to reduce the \(\alpha\)-carbon multiplets to singlets, thus improving resolution and signal-to-noise by concentrating the entire multiplet into one peak. In the \(^{13}\text{C}\{^6\text{Li}\}\) spectrum the observation of \(^{13}\text{C} \sim^7\text{Li}\) coupling from the tert-butyl \(\alpha\)-carbons composing tetramers somewhat obscures the tetramer \(\alpha\)-carbon region in the \(^6\text{Li}\) decoupled spectrum.
Figure 27 - $^{13}$C spectra of α-carbon region of $n$-propyllithium/tert-butyllithium mixture with (top) and without (bottom) $^6$Li decoupling. Temperature = -72.6°C. Total alkyl lithium concentration = 2.9F. $n$-propyl: tert-butyl = 1:2.
Variable temperature $^6$Li spectra, shown in Figure 28, also reveal the presence of new aggregates in the 1:2 solution. Attention will be focused initially on the species present in the 1:24 tube which are responsible for peaks I, II, and III. Peaks IV, V, VI, VII, and VIII will be explained later in this chapter.

Shown in Figure 29 is a $^{13}$C($^6$Li)–$^1$H HETCOR of this sample. This experiment was run in order that unambiguous assignment of the different $\alpha$-carbon $^{13}$C peaks to either an $n$-propyl or a tert-butyl group might be accomplished. Resolution in the $^1$H spectrum is not adequate to distinguish between different types of aggregates, however the observation of a $^1$H correlation in the HETCOR is sufficient to establish whether or not the $\alpha$-carbon is bonded to a proton. Resolution is critical in the $^{13}$C dimension; however, requiring that $^6$Li decoupling be written into the HETCOR pulse sequence. In a $^6$Li coupled $^{13}$C–$^1$H HETCOR, the two-dimensional correlations would be spread into large multiplets, thus limiting the information that could be gained from such an experiment. For the purpose of this work $^6$Li decoupling was written into the pulse sequence of a normal $^{13}$C–$^1$H HETCOR. A copy of the source code for this pulse sequence is listed in the appendix.

As is shown in Figure 29, of the three $\alpha$-carbons A, B, and C, only B (at 10.0 ppm) is correlated to a proton.
Figure 28 - Variable temperature $^6$Li spectra of $n$-propyllithium/tert-butyllithium mixture. Total alkyllithium concentration = 2.9F. $n$-propyl:tert-butyl = 1:2.
Figure 29 - $^{13}$C{^6}Li-^1H HETCOR. Temperature = -20 °C. $J_{1XH} = 120$. $D_1 = 2.00$ s. Total alkyllithium concentration = 2.9F. $n$-propyl:tert-butyl = 1:2.
Therefore peaks A and C are α-carbons from tert-butyl groups. This is consistent with the observed $^{13}$C-$^6$Li coupling constants for these three α-carbons, in that A and C had similar coupling constants at both high and low temperatures while B was consistently different from the other two.

To unambiguously assign the $^{13}$C peaks B and C, a $^{13}$C-$^6$Li HETCOR experiment was performed at -70°C on this mixture. This is an experiment, developed in our lab (14) (23) which makes use of the $^6$Li decoupler to establish $^{13}$C-$^6$Li correlations. This spectrum is displayed in Figure 30. In Figure 30 the vertical scale of the displayed spectrum was raised to a level where correlations for both the tetrameric α-carbons and the hexameric α-carbons were visible. Due to the difference in intensities of the peaks, tails of some very large correlations partially obscure the spectrum. Close examination of traces in the two-dimensional spectrum however, leave no doubt as to the assignment of the correlations. A series of false correlations resulting from a folded-in peak can be observed at approximately 14.1 ppm.

As would be expected, the $^{13}$C peak from the tert-butyl α-carbon (labeled A in the $^{13}$C spectrum) of the pure tert-butyl lithium tetramer correlates to the $^6$Li signal which corresponds to the pure tert-butyl lithium tetramer (labeled II in the $^6$Li spectrum). The n-propyl α-carbon (labeled B
Figure 30 - $^{13}$C-$^6$Li HETCOR of n-propyllithium/tert-butyllithium mixture. Total alkyllithium concentration = 2.9F. n-propyl:tert-butyl = 1:2.

D3 = 0.13 s. D4 = 0.0237 s. Temperature = -70°C

* indicates a peak which has been folded in from outside the spectral window.
in the $^{13}$C spectrum) correlates only to the $^6$Li peak labeled I while the tert-butyl \( \alpha \)-carbon labeled C correlates to both $^6$Li peaks I and III. This is indicative of a non-fluxional tetramer composed of three tert-butyl groups and one \( n \)-propyl group as shown in Figure 31.

In Figure 31 the alkyl groups \( n \)-propyl and tert-butyl are represented by P and B respectively. The lithiurns are labeled corresponding to the $^6$Li resonance they produce. It is obvious from this figure that in this single tetramer there are two types of lithiurns. The Li\( \text{III} \) is bonded to three tert-butyl \( \alpha \)-carbons while Li\( \text{I} \) is bonded two tert-butyl \( \alpha \)-carbons and one \( n \)-propyl \( \alpha \)-carbon. From this bonding scheme Li\( \text{I} \) would show correlations in the $^{13}$C-$^6$Li HETCOR with both the \( n \)-propyl \( \alpha \)-carbons and the tert-butyl \( \alpha \)-carbons of this tetramer, while Li\( \text{III} \) would correlate only to the tert-butyl \( \alpha \)-carbons of this tetramer. As shown in Figure 31 the two types of lithiurns in this tetramer are in a 3 to 1 ratio, therefore one would expect the $^6$Li resonances produced from these lithiurns to be in an approximate 3 to 1 ratio. This is what is observed in the $^6$Li spectra in that the intensities of peaks I and III are in a 3 to 1 ratio. The $^{13}$C-$^6$Li HETCOR confirms these two peaks to be the lithiurns displayed and labeled in Figure 31.

In comparing the two environments of the lithiurns in Figure 31, one would expect the Li\( \text{III} \) to have an environment
Figure 31 - The tetramer of composition: (tert-butyl)$_3$(n-propyl)Li$_4$. 
most similar to that of the lithiums in the pure tert-butyllithium tetramer. This is due to the fact that Li$^{\text{III}}$ is bonded to three tert-butyllithium $\alpha$-carbons in the non-fluxional tetramer whereas Li$^{\text{I}}$ is bonded to two tert-butyllithium $\alpha$-carbons and one $n$-propyl $\alpha$-carbon. Therefore, at temperatures at which this tetramer is non-fluxional, it would be expected that, of the two types of lithiums in the (tert-butyl)$_3$($n$-propyl)Li$_4$ tetramer, the chemical shift in the $^6$Li spectrum of Li$^{\text{III}}$ would be closer to that of the lithiums in the pure tert-butyllithium tetramer than would Li$^{\text{I}}$. This may be observed to be the case in the low temperature $^6$Li spectra shown in Figure 24 for the 1:24 mixture and in the low temperature $^6$Li spectrum shown in Figure 28 for the 1:2 mixture.

Thus it is established that at low $n$-propyl to tert-butyl ratios, the primary mixed aggregate formed is the (tert-butyl)$_3$($n$-propyl)Li$_4$ tetramer. This tetramer is also present in the 1:2 mixture along with other mixed aggregates discussed below. Two tetramers in each of these solutions have therefore been identified and the chemical shifts of the $^6$Li and $\alpha$-carbon $^{13}$C peaks corresponding to these tetramers have been established.

As shown in Figure 27, the 1:2 mixture contains ten $\alpha$-carbons aside from those accounted for by the (tert-butyl)$_4$Li$_4$ and (tert-butyl)$_3$($n$-propyl)Li$_4$ tetramers. These
are labeled D through M in the decoupled spectrum shown in Figure 27. Eight of these new peaks are shifted downfield from the tetramer α-carbons into a region contained from 12.7 ppm to 15.1 ppm, and possess $^{13}$C-$^6$Li coupling values equal to one of two values. All of the $^{13}$C resonances in the 12.7 to 15.1 ppm region of the spectrum exhibit $^{13}$C-$^6$Li coupling values equal to approximately 3.4 Hz or approximately 2.7 Hz. Table 11 tabulates each α-carbon peak with its coupling constant at -70°C.

Table 11

<table>
<thead>
<tr>
<th>peak</th>
<th>shift (ppm)</th>
<th>alkyl group</th>
<th>$^{13}$C-$^6$Li coupling constants</th>
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<tr>
<td>A</td>
<td>10.8</td>
<td>tert-butyl</td>
<td>5.4</td>
</tr>
<tr>
<td>B</td>
<td>10.1</td>
<td>$n$-propyl</td>
<td>6.9</td>
</tr>
<tr>
<td>C</td>
<td>9.9</td>
<td>tert-butyl</td>
<td>5.4</td>
</tr>
<tr>
<td>D</td>
<td>15.1</td>
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</tr>
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</tr>
<tr>
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<td>$n$-propyl</td>
<td>3.3</td>
</tr>
<tr>
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<td>$n$-propyl</td>
<td>3.4</td>
</tr>
<tr>
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<td>2.7</td>
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<tr>
<td>I</td>
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</tr>
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</tr>
<tr>
<td>M</td>
<td>8.9</td>
<td>tert-butyl</td>
<td>5.3</td>
</tr>
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</table>

* The coupling constant of peak L was not measurable due to poor resolution
The coupling value of approximately 3.4 Hz is consistent with the reported $^{13}\text{C}-^6\text{Li}$ coupling constant for hexameric $n$-propyllithium (18). Tert-butyllithium has a coupling constant of 4.1 Hz when bonded to four $^6\text{Li}$ nuclei, as in a fluxional tetramer (11). Thus, tert-butyllithium when bonded to six $^6\text{Li}$ nuclei, as in a fluxional hexamer, should show coupling equal to approximately $4.1 \times \frac{4}{6}$ (24) (25). This mathematical manipulation of coupling constants translates to a fluxional hexamer coupling of 2.7 Hz for a tert-butyl group, which is consistent with previously observed data for tert-butyl $\alpha$-carbons in lithium tert-butoxide/tert-butyllithium mixed hexamers (12). Based on coupling constants, the peaks in this region of the spectrum were assumed to be $\alpha$-carbons from $n$-propyl and tert-butyl groups composing fluxional hexamers. The ultimate assignment of the $\alpha$-carbon peaks to either an $n$-propyl group or a tert-butyl group is discussed below.

Two new peaks are also observed in the tetramer region of these spectra at 10.4 and 8.8 ppm. These peaks are labeled L and M respectively. The coupling of peak L is obscured in the coupled spectrum by the other large tetramer peaks A and B, but peak M has resolvable coupling at $-70^\circ\text{C}$ of 5.3 Hz.

The $^{13}\text{C}(^6\text{Li})-^1\text{H}$ HETCOR discussed above and displayed in Figure 29 was used to distinguish between $n$-propyl $\alpha$-carbons
and tert-butyl α-carbons in these new aggregates. In viewing the two-dimensional spectrum in Figure 29, one may establish whether or not correlations exist for the $^{13}$C peaks A, B, and C. However, due to the similarity in chemical shifts and lower intensity of the other α-carbons, the correlations may best be established in viewing a vertical projection of the two-dimensional spectrum shown in Figure 29. This projection is shown in Figure 32 along with the normal one-dimensional $^{13}$C spectrum.

The vertical projection resembles a one-dimensional $^{13}$C spectrum with the difference being peaks in the vertical projection arise due to proton correlations. Therefore the only $^{13}$C resonances which appear in the vertical projection are those with $^1$H correlations. The peaks which appear in the vertical projection of Figure 32 are thus the α-carbons from the $n$-propyl groups. Those α-carbons which do not appear in the vertical projection are those without proton correlations, which are the α-carbons from the tert-butyl groups.

The $^{13}$C$^6$Li-$^1$H HETCOR was run at -20°C, at which temperature the shifts of peaks H and I are different than they are at -70°C, the temperature at which the $^{13}$C-$^6$Li HETCOR was run. At -20°C peak I is downfield of peak H. This occurrence of this change in shift with change in temperature can be observed in variable temperature $^{13}$C
Figure 32 - Vertical projection of $^{13}\text{C}(^6\text{Li})-^1\text{H}$ HETCOR shown in Figure 29 (bottom) and the normal one-dimensional $^{13}\text{C}$ spectra at $-20^\circ\text{C}$ (top).
spectra of this sample.

From the data made available by this spectrum, it may be established that peaks B, D, E, F, G, I, and L are \( n \)-propyl \( \alpha \)-carbons and peaks A, C, H, J, K, and M are \( tert \)-butyl \( \alpha \)-carbons. This data is tabulated in Table 11 and is consistent with coupling values for \( n \)-propyl and \( tert \)-butyl \( \alpha \)-carbons as discussed above.

The \(^{13}\text{C}^{6}\text{Li HETCOR}\) shown in Figure 30 was used to determine which alkyl groups composed which aggregates. The information this spectrum furnishes is enormous. The correlations resulting from this experiment are shown in Table 12. Due to low intensity, correlations for the \(^{13}\text{C}\) resonances L and M are not displayed in Figure 30. For the same reasons, the \(^{6}\text{Li}\) resonances V and VIII do not appear to correlate with any \(^{13}\text{C}\) peak. When viewing traces from this spectrum however, it may be observed that peak M shows correlation peaks with both \(^{6}\text{Li}\) peaks V and VIII.

As shown in Table 12, the \(^{6}\text{Li}\) resonance labeled IV, is bonded to the \( n \)-propyl \( \alpha \)-carbons D and E, and the \( tert \)-butyl \( \alpha \)-carbon K. The \(^{6}\text{Li}\) resonance labeled VI is bonded to the \( n \)-propyl \( \alpha \)-carbon G and the \( tert \)-butyl \( \alpha \)-carbon J. The \(^{6}\text{Li}\) peak labeled VII is bonded to \( n \)-propyl \( \alpha \)-carbons F and I and \( tert \)-butyl \( \alpha \)-carbon H.

All of the \( \alpha \)-carbons bonded to the lithiums IV, VI, and VII exhibit coupling consistent with fluxional hexamers.
For a true composition determination of each hexamer one must determine how many of each type of α-carbon compose each hexamer. This may be done through $^{13}$C NMR by signal integration if the experiment is performed in a way in which the intensities of the $^{13}$C signals are truly representative of the numbers of carbons in each particular environment. Ordinary $^{13}$C spectra cannot normally be used for integration purposes as differences in relaxation rates and NOE effects may affect relative intensities of peaks. Relaxation rates and NOE effects for the n-propyl α-carbons on a given hexamer may be similar to each other, thus allowing them to be integrated relative to each other in any one-dimensional $^{13}$C spectrum. Likewise the tert-butyl α-carbons on a given hexamer may possess similar relaxation rates and NOE effects thus allowing their integration relative to one another. However, for true integration of all n-propyl and tert-butyl α-carbons relative to each other, a special one-dimensional experiment was performed.

A $^{13}$C NMR experiment which allows for accurate signal integration is one in which the observed nuclei are allowed to relax completely between pulses and NOE from decoupled protons is avoided. The NOE effect can be avoided by simply not decoupling the protons, but a $^1$H coupled $^{13}$C spectrum of this system would be cluttered with multiplets making integration very difficult. To avoid NOE and still obtain a
'H decoupled spectrum, one may run a 13C spectrum which only makes use of 'H decoupling during acquisition. Such an experiment results in a 'H decoupled spectrum, but does not allow time for NOE to build up and affect peak intensities.

In order to insure complete relaxation, the length of time it takes the nuclei of interest to relax must be known. For this reason a T1 study of the hexameric α-carbons in this system was performed. T1's generally decrease with decreasing temperature, therefore, to shorten

Table 12

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<th>13C peak</th>
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<tr>
<td>tert-butyl α-carbons</td>
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<td></td>
</tr>
<tr>
<td>H</td>
<td>VII</td>
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</tr>
<tr>
<td>J</td>
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<tr>
<td>M</td>
<td>V &amp; VIII</td>
<td>*</td>
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</table>

* - For the relative intensity study of peak M see text
the length of time required for this experiment, a
temperature of -80°C was chosen. The results of the T₁ study
revealed that at -80°C, the hexameric α-carbons of the n-
propyl groups consistently had T₁'s of approximately 0.6
seconds while the hexameric α-carbons of the tert-butyl
groups consistently had T₁'s of approximately 2.8 seconds.

A one-dimensional $^{13}$C experiment was performed on this
sample using a 90° pulse and a relaxation delay of 30
seconds. $^1$H decoupling was used only during the 1.5 second
acquisition time. This experiment allows reliable
integrations of the peaks by providing for relaxation of the
observed nuclei and avoiding the buildup of NOE. The
results of this experiment are tabulated in Table 12.

The evidence from all of the data combined suggests
that the $^6$Li peaks IV, VI, and VII are produced by three
different hexamers. This is established by the fact that
each of the $^6$Li peaks shows correlations in the $^{13}$C-$^6$Li HETCOR
only to carbons which exhibit fluxional hexamer coupling.
If each carbon in a hexamer is, over a period of time,
bonded to each lithium in a hexamer, then each lithium in
that hexamer should be equivalent.

Hexamer Fluixionality in n-Propyllithium/tert-
Butyllithium Mixed Hexamers. The information from the $^{13}$C-
$^6$Li HETCOR, when considered with the data from the peak
intensity experiment, allow for the determination of the
composition of each hexamer. From Table 12 the composition of the hexamer that produces the $^6$Li resonance labeled IV is comprised of five $n$-propyl groups and one tert-butyl group. The five $n$-propyl groups are divided into two types in a ratio of 4 to 1. This hexamer is thus consistent with a hexamer of composition $(\text{tert-butyl})(n$-propyl)$_5^6$Li$_6$ undergoing the limited fluxional exchange discussed in chapter 3.

The $^6$Li peaks labeled VI and VII are each produced by hexamers comprised of four $n$-propyl groups and two tert-butyl groups. The four $n$-propyl groups composing the hexamer which produces the $^6$Li peak labeled VI are all equivalent. The two tert-butyl groups which are part of this hexamer are also equivalent.

The four $n$-propyl groups which are part of the hexamer which produces the $^6$Li peak labeled VII, exist in two environments in a ratio of 2 to 2. The two tert-butyl groups which comprise this hexamer are equivalent with each other. This data is consistent with hexamers of composition $(\text{tert-butyl})_2(n$-propyl)$_4^6$Li$_6$ undergoing a fast limited fluxional exchange. The description of this exchange in these hexamers is very similar to the explanation for the limited fluxional exchange of the $(\text{tert-butoxide})_4(\text{tert-butyl})_2^6$Li$_6$ hexamers given in chapter 2. A brief summary of this exchange is presented here for the $(\text{tert-butyl})_2(n$-propyl)$_4^6$Li$_6$ hexamers.
Figure 33 shows the three types of structures possible for the hexamers of composition \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\). Figure 33 uses both the octahedral type structure and the simplified hexagonal structure to represent the ortho, meta, and para structures.

In this figure, each \(\text{n-propyl}\) group is represented by a \(P\) and each \(\text{tert-butyl}\) group is represented by a \(B\). Using the simplified structures one may quickly consider all possible structures which arise from the limited fluxional exchange by exchanging groups opposite to each other. This exchanging of opposite groups is not the limited fluxional exchange, but is used to examine all structures made possible by the limited fluxional exchange. A consideration of the permutations possible from exchanging opposite groups, reveals that the ortho and meta hexamers may convert between each other while the para hexamer does not convert to either the ortho or meta structures.

In considering the possible structures made possible by this exchange one may also notice that the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer maintains two types of \(\text{n-propyl}\) groups while the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer possesses only one type. Both of these observations are consistent with the observed data. Likewise the data for the hexamer of composition \((\text{tert-butyl})(\text{n-propyl})_5\text{Li}_6\) is consistent with the limited fluxional exchange in that there
Figure 33 - The three conformations possible for the hexamer of composition: (tert-butyl)$_2$(n-propyl)$_4$Li$_6$. 
are two types of $n$-propyl groups in a ratio of 1 to 4 composing this hexamer.

This limited fluxional exchange allows migration of the groups over the entire hexamer, thus causing the $\alpha$-carbons to be bonded to all six lithiums in a hexamer and causing the equivalence of all six lithiums in a hexamer. But the $n$-propyl and tert-butyl groups are not randomly distributed throughout the hexamer by this process. If fast random fluxionality occurred in these hexamers, there would be only one type of hexamer of composition $(\text{tert-butyl})_2(n$-propyl)$_4\text{Li}_6$, and in this hexamer all $n$-propyl groups would be equivalent as would be all tert-butyl groups. Likewise there would be only one type of $n$-propyl group in the hexamer of composition $(\text{tert-butyl})(n$-propyl)$_5\text{Li}_6$. Consequently, this data for these hexamers is not consistent with a hexamer undergoing fast random fluxionality.

It is of interest to note the chemical shifts of the $\alpha$-carbons from these hexamers. The assignment of the peaks according to the limited fluxional exchange is supported by the internal consistency of the chemical shifts of the individual $\alpha$-carbons.

Due to the chemical shifts of the $(\text{tert-butyl})(n$-propyl)$_5\text{Li}_6$ hexamer in comparison with the $(\text{tert-butyl})_2(n$-propyl)$_4\text{Li}_6$ hexamers it would seem that the presence of tert-butyl groups on a hexamer shift the $\alpha$-carbons of the $n$-
propyl groups upfield. This is logical, as the shift of the α-carbons of the pure n-propyllithium hexamer is reported to be 16.1 ppm (13). For this reason the most downfield peaks observed for the α-carbons of these mixed hexamers are the two types of n-propyl α-carbons in the (tert-butyl)(n-propyl)₅Li₆ hexamer. These α-carbons comprise the hexamer possessing the least number of tert-butyl groups and thus the hexamer most similar to a pure n-propyllithium hexamer.

Of the two types of n-propyl α-carbons in this (tert-butyl)(n-propyl)₅Li₆ hexamer, one type is always opposite the tert-butyl group. The other type, consisting of the other four n-propyl groups, exchanges between two different environments. In one of these environments the n-propyl group is adjacent to one n-propyl group and one tert-butyl group. In the other environment the n-propyl group is adjacent to two n-propyl groups. Of these two types of n-propyl groups, the most downfield of these would be the n-propyl groups with the least tert-butyl influence, which is the n-propyl always opposite the tert-butyl. This is consistent with the observed shift of this carbon of 15.1 ppm. This is very close to the shift of the pure n-propyllithium hexamer as might be expected, as the influence of the tert-butyl group on this n-propyl group would be minimal.

There are three different n-propyl environments for the
hexamers of the composition \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\).

These three environments are depicted in Figure 34 using the simplified model of the hexamer. It may be observed that structure \(P_x\) which originates from the ortho/meta hexamer, exchanges between two structures only one of which puts it adjacent to one tert-butyl. \(P_x\) would then have the least amount of association with the tert-butyl group and thus be the most downfield of the three. \(P'_x\), which originates from the para hexamer, exists in a single environment adjacent to one \(n\)-propyl and one tert-butyl resulting in \(P'_x\) being shifted upfield from \(P_x\). \(P'_x\), which originates from the ortho/meta hexamer, exchanges between three environments one of which is adjacent to two tert-butyl groups, thus making it the most upfield of the \(n\)-propyls.

The argument presented above for the two types of \(n\)-propyl groups in the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer (\(P'_x\) and \(P'_y\)) cannot be completely established, as it cannot be determined which of these two carbons produces peak F and which peak I. However the chemical shift argument is consistent for the other \(n\)-propyl groups and is presented for these two as a possibility.

The shifts of the \(\alpha\)-carbons of the tert-butyl groups is also internally consistent with the limited fluxional exchange. The tert-butyl group of the \((\text{tert-butyl})_2(\text{n-propyl})_5\text{Li}_6\) hexamer possesses the least amount of
Figure 34 - The three possible environments of the $n$-propyl groups in the hexamers of composition (tert-butyl)$_2$(n-propyl)$_4$Li$_6$. 
association with another tert-butyl group since it is the only tert-butyl group on this hexamer. The \( \alpha \)-carbon of this tert-butyl group is the most upfield of the hexameric \( \alpha \)-carbons leading to the assumption that association with another tert-butyl group has the effect of shifting a tert-butyl \( \alpha \)-carbon downfield.

The tert-butyl groups of both the para \((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6\) hexamer, and the ortho/meta \((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6\) hexamer, exist in hexamers in which there is another tert-butyl group. The presence of this tert-butyl group results in the shifting these \( \alpha \)-carbons downfield from the \((\text{tert-butyl})(n\text{-propyl})_3\text{Li}_6\) hexamer.

The two tert-butyl groups in the para \((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6\) hexamer are always opposite each other. This results in neither of the \( \alpha \)-carbons from these groups ever being bonded to a lithium which is simultaneously bonded to another tert-butyl \( \alpha \)-carbon. Thus, the influence of the tert-butyl groups on each other is slight relative to the ortho/meta hexamer and results in the shift of the tert-butyl \( \alpha \)-carbons from this hexamer being upfield from the tert-butyl \( \alpha \)-carbons of the ortho/meta hexamer.

The tert-butyl groups of the ortho/meta \((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6\) tert-butyl hexamer exist in an environment which is the average between two exchange structures, one of which positions the two tert-butyl groups
adjacent to each other. Thus the tert-butyl α-carbons of the ortho/meta $(\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6$ hexamer are the most downfield of the two types of tert-butyl α-carbons in the hexamers of composition $(\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6$.

The $(\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_4$ Mixed Tetramer. Peaks L and M from the $^{13}\text{C}$ spectrum shown in Figure 27 and peaks V and VIII in the $^6\text{Li}$ spectrum shown in Figure 28 are the last to be explained. Peak L at 10.5 ppm is prominent in the $^6\text{Li}$ decoupled spectrum but is difficult to observe in the coupled spectrum. The changing of this peak from a sharp singlet in the low temperature $^{13}\text{C}[^6\text{Li}]$ spectrum to a broad peak in the low temperature $^{13}\text{C}, ^6\text{Li}$ coupled spectrum confirms it to be an α-carbon. Unfortunately the magnitude of the coupling is impossible to measure due to poor resolution between this multiplet and the multiplets from the more intense tetramer α-carbon peaks. In the $^{13}\text{C}[^6\text{Li}]-^1\text{H}$ HETCOR, this peak showed a proton correlation, marking it as an $n$-propyl α-carbon. Peak L could not be assigned to a specific $^6\text{Li}$ peak with the $^{13}\text{C}-^6\text{Li}$ HETCOR, presumably due to the low intensity of the peak.

Peak M at 9.5 ppm is similar to peak L in that it broadens with increasing temperature and shows $^6\text{Li}$ coupling. This peak shows no $^1\text{H}$ correlation in the $^{13}\text{C}[^6\text{Li}]-^1\text{H}$ HETCOR establishing it as a tert-butyl α-carbon. Measurable coupling of 5.4 Hz is observed at $-70^\circ\text{C}$ for this peak. This
coupling is consistent with the coupling of the tert-butyl α-carbons from the non-fluxional tert-butyllithium tetramer and the non-fluxional \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) tetramer. This coupling value suggests this peak to originate from a third type of tetramer. In viewing traces of the \(^{13}\text{C}^{-6}\text{Li}\) HETCOR, correlations between peak M and the \(^6\text{Li}\) peaks V and VIII may be observed.

Although unambiguous assignment of these peaks cannot be made, some clues to the aggregate from which they originate are worthy of consideration. Peak M is shown to be an α-carbon from a tert-butyl group which is bonded to two types of lithiums. This carbon has measurable coupling at \(-70^\circ\text{C}\) consistent with a non-fluxional tetramer. This peak cannot be caused by the tert-butyl α-carbons comprising either the pure tert-butyllithium tetramer or the tetramer of composition \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) as the chemical shifts for the α-carbons of these tetramers has already been established. The only other mixed tetramers which might be produced are tetramers of composition \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) and those of composition \((\text{tert-butyl})(\text{n-propyl})_3\text{Li}_4\). This indicates that there must be a corresponding \(n\)-propyl α-carbon for peak M. The only \(n\)-propyl peak which has not been accounted for is peak L. The presence of hexamers containing alkoxide groups formed from adventitious oxygen has been ruled out by the fact that no
$^{13}$C peak is observed downfield of 30 ppm.

Intensity determination of peaks L and M was performed as described above for the hexamers. The intensity study determined that peak's L and M are in a ratio of 1 to 1. This indicates that if these peaks are from the same tetramer, this tetramer is composed of two tert-butyl groups and two n-propyl groups.

The assumption that these two peaks comprise a tetramer of composition \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\), is consistent with chemical shift arguments. The tert-butyl α-carbons from the tetramer of composition \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) are shifted approximately 1 ppm upfield from the α-carbons of the pure tert-butyllithium tetramer. The chemical shift of peak M is approximately 1 ppm upfield from the \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) tetramer, consistent with the replacement of a second tert-butyl group with an n-propyl group.

Comparisons between the two types of n-propyl α-carbons fail to yield solid results as there is not a pure n-propyllithium tetramer for comparison, however the position of peak L is downfield of the n-propyl α-carbon from the \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) tetramer. This downfield shift is consistent with the expected shift towards the pure n-propyllithium aggregates.

The presence of this non-fluxional tetramer would lead
to the presence of two types of lithiums as displayed in Figure 35. The lithiums marked with an asterisk in Figure 35 are bonded to two n-propyl groups and one tert-butyl group. The unmarked lithiums are bonded to one n-propyl group and two tert-butyl groups.

In a non-fluxional tetramer the nearest neighbor environment of the lithiums bonded to two tert-butyl groups and one n-propyl group in a \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) tetramer is identical to the three equivalent lithiums in the \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) tetramer. Thus the chemical shifts in the \(^6\text{Li}\) spectrum for these two lithiums would be expected to be similar. The \(^6\text{Li}\) peak labeled I, is the peak in question for the \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) tetramer. The \(^6\text{Li}\) peak VIII is 0.02 ppm upfield of peak I and is one of the two peaks to which the tert-butyl \(\alpha\)-carbon M shows a correlation in the \(^{13}\text{C-}^6\text{Li}\) HETCOR. This data makes it likely that it is the peak which arises due to the unmarked lithiums in Figure 35.

The other \(^6\text{Li}\) peak to which the tert-butyl \(\alpha\)-carbon M is bonded, is peak V. If this peak is the lithium bonded to two n-propyl groups and one tert-butyl group in the \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) tetramer it would be expected to be shifted toward the pure n-propyllithium aggregates which have chemical shifts of approximately 2.0 ppm at -70°C (19). Thus the chemical shifts of the \(^6\text{Li}\) peaks V and VIII are
Figure 35 - Tetramer of composition: $(\text{tert-butyl})_2(n\text{-propyl})_2\text{Li}_4$. 
consistent with what would be expected from a \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) tetramer.

Both \(^6\text{Li}\) peaks V and VIII should show correlations with the \(\text{n-propyl} \alpha\)-carbon peak L if the assumptions about the \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) mixed tetramer is correct. The reason these correlations do not appear is a combination of intensity and coupling constants. This inconsistency in the data is discussed further in the \(\text{n-butyllithium/tert-butyllithium}\) mixed systems reported later in this chapter. The presence of the \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) mixed tetramer is further supported in the exchange process section below. All of this data combined, strongly indicates the existence of this tetramer. The aggregate composition data for the \(\text{n-propyllithium/tert-butyllithium}\) mixture is summarized in Table 13.

**Interaggregate Exchange Processes in the \(\text{n-Propyl/tert-Butyl}\) System.** Figure 28 displays variable temperature \(^6\text{Li}\) spectra of the 1:2 sample discussed above. Peaks I and III are coalesced at room temperature into one broad peak. Between +23.0°C and -27.2°C, this peak separates into peaks I and III which possess an intensity ratio of 3 to 1. As described above, this is consistent with the fluxionality of the \((\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4\) tetramer slowing to the non-fluxional limit with decreasing temperature. This exchange process is discussed later in this chapter.
At 23.0°C, peaks IV, V, VI, VII, and VIII are all coalesced into one peak. This is consistent with these aggregates participating in interaggregate exchange. At -27.2°C, peak VI becomes sharp. This peak correlated with the alkyl groups making up the para \((\text{tert-butyl})_2(n-\text{propyl})_4\text{Li}\) hexamer, indicating that the para \((\text{tert-butyl})_2(n-\text{propyl})_4\text{Li}_6\) hexamer reaches the slow limit of interaggregate exchange before either the ortho/meta \((\text{tert-butyl})_2(n-\text{propyl})_4\text{Li}_6\) or the \((\text{tert-butyl})(n-\text{propyl})_5\text{Li}_6\) hexamer. This is further supported when viewing the variable temperature \(^{13}\text{C}\) spectra shown in Figure 36. It may be observed that, as temperature decreases, coupling is observable in the peaks corresponding to the para \((\text{tert-butyl})_2(n-\text{propyl})_4\text{Li}_6\) α-carbons (peak G for the tert-butyl α-carbon and peak J for the n-propyl α-carbon) at -22.1 °C, whereas the peaks corresponding to the α-carbons of the ortho/meta \((\text{tert-butyl})_2(n-\text{propyl})_4\text{Li}_6\) hexamer, the \((n-\text{propyl})_5(\text{tert-butyl})\text{Li}_6\) hexamer and the \((\text{tert-butyl})_2(n-\text{propyl})_2\text{Li}_4\) tetramer do not show measurable coupling until -52.4°C.

Two-dimensional exchange spectroscopy was used to aid in the elucidation of the exchange processes occurring in this system. A 2DEXSY spectrum of this system at -40 °C is shown in Figure 37. This spectrum revealed that, at this temperature, the tert-butyl groups of the \((\text{tert-butyl})(n-\text{propyl})_4\text{Li}_6\) hexamer (peak K) were exchanging with the tert-
Figure 36 - Variable temperature $^{13}$C spectra of the hexameric $\alpha$-carbon region of $n$-propyllithium/tert-butyllithium mixture. Total alkyl lithium concentration = 2.9F. $n$-propyl:tert-butyl = 1:2.
butyl groups of the \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_4\) tetramer (peak M). The tert-butyl groups of the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer (peak H) were also exchanging with the tert-butyl groups of the \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) tetramer (peak M). But the tert-butyl groups from the \((\text{tert-butyl})(\text{n-propyl})_6\) hexamer (peak K) were not exchanging directly with the tert-butyl groups of the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer (peak H).

This spectrum also reveals the n-propyl exchange. The n-propyl groups of both the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_6\) (peaks I and F), and the \((\text{tert-butyl})(\text{n-propyl})_6\) hexamers (peaks D and E) were exchanging with the n-propyl groups of the \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) tetramer (peak L) but not with each other. Random fluxionality of the \((\text{tert-butyl})(\text{n-propyl})_6\) hexamer may be occurring at this temperature, as revealed by the presence of cross peaks between the two types of n-propyl groups in this hexamer (peaks D and E). However, random fluxionality is not occurring within the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_6\) hexamer as the two types of n-propyl groups in this hexamer are not exchanging with each other. The random fluxionality of the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_6\) hexamer would also be manifested by the exchange between the n-propyl groups of ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_6\) hexamer (peaks F and I) with those of the para \((\text{tert-butyl})_2(\text{n-}
Figure 37 - $^1$H $^1$C 2DEXSY of the $\alpha$-carbon region of the $n$-propyllithium/tert-butyllithium mixture. Total alkyl-lithium concentration = 2.9F. $n$-propyl:tert-butyl = 1:2. Temperature = -40°C. $T_{\text{mix}} = 0.75$ s. D1 = 0.5s.
propyl)$_4$Li$_6$ hexamer (peak G). An exchange between the tert-butyl groups of the ortho/meta (tert-butyl)$_2$(n-propyl)$_4$Li$_6$ hexamer (peak H) with those of the para (tert-butyl)$_2$(n-propyl)$_4$Li$_6$ hexamer (peak J) would also indicate a random fluxionality of the hexamer of composition (tert-butyl)$_2$(n-propyl)$_4$Li$_6$. The fact that these exchanges are not observed in the 2DEXSY spectrum of this system at -40°C establishes that interaggregate exchange between the ortho/meta (tert-butyl)$_2$(n-propyl)$_4$Li$_6$ hexamer and the (tert-butyl)$_2$(n-propyl)$_2$Li$_2$ tetramer is occurring faster than random fluxionality in the hexamers of composition (tert-butyl)$_2$(n-propyl)$_4$Li$_6$.

Quantification of these exchanges using $^{13}$C 2DEXSY was not practical due to the large spectral width necessary to include all exchanging sites. This large spectral width, coupled with the fact that many of these peaks have very similar chemical shifts, make for very long experiments and unreliable intensity determination. As may be observed in the low temperature $^6$Li spectra shown in Figure 28, resolution between the two types of hexamers of composition (tert-butyl)$_2$(n-propyl)$_4$Li$_6$ is very poor, thus making $^6$Li 2DEXSY unreliable for quantification.

Qualitatively, the information provided by the 2DEXSY spectrum is invaluable. Fraenkel has postulated the existence of a biaggregate of composition $R_{12}$Li$_{12}$ (18) to
account for the interaggregate exchange of some alkyllithium hexamers. His theory is based primarily on large values for \( \Delta S^* \) he has discovered when quantifying interaggregate exchange of alkyllithium hexamers. It might be supposed that if two hexamers had to come together for interaggregate exchange to occur, according to equation 31 below,

\[
2R_6\text{Li}_6 \quad \longrightarrow \quad R_{12}\text{Li}_{12} \quad \longrightarrow \quad 2R_6\text{Li}_6
\]  

[31]

that the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer would be the most sterically prohibitive of this process. The ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer and the \((\text{tert-butyl})(\text{n-propyl})_4\text{Li}_6\) hexamer each possess open faces which are bordered only by faces occupied by \(\text{n-propyl}\) groups, whereas each open face in the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer is bordered by a face occupied by a tert-butyl group. This may be indicative of interaggregate exchange being brought about by two hexamers approaching each other at each hexamer's open face, then combining in some manner, redistributing the alkyl groups, and dissociating into two hexamers.

The exchange between the \((\text{tert-butyl})(\text{n-propyl})_4\text{Li}_6\) hexamer with the \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) tetramer and the exchange between the ortho/meta \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer with the \((\text{tert-butyl})_2(\text{n-propyl})_2\text{Li}_4\) tetramer, both
seem to support a dissociative theory of interaggregate exchange similar to Brown's theory. Brown suggested that hexamers might dissociate into tetramers, trimers, or dimers, then reassociate to form hexamers in which the alkyl groups have been redistributed (26). Certainly the hexamers in this system cannot exchange with the \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_4\) tetramer without some manner of dissociation, therefore a dissociative mechanism would seem to be a credible explanation of this process. However, since at \(-40^\circ\text{C}\) the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer does not participate in this exchange, not only does the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer not dissociate at this temperature, the recombination of the lower aggregates into hexamers must not form the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer. If the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer could be formed by the recombination of the lower aggregates, it would act as a 'sink' into which the lower aggregates proceeded and did not return.

A logical explanation of the exclusion of the para \((\text{tert-butyl})_2(\text{n-propyl})_4\text{Li}_6\) hexamer would be that the dissociative process is prompted by the contact between two hexamers, perhaps even to the extent of the formation of the biagggregate referred to above. This biagggregate may then dissociate into monomers, dimers, trimers, tetramers, or hexamers which may or may not have a detectable existence.
If this process occurs, the recombination of these lower aggregates must then be preferential toward the ortho/meta
\((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6\) hexamer over the para \((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}\) hexamer.

Clearly the process of interaggregate exchange is perplexing. The work reported here provides much information about this process and also demonstrates that mixed hexamer systems are an excellent tool for studying these exchange processes. Table 13 summarizes the assignments of the \(\alpha\)-carbons of the \(n\text{-propyllithium/tert-butyllithium}\) mixed hexamers.

<table>
<thead>
<tr>
<th>(13^C) peak</th>
<th>Aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n\text{-propyl }\alpha\text{-carbons} )</td>
<td>((\text{tert-butyl})_3(n\text{-propyl})\text{Li}_4)</td>
</tr>
<tr>
<td>B (tert-butyl)((n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>D (tert-butyl)((n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>E (tert-butyl)((n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>F ortho/meta ((\text{tert-butyl})_3(n\text{-propyl})\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>G para ((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>I ortho/meta ((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>L ((\text{tert-butyl})_3(n\text{-propyl})_4\text{Li}_4)</td>
<td></td>
</tr>
<tr>
<td>tert-butyl (\alpha\text{-carbons} )</td>
<td>((\text{tert-butyl})_4\text{Li}_4)</td>
</tr>
<tr>
<td>A ((\text{tert-butyl})_4\text{Li}_4)</td>
<td></td>
</tr>
<tr>
<td>C ((\text{tert-butyl})_3(n\text{-propyl})\text{Li}_4)</td>
<td></td>
</tr>
<tr>
<td>H ortho/meta ((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>J para ((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>K ((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_6)</td>
<td></td>
</tr>
<tr>
<td>M ((\text{tert-butyl})_2(n\text{-propyl})_4\text{Li}_4)</td>
<td></td>
</tr>
</tbody>
</table>

Table 13

Summary of the assignments of the \(\alpha\)-carbons of the \(n\text{-propyllithium/tert-butyllithium}\) mixture.
**n-Butyllithium/tert-Butyllithium Mixtures.** In hydrocarbon solution n-butyllithium is very similar to n-propyllithium. At low temperatures, both exist as a mixture of hexamers, octamers, and at least one type of nonamer (13). $^{13}C-{^6}Li$ coupling had not been observed for n-butyllithium in hydrocarbon solvent, presumably due to fast interaggregate exchange (19). In the study of mixtures of n-butyllithium and tert-butyllithium, knowledge gained from the n-propyllithium/tert-butyllithium proved to be useful for the assignment of peaks to specific hexamers and tetrammers. In order to continue the study of mixed alkyllithium systems, an NMR sample was prepared of a mixture of n-butyllithium and tert-butyllithium. This sample was contained in a 10 mm NMR tube and was IF in both n-butyllithium and tert-butyllithium.

Shown in Figure 38 are variable temperature $^6Li$ spectra of this sample. It is immediately obvious that these spectra are very similar to the $^6Li$ spectra obtained from the n-propyllithium /tert-butyllithium mixture. The low temperature spectrum reveals eight $^6Li$ resonances. These are labeled X through XVII starting with X as the most downfield resonance. Based on chemical shifts, peak XVI is known to be the pure tert-butyllithium tetramer.

Shown in Figure 39 are $^6Li$ coupled and decoupled, $^{13}C$ spectra of the $\alpha$-carbon region of this sample at -70°C.
Figure 38 - Variable temperature $^6$Li spectra of $n$-butyllithium/tert-butyllithium mixture. Total alkyl lithium concentration = 2F. $n$-butyl:tert-butyl = 1:1.
These spectra are somewhat more complicated than the \textit{n}-propyllithium/tert-butyllithium mixtures due to the presence of the terminal methyl carbon of the \textit{n}-butyl group at approximately 13.5 ppm. However when comparing the \textit{6}Li coupled \textit{13}C spectrum with the \textit{6}Li decoupled \textit{13}C spectrum one may easily discern the \textit{\alpha}-carbon peaks from other \textit{13}C peaks by observing the collapse of the \textit{\alpha}-carbon multiplets upon using \textit{6}Li decoupling. Another complicating feature of this spectrum is the fact that the \textit{\alpha}-carbons of the \textit{n}-butyl groups which show coupling consistent with fluxional hexamers are shifted to the same region of the spectrum as the \textit{\alpha}-carbons of the tert-butyl groups showing tetrameric coupling.

As in the \textit{n}-propyllithium/tert-butyllithium mixture, there is some pure tert-butyllithium tetramer in this solution. The \textit{13}C resonance for the \textit{\alpha}-carbon of this tetramer is identifiable by its chemical shift of 10.7 ppm. This peak is labeled GG in the \textit{13}C\{\textit{6}Li\} spectrum. At least one pure \textit{n}-butyllithium aggregate is identifiable at 11.6 ppm. This peak is labeled DD in the \textit{13}C\{\textit{6}Li\} spectrum. Pure \textit{n}-butyllithium should have at least three detectable \textit{\alpha}-carbons at this temperature in the 11 to 13 ppm region (13). At the low concentration of the pure \textit{n}-butyllithium aggregates in this sample, only one \textit{\alpha}-carbon was detectable.

A \textit{13}C\{\textit{1}H\} HETCOR, which utilized \textit{6}Li decoupling, was
performed on this sample in order to distinguish \( n \)-butyl \( \alpha \)-carbons from \( tert \)-butyl \( \alpha \)-carbons. This experiment was performed at \(-70^\circ C\). A vertical projection, which reveals only those peaks which show proton correlations is shown in Figure 40 along with a normal one-dimensional \( ^{13}C \) spectrum acquired at \(-70^\circ C\). From this figure one can readily differentiate between these \( n \)-butyl and \( tert \)-butyl \( \alpha \)-carbons. The data provided by this HETCOR, as well as coupling constants and chemical shifts at \(-70^\circ C\) are tabulated in Table 14.

The \( ^{13}C \)-\( ^{6}Li \) coupling constants for \( n \)-butyllithium reported here are the first for any \( n \)-butyllithium compound in hydrocarbon solvent. The coupling value for the \( n \)-butyllithium dimer in THF has been reported to be 7.8 Hz \( ^{27} \). The compound exists in ether as a tetramer with \( ^{13}C \)-\( ^{7}Li \) coupling of 15 Hz \( ^{28} \). This translates to a \( ^{13}C \)-\( ^{6}Li \) coupling constant of 5.7 Hz. Both the tetramer and hexamer \( \alpha \)-carbon coupling of \( n \)-butyllithium are very similar to those for \( n \)-propyllithium in the corresponding aggregate. This supports the theory that fast interaggregate exchange has been the prohibitive factor in observing coupling in \( n \)-butyllithium \( ^{12} \).

The similarities of the \( tert \)-butyl \( \alpha \)-carbons in this mixed system, with those of the \( n \)-propyllithium/\( tert \)-butyllithium mixed system are readily apparent. All of the
Figure 40 - $^{13}$C spectrum (top) and vertical projection from $^{13}$C($^6$Li)-$^1$H HETCOR (bottom) of n-butyllithium/tert-butyllithium mixture. Total alkyllithium concentration = 2F. n-butyl:tert-butyl = 1:1. J1XH = 120. D1 = 2s. Temp = -70°C
tert-butyllithium peaks in this system have corresponding peaks in the \textit{n}-propyllithium/tert-butyllithium mixed system. For this reason one might conclude the mixed aggregates formed are the same. In order to test this theory, a $^{13}\text{C-}^6\text{Li}$ HETCOR experiment was run on this system.

Figure 41 displays the $^{13}\text{C-}^6\text{Li}$ HETCOR. As might have been anticipated, resolution in this spectrum is

\begin{table}[h]
\centering
\caption{Coupling constants and chemical shifts of the $\alpha$-carbons of the alkyl groups in the \textit{n}-butyllithium/tert-butyllithium mixture}
\begin{tabular}{llll}
\hline
peak & shift (ppm) & alkyl group & $^{13}\text{C-}^6\text{Li}$ coupling constants \\
\hline
AA & 13.9 & tert-butyl & 2.7 \\
BB & 13.4 & tert-butyl & 2.7 \\
CC & 12.7 & tert-butyl & 2.7 \\
DD & 11.6 & \textit{n}-butyl & * \\
EE & 11.0 & \textit{n}-butyl & ** \\
FF & 10.9 & \textit{n}-butyl & 3.4 \\
GG & 10.8 & tert-butyl & 5.4 \\
HH & 10.5 & \textit{n}-butyl & ** \\
II & 10.2 & \textit{n}-butyl & 3.4 \\
JJ & 9.9 & \textit{n}-butyl & ** \\
KK & 9.8 & tert-butyl & 5.3 \\
LL & 8.9 & tert-butyl & 5.3 \\
MM & 6.4 & \textit{n}-butyl & 6.5 \\
NN & 6.0 & \textit{n}-butyl & 6.8 \\
\hline
\end{tabular}
\end{table}

* - Peak DD is the \textit{n}-butyllithium aggregate. Coupling is immeasurable due to interaggregate exchange

** - Resolution problems prevented the obtainment of the coupling constants of these $\alpha$-carbons
Figure 41 - $^{13}$C-$^6$Li HETCOR of $n$-butyllithium/tert-butyllithium mixture. Total alkylolithium concentration = 2F. $n$-butyl:tert-butyl = 1:1. Temperature = -70°C. D3 = 0.13 s. D4 = 0.0237 s.
significantly worse than the corresponding $n$-propyllithium/tert-butyllithium experiment. With careful viewing of traces; however, one may establish the bonding scheme of these aggregates. The correlations between the $\alpha$-carbons and the lithiums to which they are bonded are tabulated in Table 15.

Table 15
$^{13}$C-$^6$Li correlations in the $n$-butyllithium/tert-butyllithium mixtures.
Total alkyllithium concentration = $2F$.
$n$-butyl:tert-butyl = 1:1.

<table>
<thead>
<tr>
<th>$^{13}$C peak</th>
<th>$^6$Li peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-butyl $\alpha$-carbons</td>
<td></td>
</tr>
<tr>
<td>DD</td>
<td>*</td>
</tr>
<tr>
<td>EE</td>
<td>X</td>
</tr>
<tr>
<td>FF</td>
<td>X</td>
</tr>
<tr>
<td>HH</td>
<td>XIII</td>
</tr>
<tr>
<td>II</td>
<td>XII</td>
</tr>
<tr>
<td>JJ</td>
<td>XIII</td>
</tr>
<tr>
<td>MM</td>
<td>**</td>
</tr>
<tr>
<td>NN</td>
<td>XVII</td>
</tr>
<tr>
<td>tert-butyl $\alpha$-carbons</td>
<td></td>
</tr>
<tr>
<td>AA</td>
<td>XIII</td>
</tr>
<tr>
<td>BB</td>
<td>XII</td>
</tr>
<tr>
<td>CC</td>
<td>X</td>
</tr>
<tr>
<td>GG</td>
<td>XVI</td>
</tr>
<tr>
<td>KK</td>
<td>XV &amp; XVII</td>
</tr>
<tr>
<td>LL</td>
<td>XI &amp; XIV</td>
</tr>
</tbody>
</table>

* - The correlation from the $n$-butyllithium aggregate was not observable.
** - Peak MM will be explained below.
The tert-butyllithium tetramer α-carbon GG shows a correlation with the 6Li peak labeled XVI. This is in agreement with reported values for chemical shifts of both the 13C α-carbon and the 6Li peak for this tetramer.

The α-carbon labeled KK is a tert-butyl α-carbon and shows coupling consistent with a non-fluxional tetramer. This peak shows correlations in the 13C-6Li HETCOR with both the lithium peak labeled XV and that labeled XVII. The α-carbon labeled NN is an n-butyl α-carbon which possesses a coupling constant consistent with a non-fluxional tetramer and is bonded to the 6Li labeled XVII. The 6Li peaks XV and XVII are in an intensity ratio of 3 to 1. All of this data is consistent with a non-fluxional tetramer composed of three tert-butyl groups and one n-butyl group.

Each 6Li peak that shows coupling consistent with a fluxional hexamer, arises because of one hexamer. This is known by the fact that if the α-carbons show coupling to six lithiums, then, over a period of time, each alkyl group is bonded to each lithium. This brings equivalence to all the lithiums in the hexamer. With this knowledge, and the data provided by the 13C-6Li HETCOR, the composition of each hexamer may be established. Intensity determinations were not run on this sample due to the severe overlap of peaks. However the similarities between this system and the n-propyllithium/tert-butyllithium system leave no doubt as to
the composition of these aggregates.

The $^{13}$C-$^6$Li HETCOR revealed that $^6$Li peak X is bonded to two types of $n$-butyl $\alpha$-carbons ($^{13}$C peaks EE and FF) and one type of tert-butyl $\alpha$-carbon ($^{13}$C peaks CC). Peaks EE and FF are in an approximate intensity ratio of 4 to 1. Both the $^6$Li peak X and the tert-butyl $\alpha$-carbon peak CC have corresponding peaks in the $n$-propyllithium/tert-butyllithium system. The chemical shift of $^{13}$C peak CC is identical to the $^{13}$C peak in the $n$-propyllithium/tert-butyllithium mixture which corresponded to the $\alpha$-carbon of the tert-butyl group from the $(\text{tert-butyl})(n\text{-propyl})_5$Li$_6$ hexamer. The chemical shift of the $^6$Li peak X is identical with the $^6$Li peak which corresponded to the $(\text{tert-butyl})(n\text{-propyl})_5$Li$_6$ hexamer. The $^6$Li peak X must then correspond to a hexamer of composition $(n\text{-butyl})_5(\text{tert-butyl})$Li$_6$ undergoing the limited fluxional exchange.

The $^6$Li peak XII has the same chemical shift as the $^6$Li peak in the $n$-propyllithium/tert-butyllithium system which corresponded to the para $(\text{tert-butyl})_2(n\text{-propyl})_4$Li$_6$ hexamer. In the $^{13}$C-$^6$Li HETCOR, peak XII correlated with one type of $n$-butyl $\alpha$-carbon ($^{13}$C peak II) and one type of tert-butyl $\alpha$-carbon ($^{13}$C peak BB). The chemical shift of $^{13}$C peak BB is identical with that of the $\alpha$-carbon of the tert-butyl group of the para $(\text{tert-butyl})_2(n\text{-propyl})_4$Li$_6$ hexamer. This data suggests this to be the $(n\text{-butyl})_4$ para $(\text{tert-butyl})_2$Li$_6$. 
hexamer undergoing the limited fluxional exchange.

Comparison of the $^6\text{Li}$ peak XIII with the $^6\text{Li}$ spectra from the $n$-propyllithium/tert-butyllithium system suggests this peak to be caused by the lithiums in the $(n$-butyl)$_4$ ortho/meta (tert-butyl)$_2\text{Li}_6$ hexamer. The $^{13}\text{C}$-$^6\text{Li}$ HETCOR revealed that $^6\text{Li}$ peak XIII is bonded to two types of $n$-propyl $\alpha$-carbons ($^{13}\text{C}$ peaks HH and JJ) and one type of tert-butyl $\alpha$-carbon ($^{13}\text{C}$ peak AA). The approximate intensity ratio of peaks HH and JJ is 1 to 1 and the chemical shift of peak AA is identical with the chemical shift of the tert-butyl $\alpha$-carbon which corresponded to the ortho/meta (tert-butyl)$_2(n$-propyl)$_4\text{Li}_6$ hexamer undergoing the limited fluxional exchange.

From this information it may be concluded that the $n$-butyllithium/tert-butyllithium hexamers are very similar to the $n$-propyllithium/tert-butyllithium hexamers. In each system the maximum number of tert-butyl groups which may exist on a hexamer is two. The hexamers in each system are also consistent with hexamers undergoing the limited fluxional exchange and are not consistent with randomly fluxional hexamers.

The $^{13}\text{C}$ $\alpha$-carbon peak labeled LL is a tert-butyl $\alpha$-carbon with a chemical shift of 8.9 ppm. This chemical shift and the $^{13}\text{C}$-$^6\text{Li}$ coupling constant of 5.3 Hz corresponds with the tert-butyl $\alpha$-carbon from what was hypothesized to
be the (tert-butyl)$_2$(n-propyl)$_2$Li$_4$ tetramer in the n-propyl/tert-butyl system. The $^{13}$C-$^6$Li HETCOR revealed correlations between this peak and two $^6$Li peaks. One of these is a very small peak labeled XIV, which is 0.02 ppm downfield of $^6$Li peak XV. The other correlation is to a very small peak labeled XI, shifted approximately 0.7 ppm downfield of the tert-butyl lithium tetramer.

Although accurate integrations cannot be obtained from the $^6$Li spectrum, visual inspection would indicate an approximate one to one ratio of these two peaks. The reason accurate integrations cannot be obtained from this spectrum is the poor resolution between peaks XV and XVI. This similarity in chemical shift is to be expected as the environments of these two lithiums are very similar. At -70°C, both of these tetramers are non-fluxional (as revealed by their $\alpha$-carbon coupling) rendering each of these lithiums bonded to two tert-butyl groups and one n-butyl group. This similarity of environments causes their chemical shifts to be very similar.

The $^{13}$C peak labeled MM would seem to be the n-butyl $\alpha$-carbon corresponding to this (tert-butyl)$_2$(n-propyl)$_2$Li$_4$ tetramer, as it is one of only two n-butyl $\alpha$-carbons showing non-fluxional tetrameric coupling. The $^{13}$C peak labeled NN is the other n-butyl $\alpha$-carbon peak with tetrameric coupling but it as already been accounted for as the n-butyl $\alpha$-carbon
of the \((n\text{-butyl})(\text{tert-butyl})_3\text{Li}_4\) tetramer. Peak MM however, did not show a \(^6\text{Li}\) correlation in the \(^{13}\text{C}-^6\text{Li}\) HETCOR. This may be explained by a combination of two reasons.

As explained in the experimental section of this chapter, the HETCOR experiment must be optimized for a particular coupling value \((23)\). In this particular system at \(-70^\circ\text{C}\) there are four basic coupling situations: tert-butyl \(\alpha\)-carbons bonded to three \(^6\text{Li}\) nuclei, tert-butyl \(\alpha\)-carbons bonded to six \(^6\text{Li}\) nuclei, \(n\text{-butyl}\) \(\alpha\)-carbons bonded to three \(^6\text{Li}\) nuclei, and \(n\text{-butyl}\) \(\alpha\)-carbons bonded to six \(^6\text{Li}\) nuclei. This experiment was optimized for the hexameric coupling values of 2.7 as an approximate midpoint of the hexameric coupling of the tert-butyl \(\alpha\)-carbons and the \(n\)-butyl \(\alpha\)-carbons. This was done because the intensity of the hexamers was low compared with the tetrameric \(\alpha\)-carbons. Correlations were prominent for the pure tert-butyllithium tetramer, and the \((n\text{-butyl})(\text{tert-butyl})_3\text{Li}_4\) tetramer, mainly due to their large concentration in this solution. Peak MM, the \(n\)-butyl \(\alpha\)-carbon of the \((n\text{-butyl})_3(\text{tert-butyl})_2\text{Li}_4\) tetramer, did not show a \(^6\text{Li}\) correlation because it is very low in intensity, and its coupling constant is most different from the coupling value for which this experiment was optimized. Peak LL, which did reveal a \(^6\text{Li}\) correlation, is of approximately equal intensity as peak MM but its coupling value of 5.3 Hz is closer to the value for which
this experiment was optimized.

These reasons for not observing the correlation that should appear between $^{13}$C peak MM and $^6$Li peaks XI and XVII are also responsible for the non-observance of the correlations between the $n$-propyl $\alpha$-carbon and the two lithiums of the (tert-butyl)$_2$($n$-propyl)$_2$Li$_4$ tetramer. The supporting data in both of these systems strongly supports the existence of this tetramer as well as its role in the interaggregate exchange process of the hexamers.

**Exchange Processes in the $n$-Butyl/tert-Butyl System.**

One important point from the study of this system is that all of the hexamers studied are consistent with hexamers undergoing the limited fluxionality observed for the lithium tert-butoxide/tert-butyllithium system discussed in chapter 3, as well as the $n$-propyllithium/tert-butyllithium system discussed earlier in this chapter. The coupling values observed for the $\alpha$-carbons at the lowest temperatures studied (as low as $-85^\circ$C) were consistent with carbons bonded to six lithiums. Each hexamer consistently produced only one signal in the $^6$Li spectra. These coupling values and $^6$Li spectra require fast fluxionality, yet non-equivalencies occur which are not consistent with random fluxionality. The non-equivalencies observed were consistent with the proposed limited fluxionality.

This mixed system also provided an opportunity to study
the nature of interaggregate exchange. When viewing the variable temperature $^6$Li spectra shown in Figure 38, one observes the same effect previously noticed in the n-propyl/tert-butyl system, that all the hexamers are interaggregately exchanging at room temperature. As the temperature is lowered the (n-butyl)$_4$ para (tert-butyl)$_2$Li$_6$ hexamer reaches the slow limit of interaggregate exchanging by -31.9°C and the ortho/meta and (n-butyl)$_5$(tert-butyl)Li$_6$ by -62.4°C.

Variable temperature $^{13}$C spectra are in agreement with this finding in that coupling is observed for the tert-butyl α-carbons of the (n-butyl)$_4$ para (tert-butyl)$_2$Li$_6$ hexamer before it may be observed for any of the tert-butyl α-carbons of either the (n-butyl)$_4$ ortho/meta (tert-butyl)$_2$Li$_6$ or (n-butyl)$_5$(tert-butyl)Li$_6$ hexamers. Coupling for the n-butyl α-carbon of the (n-butyl)$_4$ para (tert-butyl)$_2$Li$_6$ hexamer becomes observable at -20°C, however comparison with other n-butyl α-carbons is not possible due to poor resolution. Observation of coupling for the α-carbons of the (n-butyl)$_4$ ortho/meta (tert-butyl)$_2$Li$_6$ and (n-butyl)$_5$(tert-butyl)Li$_6$ hexamers coincides with the observation of coupling for the α-carbons of the (n-butyl)$_2$(tert-butyl)$_2$Li$_4$ tetramer.

All of this information points to a system wherein the hexamers and the (n-butyl)$_2$(tert-butyl)$_2$Li$_4$ tetramer are
interaggregately exchanging at room temperature. As
temperature decreases the interaggregate exchange slows to
the limit at which $^{13}$C-$^6$Li coupling may be observed for the
$\alpha$-carbons. This slowing of interaggregate exchange is
preferential toward the para hexamer, as was observed for
the $n$-propyl/tert-butyl system.

Due to the similarities between the $n$-propyl/tert-butyl
system and the $n$-butyl/tert-butyl system it would seem
reasonable to assume the interaggregate exchange of the ($n$-
butyl)$_4$ ortho/meta (tert-butyl)$_2$Li$_6$ hexamer and ($n$-butyl)$_5$
(tert-butyl)Li$_6$ hexamer proceeded through the ($n$-butyl)$_2$
(tert-butyl)$_2$Li$_4$ tetramer. As discussed for the $n$-
propyl/tert-butyl mixed hexamers, an explanation for this
preferential exclusion of the para hexamer from the
interaggregate exchange as well as the mechanism whereby the
other hexamers exchange with the ($n$-butyl)$_2$(tert-butyl)$_2$Li$_4$
tetramer can only be speculated upon at this time. Shown in
Table 16 is a summary of the assignments of the $\alpha$-carbons of
the $n$-butyllithium/tert-butyllithium mixture.

**Tetramer Fluxionality in the Mixed $n$-Alkyl/tert-Butyl
Systems.** Although, as explained above, quantification of
the hexamer interaggregate exchange could not be performed
using 2DEXSY, both systems included an abundance of ($n$-
alcohol)(tert-butyl)$_3$Li$_4$ tetramers which were ideally suited
for $^6$Li 2DEXSY quantification. The $^6$Li spectra of these
Table 16
Summary of the assignments of the α-carbons of the n-butyllithium/tert-butyllithium mixture

<table>
<thead>
<tr>
<th>¹³C peak</th>
<th>Aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butyl α-carbons</td>
<td></td>
</tr>
<tr>
<td>EE</td>
<td>(n-butyl)₅(tert-butyl)Li₆</td>
</tr>
<tr>
<td>FF</td>
<td>(n-butyl)₅(tert-butyl)Li₆</td>
</tr>
<tr>
<td>HH</td>
<td>(n-butyl), ortho/meta (tert-butyl)₂Li₆</td>
</tr>
<tr>
<td>II</td>
<td>(n-butyl), para (tert-butyl)₂Li₆</td>
</tr>
<tr>
<td>JJ</td>
<td>(n-butyl), ortho/meta (tert-butyl)₂Li₆</td>
</tr>
<tr>
<td>MM</td>
<td>(n-butyl)₃(tert-butyl)₂Li₄</td>
</tr>
<tr>
<td>NN</td>
<td>(n-butyl)₂(tert-butyl)₂Li₄</td>
</tr>
<tr>
<td>tert-butyl α-carbons</td>
<td></td>
</tr>
<tr>
<td>AA</td>
<td>(n-butyl)₅(tert-butyl)₂Li₆</td>
</tr>
<tr>
<td>BB</td>
<td>(n-butyl)₅(tert-butyl)₂Li₆</td>
</tr>
<tr>
<td>CC</td>
<td>(n-butyl)₅(tert-butyl)Li₆</td>
</tr>
<tr>
<td>GG</td>
<td>(tert-butyl)₄Li₄</td>
</tr>
<tr>
<td>KK</td>
<td>(n-butyl)(tert-butyl)₂Li₄</td>
</tr>
<tr>
<td>LL</td>
<td>(n-butyl)₂(tert-butyl)₂Li₄</td>
</tr>
</tbody>
</table>

systems (shown in Figures 5 and 15) revealed that at temperatures at which fluxionality of these tetramers is slow, resolution is sufficient to use ⁶Li 2DEXSY to quantitate these exchange processes. This system thus provides an excellent means for studying tetramer fluxionality.

A ⁶Li 2DEXSY spectrum of the n-propyl/tert-butyl mixture is shown in Figure 42. Cross peaks between the (tert-butyl)₃(n-propyl)Li, ⁶Li peaks (I and III) reveal an exchange between these two peaks. The exchange rates were
Figure 42 - $^6$Li 2DEXSY of (tert-butyl)$_3$(n-propyl)Li$_4$ tetramer. Concentration of tetramer = 0.35M.
Temperature = -43.9°C. $T_{\text{mix}} = 28.0$ s. $D_1 = 10$ s.
calculated from the intensities of the cross peaks and the diagonal peaks, in the manner first proposed by Perrin (29) and used extensively by Abel (30). Appropriate mix times were calculated according to equation 18 in chapter 2 (31). The variable temperature $^6$Li 2DEXSY results are tabulated in Table 17 and the Eyring plot is shown in Figure 43.

Table 17

Rates of fluxionality of the (tert-butyl)$_3$(n-propyl)Li$_4$ tetramer.
Concentration of the tetramer is 0.35 M.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>$t_m$(s)</th>
<th>Rate(s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP551X</td>
<td>-43.9</td>
<td>28.0</td>
<td>.021</td>
</tr>
<tr>
<td>DP549X</td>
<td>-40.9</td>
<td>13.4</td>
<td>.033</td>
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<tr>
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<td>9.0</td>
<td>.11</td>
</tr>
<tr>
<td>DP540X</td>
<td>-28.7</td>
<td>6.6</td>
<td>.24</td>
</tr>
</tbody>
</table>

$\Delta H^* = 17.9 \pm 1.5$ kcal/mol $\Delta S^* = 14.4 \pm 6.4$ eu

The fluxionality of the (n-butyl)(tert-butyl)$_3$Li$_4$ tetramer was also examined in this study. Two samples were prepared, one of which contained an n-butyl to tert-butyl ratio of 1 to 1 and was 0.13M of the (n-butyl)(tert-butyl)$_3$Li$_4$ tetramer. The other sample contained an n-butyl to tert-butyl ratio of 1 to 15 and was 0.03M of the (n-butyl)(tert-butyl)$_3$Li$_4$ tetramer. Variable temperature $^6$Li 2DEXSY experiments were performed on these samples and the
results are tabulated in Table 18. The resulting Eyring plot, shown in Figure 44, showed there to be no concentration dependence and therefore the fluxionality of this tetramer was determined to be first order. The activation parameters arrived at for the fluxionality of the (tert-butyl)₃(n-propyl)Li₄ tetramer were

\[ \Delta H^* = 17.9 \pm 1.5 \text{ kcal/mol and } \Delta S^* = 14.4 \pm 6.4 \text{ eu.} \]

Table 18

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>( t_m (\text{s}) )</th>
<th>Rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP526X</td>
<td>-39.1</td>
<td>16.0</td>
<td>.043</td>
</tr>
<tr>
<td>DP521X</td>
<td>-28.7</td>
<td>6.0</td>
<td>.22</td>
</tr>
<tr>
<td>[3:1]=0.03M</td>
<td>-33.5</td>
<td>9.5</td>
<td>.093</td>
</tr>
<tr>
<td>DP535X</td>
<td>-22.5</td>
<td>2.5</td>
<td>.54</td>
</tr>
</tbody>
</table>

\[ \Delta H^* = 17.5 \pm 1.0 \text{ kcal/mol } \quad \Delta S^* = 13.3 \pm 3.0 \text{ eu.} \]

The resulting activation parameters for the (n-butyl)(tert-butyl)₃Li₄ tetramer fluxionality were \( \Delta H^* = 17.5 \pm 1.0 \) kcal/mol and \( \Delta S^* = 13.3 \pm 3.0 \) eu. Multiple concentrations of the (tert-butyl)₃(n-propyl)Li₄ tetramer were not examined with 2DEXSY but variable temperature one-dimensional \(^6\text{Li}\)
Figure 43 - Eyring plot of the (tert-butyl)$_3$(n-propyl)Li$_4$ tetramer. Concentration of the tetramer is 0.35 M.

$\Delta H^* = 17.9 \pm 1.5 \text{ kcal/mol}$  $\Delta S^* = 14.4 \pm 6.4 \text{ eu}$
Figure 44 - Eyring plot for the (n-butyl)(tert-butyl)_4 Li tetramer fluxionality. The concentration of the tetramer is 0.03 M for the x, and 0.13 M for the *. \( \Delta H^* = 17.5 \pm 1.0 \text{ kcal/mol} \quad \Delta S^* = 13.3 \pm 3.0 \text{ eu} \)
spectra of different concentrations of this tetramer ranging from 0.01 M to 0.35 M were examined with no significant change in the lineshapes in the spectra. This fact, along with the fact that this tetramer has obvious similarities to the \((n\text{-butyl})(\text{tert-buty})_3\text{Li}_4\) tetramer, lead to the conclusion that the fluxionality of the \((\text{tert-buty})_3(\text{n-propyl})\text{Li}_4\) is first order.

The fluxionality of alkyllithium tetramers has been studied in the past. The activation parameters for the fluxionality of several different alkyllithium tetramers are tabulated in Table 19.

Table 19

<table>
<thead>
<tr>
<th>tetramer</th>
<th>(\Delta H^*(\text{kcal/mol}))</th>
<th>(\Delta S^*(\text{eu}))</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>sec-pentyl lithium</td>
<td>9.1 ± 0.9</td>
<td>-16 ± 4</td>
<td>7</td>
</tr>
<tr>
<td>iso-propyl lithium</td>
<td>13 ± 2</td>
<td>-3 ± 8</td>
<td>7</td>
</tr>
<tr>
<td>tert-butyllithium</td>
<td>25 ± 0.1</td>
<td>44 ± 1</td>
<td>4</td>
</tr>
<tr>
<td>(tert-butoxide)(tert-butyl)_3Li_4</td>
<td>14.8 ± 0.8</td>
<td>0.9 ± 3.0</td>
<td>32</td>
</tr>
<tr>
<td>(tert-butoxide)(tert-butyl)_3Li_4</td>
<td>13.7 ± 1.0</td>
<td>-4.7 ± 3.6</td>
<td>*</td>
</tr>
<tr>
<td>(tert-buty)_3(n-propyl)Li_4</td>
<td>17.9 ± 1.5</td>
<td>14.4 ± 6.4</td>
<td>*</td>
</tr>
<tr>
<td>(n-buty)_3(tert-butyl)_3Li_4</td>
<td>17.5 ± 1.0</td>
<td>13.3 ± 3.0</td>
<td>*</td>
</tr>
</tbody>
</table>

* - This work.

The mixed tetramer \((\text{tert-butoxide})(\text{tert-buty})_3\text{Li}_4\) has been studied with line-shape-analysis resulting in activation parameters of \(\Delta H^* = 14.8 \pm 0.8 \text{ kcal/mol}\) and \(\Delta S^*\)
\[ 0.9 \pm 3 \text{ eu} \quad (32) \]. The fluxionality of this same tetramer was studied using 2D EXSY as discussed in chapter 2. The resulting activation parameters were calculated to be \( \Delta H^* = 13.7 \pm 1.0 \text{ kcal/mol} \) and \( \Delta S^* = -4.7 \pm 3.6 \text{ eu} \).

The activation enthalpies reported here for the (tert-butyl)\(_3\)(n-propyl)Li\(_4\) tetramer and the (n-butyl)(tert-butyl)Li\(_4\) tetramer are similar to the sec-pentyl lithium tetramer and the isopropyl lithium tetramer, and also in very good agreement with the activation enthalpy for the fluxionality of the (tert-butoxide)(tert-butyl)Li\(_4\) mixed tetramer.

When considering the mechanism for alkyllithium tetramer fluxionality, there are three proposed mechanisms. Dissociation of the tetramer into two dimers followed by rotation and recombination is a possible mechanism. Such a mechanism would be manifested by a large positive entropy of activation. It has also been reported that the enthalpy of activation for the dissociation of the tert-butyllithium tetramer into dimers is \( 24 \pm 6 \text{ kcal/mol} \quad (3) \). However, Dixon has argued that 24 kcal/mol is much too low for the dissociation of alkyllithium tetramers to dimers \( (33) \). On the basis of PRDDO molecular orbital calculations, he found there to be a difference of 43 kcal/mol between the methyllithium tetramer and dimers. He found very little difference in energy however, between the tetramers and a
planar eight-membered ring intermediate, first proposed by Brown (34) to account for alkyllithium tetramer fluxionality. Although no such planar ring structures have been observed in alkyllithium compounds in their ground state, such structures have been reported for related copper compounds (35) (36).

Molecular orbital arguments were used to propose an over-the-edge mechanism for the inversion at the α-carbon of primary alkyl groups (37). In such a mechanism the carbon bonded to lithium undergoes a change to sp² hybridization as the alkyl group migrates over-the-edge, thus accomplishing fluxionality. It was suggested that such a mechanism would not occur for secondary or tertiary alkyl groups due to steric interaction between the groups attached to the α-carbon and the lithium core (37). The tetramers in this study both contained three tert-butyl groups, therefore such a mechanism seems unlikely in these tetramers. However, if alkyllithium tetramers are primarily ionic in nature, as has been suggested (38), an over-the-edge movement of the alkyl groups around the lithium core might proceed even for tertiary alkyl groups. Such a movement of the alkyl groups would cause the α-carbons to show coupling to all four lithums in a tetramers and provide for the high temperature equivalence of the two types of lithums in these tetramers. It is unclear how such a process would affect the entropy of
activation.

Considering the data on the two mixed tetramers presented in this study, the dissociation of these tetramers into dimers does not seem to be a likely mechanism of fluxionality. The fact that no interaggregate exchange is observed in these tetramers makes it difficult to explain the large difference in the rate of fluxionality versus the rate of interaggregate exchange if dissociation into dimers were the mechanism of fluxionality. Also, the activation parameters do not suggest an intermediate which is highly entropically favored.

When considering the other two theories about the mechanism of alkyllithium tetramer fluxionality, it is important to note the observance of $^{13}$C-$^6$Li coupling in the $^{13}$C spectra. For example, in the (tert-butyl)$_3$(n-propyl)Li$_4$ tetramer, when the temperature of the system is decreased, both types of $\alpha$-carbons in this tetramers convert from fluxional to non-fluxional coupling values at approximately the same temperature. This would be required if the mechanism of fluxionality proceeded by the eight-membered ring intermediate; however, as explained below, it is not required for a non-random over-the-edge mechanism. The $^{13}$C and $^6$Li NMR spectra are consistent with an eight-membered ring intermediate. The activation entropies of these tetramers indicate that the fluxionality intermediate is
somewhat entropically favored, this might be due to the increased degrees of freedom obtained in the planar ring over the tetramer.

An over-the-edge mechanism is consistent with the data reported here, however, each of the types of tetramers examined contained three tert-butyl groups. This is inconsistent with the molecular orbital argument upon which this theory was based. Such an exchange mechanism would be more likely if the tetramers, or the intermediates through which fluxionality occurred, were primarily ionic. Such a mechanism would account for the observed $^{13}$C-$^6$Li coupling and the $^6$Li spectra observed.

If an over-the-edge mechanism does occur in these systems, there is not a preference for movement of the tert-butyl groups over an $n$-propyl or an $n$-butyl group. This is required by the fact that in either type of tetramer, both types of $\alpha$-carbons on that tetramer convert from fluxional tetrameric coupling to non-fluxional tetrameric coupling at approximately the same temperature. For example, if in the (tert-butyl)$_3$(n-propyl)Li tetramer, the tert-butyl groups migrated more quickly than the $n$-propyl group, there would be a temperature span in which the $\alpha$-carbon from the $n$-propyl group would exhibit coupling to three lithiums while the $\alpha$-carbons from the tert-butyl groups would exhibit coupling to four lithiums. The converse of this deduction
is not necessarily true, in that movement of the \(n\)-propyl group must be accompanied by movement of at least two tert-butyl groups. Such a movement would result in both types of \(\alpha\)-carbons going from displaying non-fluxional to fluxional coupling simultaneously.

The observance of coupling in the \((n\text{-butyl})(\text{tert-butyl})_3\text{Li}_4\) tetramer is similar to the \((\text{tert-butyl})_3(n\text{-propyl})\text{Li}_4\) tetramer in that both types of \(\alpha\)-carbons in this tetramer convert from fluxional to non-fluxional couplings at approximately the same temperature. Therefore, it may be concluded that if the fluxionality of these tetramers does proceed by an over-the-edge mechanism, the tendency for the \(n\text{-propyl}\) or the \(n\text{-butyl}\) group to migrate over the tetramer is at least as great as that tendency in the tert-butyl group.

The work reported here does not rule out either the planar eight-membered ring or the over-the-edge mechanism. As discussed above, if the over-the-edge mechanism is operative in these tetramers, movement of the two primary alkyl groups occurs at least as fast as movement of the tert-butyl groups.

Experimental

Sample preparation. The tert-butyllithium used in this
study was from the same source as that used in chapter 3. For experimental procedures of this synthesis see the experimental sections of chapters 2 and 3. The syntheses of both n-propyllithium and n-butyllithium are discussed below relative to the synthesis of tert-butyllithium as all three syntheses are very similar.

The starting reagent in the synthesis of n-propyllithium was n-propyl chloride. This, of course, eliminated the halogenation reaction from the general synthetic scheme. The preparation of the bis(n-propyl) mercury compound from the halide proceeded according to the synthetic reactions discussed for the bis(tert-butyl)mercury from the corresponding tert-butyl chloride. A 156.8 gram (2 mols) portion of n-propyl chloride was used in the initial Grignard synthesis. A 42% yield of 102.3 grams (0.42 mols) of bis(n-propyl) mercury were obtained. Bis(n-propyl) mercury is a clear viscous liquid. This liquid was distilled at 52°C and 2 torr. The $^{13}$C NMR spectrum showed $^{13}$C shifts of 47.3 ppm, 22.7 ppm, and 20.1 ppm. These shifts are consistent with previously reported $^{13}$C chemical shifts for bis(n-propyl)mercury (39).

A 7.2 gram (0.03 mols) portion of bis(n-propyl)mercury was combined with excess $^{6}$Li-enriched lithium metal and cyclopentane in a reaction vessel. The reaction vessel was then flame sealed and placed on a shaker table for 15 days.
After this time period, the reaction mixture was analyzed by $^{13}$C NMR and shown to contain the desired product $n$-propyllithium. The room temperature $^{13}$C NMR spectrum showed peaks at 16.1 ppm, 22.4 ppm, and 22.3 ppm. These shifts are consistent with previously reported $^{13}$C NMR data on $n$-propyllithium (13).

The cyclopentane solvent was cryopumped from the reaction mixture leaving behind 2.3 grams (.047 mols) of liquid $n$-propyllithium which was a 78% yield based on the amount of mercury compound used. The $n$-propyllithium was transferred in the glove box to a vessel equipped with a high-vacuum roto-flow stopcock. This stock solution of $n$-propyllithium was stored in the glove box and was the source of all $n$-propyllithium used in this study.

The synthesis of $n$-butyllithium began with 184.8 grams (2 mols) of $n$-butyl chloride. The synthetic process was identical to that of $n$-propyllithium. Bis($n$-butyl)mercury was obtained in a 52% yield (0.52 mols, 136.5 grams of bis($n$-butyl) mercury). Bis($n$-butyl)mercury was a viscous liquid which was purified by vacuum distillation at 120°C and 23 torr. The room temperature $^{13}$C NMR spectrum revealed $^{13}$C peaks at 44.7 ppm, 31.5 ppm, 28.4 ppm, and 14.4 ppm which was consistent with previously reported data. As was the $^{1}J(^{199}$Hg-$^{13}$C) coupling constant of 662 Hz (39).

8.1 grams (0.03 mols) of bis($n$-butyl)mercury was used
to prepare a reaction vessel for the production of n-butyllithium. A 78% yield of n-butyllithium (3.15 grams, 0.05 mols) was obtained. The viscous liquid had $^{13}$C chemical shifts at 11.7 ppm, 30.9 ppm, 31.5 ppm, and 13.0 ppm at room temperature. This is consistent with previously reported $^{13}$C data for n-butyllithium (13). The n-butyllithium was stored in a vessel equipped with a high-vacuum roto-flow stopcock. This vessel was kept in the glove box and used as the stock supply of n-butyllithium for this study.

The manipulations of the alkyllithium mixtures were all done in the argon-filled drybox described in chapter 2. The mixtures were prepared by dissolving the appropriate amount of each alkyllithium compound in half the amount of solvent necessary to prepare the NMR tube. These amounts are 0.45 ml for a 5 mm NMR tube and 1.55 ml for a 10 mm tube. These solutions were then mixed in an NMR tube. The NMR tube was then fitted with a stopcock assembly and removed from the drybox. This tube was then degassed a minimum of three times using the freeze-pump-thaw method. The sample tube was then flame sealed and allowed to warm up overnight. The solvent used in these solutions was 92% cyclopentane (Wiley Organics 99.9%) and 8% d$^{10}$ cyclopentane (MSD isotopes 98.8% D).

The $n$-propyllithium/tert-butyllithium mixture which contained an $n$-propyl:tert-butyl ratio of 1:24 was prepared
by dissolving 0.030 grams (0.48 millimols) of tert-butyllithium in 0.45 ml of the cyclopentane solution and then mixing this solution with 0.001 grams (0.02 millimols) of n-propyllithium which had previously been dissolved in 0.45 ml of the cyclopentane solution. This created a tube which contained 0.13 M of the tert-butyllithium tetramer and 0.02 M of the\( (\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4 \) tetramer. This tube was used in the initial investigation of the\( (\text{n-propyl})_4\text{Li} \) tetramer.

A second n-propyllithium/tert-butyllithium sample tube was prepared to be a 1:2 ratio of n-propyl:tert-butyl. This sample was prepared by dissolving 0.378 grams (6 millimols) of tert-butyllithium in 1.55 ml of the cyclopentane solution, and then mixing this with a 1.55 ml cyclopentane solution containing 0.147 grams (3 millimols) of tert-butyllithium. This resulted in a solution which was 2.9 F in alkyllithium compound and contained a 1:2 ratio of n-propyllithium:tert-butyllithium. This mixture resulted in a tube which contained a large amount of hexamers and was 0.35 M in the\( (\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4 \) tetramer. The concentration of the\( (\text{tert-butyl})_3(\text{n-propyl})\text{Li}_4 \) was determined from the total concentration and integrations of the \(^{6}\text{Li} \) spectra.

The n-butyllithium/tert-butyllithium mixtures were prepared in a similar fashion. The sample tube which
contained an n-butyl to tert-butyl ratio of 1 to 1 was prepared with 0.206 grams (3.27 millimols) of tert-butyllithium and 0.195 grams (3.10 millimols) of n-butyllithium. The total volume of this solution in the sample tube was 3.1 ml, making it 1F in each of the alkyllithium compounds in the solution. The resulting concentration of the \((n\text{-butyl})(\text{tert-butyl})_3\text{Li}_4\) tetramer was determined from the total concentration and integrations of the \(^6\text{Li}\) spectra to be 0.13M.

A second sample tube was prepared to have an n-butyl to tert-butyl ratio of 1 to 15. This tube was prepared with 0.220 grams (3.5 millimols) of tert-butyllithium and 0.015 grams (0.24 millimols) of n-butyllithium. The total volume of this solution was 3.1 ml making it 1.2F in alkyllithium compound. The resulting concentration of the \((n\text{-butyl})(\text{tert-butyl})_3\text{Li}_4\) tetramer was 0.07M.

**NMR Experiments.** The one-dimensional \(^6\text{Li}\) spectra were typically acquired with the following parameters. The resonance frequency of \(^6\text{Li}\) at 7.4 Tesla is 44.1 MHz. 1024 data points were collected over a spectral width of approximately 65 Hz with an acquisition time of approximately 10 seconds. Before Fourier transformation the number of data points was zero-filled to 2048. This provided a data point density of about 0.1 Hz/data point. Due to the high abundance of \(^6\text{Li}\) in these compounds, pulse
widths of 2μseconds were sufficient to obtain adequate signal. With short pulse widths and long acquisition times no delay was needed to ensure relaxation of the nuclei.

The \(^{13}\)C spectra acquired on the VXR-300 typically observed a 3500 Hz spectral width. This allowed observation of all \(^{13}\)C shifts in the compound. One-dimensional \(^{13}\)C spectra which accompany two-dimensional spectra usually were obtained with the reduced window used in the two-dimensional spectra. In all cases in this chapter the reduced window encompassed the \(\alpha\)-carbon region of the \(^{13}\)C spectra. This resulted in a spectral width of approximately 500 Hz for the \(n\)-propyllithium/tert-butyllithium system and approximately 800 Hz for the \(n\)-butyllithium/tert-butyllithium system. The number of data points collected was approximately 15000, which was subsequently zero-filled to 30000 before Fourier transformation. Typically an acquisition time of 3 seconds was used with a 60° pulse for the one-dimensional spectra.

As discussed in chapter one, a 10 mm probe has been modified to allow \(^6\)Li decoupling through the lock coil. To obtain \(^{13}\)C\({}^6\)Li\({}^1\)H spectra, the exact frequency necessary to decouple the \(^6\)Li nuclei must be computed. This is done by obtaining a \(^6\)Li spectrum through the decoupler coil. The spectrum was then examined and the desired decoupler frequency found by positioning a cursor at that frequency in the spectrum. Once the cursor is in position the exact
The frequency of the cursor is determined by equation 32 below.

\[ V_{Li} = SPFREQ + TO - SW/2 + DIFF \]  

In this equation SPFREQ is the spectrometer output frequency in Hz, TO is the transmitter offset in Hz, SW/2 is the spectral width divided by 2 and DIFF is the difference in Hz between the observed peak and upfield edge of the spectral window (23). This equation is invoked on the VXR-300 by displaying the \(^6\)Li spectrum, placing the cursor on the desired decoupler position and then using the macro SETDMX. This macro will then return the \( V_{Li} \) needed. The value of \( V_{Li} - 10 \text{MHz} \) is then entered manually into the PTS-160 synthesizer. The \(^6\)Li decoupler was set in a continuous wave mode and the output from the \(^6\)Li decoupler was adjusted to deliver 10 watts of power to the \(^6\)Li coil of the triple resonance probe.

As mentioned in chapter one, the capacitance of the lock coil in this probe was modified to resonate at the \(^6\)Li frequency, therefore samples run using \(^6\)Li decoupling must be performed unlocked. Since a lock coil is not available in this probe, shimming is done through the observe coil. This is accomplished by tuning the observe coil to the \(^2\)H resonance frequency (42 MHz at this field strength) and connecting the lock cable to the observe coil. In this
manner the lock signal may be observed and used to shim. Upon running the experiment the observe coil must be retuned to the $^{13}$C resonance frequency and the lock must be turned off.

The pulse sequence for the $^{13}$C-$^1$H HETCOR used in these systems was modified to allow $^6$Li decoupling. A copy of the source code for this pulse sequence is listed in the appendix. The setting of the $^6$Li decoupler frequency was performed according to the method discussed above. To prevent an abundance of folding-in of the signal, the $^{13}$C spectral width was set to 2500 Hz. The $^1$H spectral width was 1400 Hz. A $^{13}$C-$^1$H coupling of 120 Hz was estimated and entered into the parameters as $J_{1XH}$. A 90° pulse of 21 $\mu$seconds was used on the $^{13}$C nuclei and a 90° pulse of 44.9 $\mu$seconds was performed on the $^1$H nuclei through the decoupler coil. 2048 data points were collected in the F2 dimension and 32 increments were performed resulting in 32 data points in the F1 dimension. The number of transients per increment was 800. A delay of 2 seconds was used to relax the $^1$H nuclei sufficiently to obtain adequate signal. Before performing the Fourier-transform, the F2 dimension was zero-filled to 4096 points and the F1 dimension was zero-filled to 128 points. No line broadening or resolution enhancement were used in the displayed spectrum. The time required from start to completion of these experiments was
approximately 12 hours.

It was found the most informative means of displaying this spectrum was to display a vertical projection of the F2 (\(^{13}\)C) dimension. Such a projection displays only peaks with proton correlation thus distinguishing the primary \(\alpha\)-carbons from the tert-butyl \(\alpha\)-carbons.

The \(^{13}\)C-\(^{6}\)Li HETCOR was performed as described in reference 23. The spectral width of the \(^{13}\)C dimension in this experiment must only contain the \(\alpha\)-carbon region, thus the spectral width for the \(^{13}\)C dimension of the \(n\)-propyl/tert-butyl system was 550 Hz and the spectral width for the \(n\)-butyl/tert-butyl system was 800 Hz. The spectral width necessary to contain the entire \(^{6}\)Li spectrum was the same in both experiments. Both experiments made use of spectral widths in the \(^{6}\)Li dimension of approximately 50 Hz.

The number of data points collected in the F2 dimension was 2048 while the number of increments performed was 32. These values were zero-filled to 4096 and 128 respectively before Fourier-transformation. The number of transitions per increment was 256. A relaxation delay of 25 seconds was used to allow relaxation of both the \(^{13}\)C and \(^{6}\)Li nuclei. The 90° pulse on the \(^{13}\)C nuclei was 21.0\(\mu\)s and the 90° pulse used on the \(^{6}\)Li nuclei through the decoupler coil was 696.0\(\mu\)s.

The mix time for this experiment was set as described
in reference 23. In this experiment, the mix time is divided into two time variables, D3 and D4. These time variables are set based on coupling values. In the systems studied in this chapter, $^{13}$C-$^6$Li coupling values range from 2.7 Hz to 6.8 Hz. For these systems intermediate values were chosen taking into account peak intensities. For both of the HETCOR experiments performed on these systems, a D4 value of 0.0237 seconds and a D3 of 0.13 seconds was chosen. Initially, attention was focused on the hexamers which were low in intensity compared to the tetramers, therefore, the D3 and D4 values were weighted towards the hexameric coupling values.

As explained in the text of this chapter, most of the $\alpha$-carbons exhibiting tetrameric couplings showed correlations in the two-dimensional spectrum. However, in both cases, the primary alkyl $\alpha$-carbons of the 2:2 tetramer did not reveal a correlation. As discussed in the text, this is caused by the low intensity of the peak along with the large difference in $^{13}$C-$^6$Li coupling constants between this $\alpha$-carbon and the hexameric $\alpha$-carbons towards which this experiment was weighted. In both $^{13}$C-$^6$Li HETCOR experiments performed on these mixtures, the time required from start to finish of the experiment was approximately 50 hours.

The two-dimensional exchange spectra were acquired in a manner similar to those acquired in chapter 2. Mix times
and relaxation delays were temperature dependent and are
different for each experiment. The mix times were arrived
at according to the equation discussed in the text. The
relaxation delays (D1) were typically 3 times T1 of the
observed nuclei.

The spectral width used was 50 Hz. The number of data
points collected in the F2 dimension was 1024 and the number
of increments used for the F1 dimension was 128. These
values were zero-filled before Fourier-transformation to
2048 and 256 respectively. The spectra were not folded
before intensity determination. Intensity determination was
performed as described in chapter 2. The computer program
D2DNMR, discussed in chapter 2 was used to arrive at
exchange rates.

The Eyring plots produced from these exchange rates
were made by fitting the points to a straight line using a
least squares analysis. The error bounds reflect only the
fitting of the points to a straight line and are at one
standard deviation.

The T1 experiments were run using the standard
inversion recovery pulse sequence (40) (41) available on the
VXR-300. This pulse sequence makes use of minimum and
maximum T1's expected, to set incremented delay values. The
longest delay is set to 5 times the expected maximum T1 to
insure complete relaxation.
Temperature measurement. A methanol NMR thermometer was used on each 2DEXSY experiment to measure the temperature of the probe. As discussed in chapter 3, the methanol thermometer makes use of the fact that the proton shifts in methanol are temperature dependent; therefore, these shifts can be used to measure the temperature of the NMR probe.

This measurement is accomplished by inserting a neat methanol sample into the probe and setting the variable temperature controller to the desired temperature. After waiting a minimum of 15 minutes to insure that the methanol has reached the desired temperature, a proton spectrum is acquired. The cursors are then positioned on the proton peaks and the macro TEMCAL(M) is run. This macro uses the cursor positions to return the temperature of the methanol.

As discussed in chapter 3, this type of temperature measurement does not allow for the proton decoupling used during the 2DEXSY experiments. To determine actual probe temperature, a temperature study was done relating the methanol chemical shift thermometer to an actual ethanol thermometer subjected to proton decoupling identical to that used during the 2DEXSY experiment. This thermometer was placed inside a 10 mm NMR tube containing cyclopentane, inserted into the probe and the temperature allowed to equilibrate to that of the probe for a minimum of 15 minutes. This tube was then quickly removed and the
temperature recorded. The methanol chemical shift thermometer was then placed in the probe and allowed to equilibrate. A proton spectrum was then acquired and used to determine the probe temperature. The ethanol thermometer generally recorded a temperature approximately 2°C warmer than the methanol chemical shift thermometer, presumably due to the proton decoupling used in the experiment.

The thermometer temperatures were then plotted against the methanol chemical shift temperatures. Before each experiment the methanol chemical shift thermometer was used to determine the temperature without proton decoupling and then this temperature was adjusted according to the ethanol thermometer temperatures. With this method the cumbersome task of using the ethanol thermometer could be avoided for each experiment and replaced by the relatively simple task of using the methanol chemical shift thermometer.
CHAPTER BIBLIOGRAPHY


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CHAPTER 5

n-PROPYLLITHIUM/n-BUTYLLITHIUM MIXED HEXAMERS
AND RACEMIC 2-METHYLBUTYLLITHIUM
MIXED HEXAMERS

Introduction

The fluxionality of alkyllithium hexamers has, in the past, been a matter of speculation (1)(2)(3). The information presented in chapters 3 and 4 about hexameric intraaggregate exchange has provided the first information about the nature of this exchange process. It may be concluded from the data presented in chapters 3 and 4 that limited fluxionality occurs in the alkyllithium hexamers examined. The hexamers studied in these chapters are not representative of alkyllithium hexamers in general in that they are composed of either both tert-butyl and tert-butoxide groups or tert-butyl and a straight chain alkyl group. In general, these hexamers are composed of two types of groups, one of which is much more sterically demanding than the other. One might suggest that the limited fluxionality is peculiar to hexamers which contain a bulky alkyl group such as a tert-butyl group.

To determine if limited fluxionality is a process common to alkyllithium hexamers, n-propyllithium/n-butyllithium mixed hexamers and 2-methylbutyllithium hexamers were examined. The n-propyllithium/n-butyllithium...
mixture contains only alkyllithium compounds which are known to form hexamers (4)(5)(6)(7). Therefore, the mixed hexamers this mixture produces would be representative of alkyllithium hexamers in general.

2-Methylbutyllithium has the desired trait of producing pure alkyllithium hexamers, while at the same time providing non-equivalent sites within these hexamers due to the presence of a chiral carbon. Both features are necessary in order to determine if pure alkyllithium hexamers undergo the limited fluxionality observed for the mixed hexamers in chapters 3 and 4.

Fraenkel has studied 2-methylbutyllithium in depth (8) using $^1$H NMR, and has determined there to be four sets of diastereomeric hexamers composed of the different optical isomers of this compound. Using the R and S designations for the optical isomers of 2-methylbutyllithium, these four sets of diastereomers are: $R_6 + S_6$, $R_4S + S_3R$, $R_4S_2 + S_4R_2$, and $R_3$. The pairs of hexamers which are grouped together, such as $R_6$ and $S_6$, are enantiomeric and thus are indistinguishable with NMR. Fraenkel has shown the existence of these diastereomers in both 2-methylbutyllithium and the optically active secondary alkyllithium compound, sec-butyllithium (9).

Thomas has reported the observation of coupling in 2-methylbutyllithium of 3.4 Hz and noted this coupling to be
obscured by the presence of multiple α-carbons (10) (11). The multiple α-carbons were supposed to indicate the existence of different diastereomers composed of the different proportions of the optical isomers as Fraenkel had earlier indicated. The presence of these different types of hexamers in a pure alkyl lithium system provides an ideal situation for study of the limited fluxional exchange proposed in chapters 2 and 3.

Results and Discussion

*n*-Propyllithium/*n*-Butyllithium mixtures. A sample tube containing 1.6F *n*-propyllithium and 1.3F *n*-butyllithium in cyclopentane solvent was prepared in order to determine if these mixed aggregates would be formed in a mixture of primary alkyl lithium compounds. The resulting mole ratio of *n*-propyllithium to *n*-butyllithium was 1.2 to 1.

*n*-Propyllithium in hydrocarbon solvent had been studied in the past and had shown low temperature α-carbon couplings consistent with hexamers, octamers, and nonamers (4)(5)(6). The 6Li spectra of *n*-propyllithium in these past studies had revealed three large peaks and two smaller peaks, consistent with the conclusions that, at low temperature, *n*-propyllithium existed as hexamers, octamers, and three kinds of nonamers (4).
Li spectra of the n-propyllithium/n-butyllithium mixture are shown in Figure 45. These spectra are nearly identical with spectra shown in references 4 and 6. This indicates that the n-propyllithium/n-butyllithium mixture behaves in a manner very similar to n-propyllithium. n-Butyllithium has also been studied in the past with the findings being not quite as clear as the n-propyllithium system in that $^{13}$C-$^6$Li coupling was not observable and the $^6$Li spectra showed peaks not quite as well resolved (6). However it was assumed, due to the similarities in the two systems, that n-butyllithium also existed at low temperatures as hexamers, octamers, and nonamers (6).

The $^6$Li spectra in Figure 45 indicate that in the n-propyllithium/n-butyllithium mixture, the presence of the n-propyl group slows the interaggregate exchange of these aggregates to values somewhere between pure n-propyllithium aggregates and pure n-butyllithium aggregates. Figure 46 displays both $^6$Li coupled and decoupled $^{13}$C spectra at -77°C. These spectra reveal many types of different hexamers, octamers, and nonamers. In the coupled spectrum the three broad peaks at 18.4 ppm, 17.4 ppm, and 15.5 ppm, are identical to shifts observed in the pure n-propyllithium aggregates (4) (6) and are thus assigned accordingly to the n-propyl $\alpha$-carbons of the nonamer, octamer, and hexamer respectively.
Figure 45 - Variable temperature $^6\text{Li}$ spectra of $n$-Propyllithium/$n$-butyllithium mixture. Total alkyllithium concentration = 1.3F. $n$-Propyl:$n$-butyl = 1.2:1.
Figure 46 - $^{13}$C spectra with (top) and without (bottom) $^6$Li decoupling of n-propyllithium/n-butyllithium mixture. Total alkyllithium concentration = 1.3F. N-propyl:n-butyl = 1.2:1. Temp = -75°C.
The chemical shift of the α-carbons of n-butyllithium hexamers in hydrocarbon is 11.7 ppm (6). This shift corresponds well with an α-carbon shift in Figure 46, thus this peak is assumed to be the n-butyl α-carbons of the hexamers in the n-propyllithium/n-butyllithium mixture. In comparison with the n-propyllithium system, the α-carbon shifts at 13.4 ppm, and 14.3 ppm can be assigned to the n-butyl α-carbons of the octamer and nonamer respectively. The intense sharp peaks in the 13.5 ppm region of this spectra are from the methyl carbon of the n-butyl groups. This assignment is based on chemical shift comparison with pure n-butyllithium (13). The splitting of this peak into multiple peaks in Figure 46 indicates the presence of many different types of aggregates, as would be expected in such a mixed system.

The $^{13}$C{"Li} spectrum at the top of Figure 46 reveals each α-carbon peak is actually composed of several different types of aggregates. Considering there are seven types of hexamers possible, and in each hexamer there are non-equivalent sites, one would expect many peaks for the hexamers, and multiple peaks for the octamers, and nonamers. This is what is revealed in Figure 46, in that each broad α-carbon peak in the ⁶Li coupled $^{13}$C spectrum is shown to be composed of several different peaks in the $^{13}$C{⁶Li} spectrum. Due to the similarities observed in the n-propyllithium and
n-butyllithium systems, one would expect there to be only very small chemical shift differences between the non-equivalent sites within the aggregates. This is observed in that it is impossible to determine in the spectra shown in Figure 46, how many different α-carbon sites there are in all of the hexamers combined, and thus it is also impossible to determine the number of non-equivalent sites in a specific hexamer.

It is thus determined that in an n-propyllithium/n-butyllithium mixture, mixed aggregates are formed including mixed octamers and mixed nonamers. No new information concerning the nature of fluxionality or interaggregate exchange is revealed in the study of this system. The chemical shifts of n-butyl α-carbons in pure n-butyllithium octamers and nonamers had not been revealed prior to this study, but may be inferred from this study to be approximately 13.4 ppm and 14.3 ppm respectively.

2-Methylbutyllithium. Shown in Figure 47 are variable temperature 6Li spectra of 2-methylbutyllithium in cyclopentane solution. These spectra are referenced to the reported shift of 2-methylbutyllithium (10). It may be observed in these spectra that the 6Li peak is broad at +12.3°C and, by -42.7°C, splits into four peaks. As temperature further decreases, these peaks broaden further due to decreasing T2.
Figure 47 - Variable temperature $^6$Li spectra of 2-methylbutyllithium. Sample is 2F 2-methylbutyllithium in cyclopentane.
Applying resolution enhancement to the -42.7°C spectrum in Figure 47 results in the spectrum shown in Figure 48. In this spectra there are four well-defined peaks which are labeled XX through XXIII. Integration of the spectrum in Figure 48 results in intensities listed in Table 20. These intensities must be taken as approximate since they are obtained from a resolution enhanced spectrum.

<table>
<thead>
<tr>
<th>Li peak</th>
<th>intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td>4.6</td>
</tr>
<tr>
<td>XXI</td>
<td>20.8</td>
</tr>
<tr>
<td>XXII</td>
<td>45.6</td>
</tr>
<tr>
<td>XXIII</td>
<td>29.0</td>
</tr>
</tbody>
</table>

Concentration of 2-methylbutyllithium was 2F. Temperature of spectrum from which the intensities were taken was -42.7°C.

Assuming a random distribution of the $R$ and $S$ isomers of the 2-methylbutyl group results in a binomial distribution of the different diastereomeric hexamers discussed above. Thus the relative amounts of each of the four diastereomeric hexamers would be the coefficients in the expansion of $(x+y)^6$. These expected amounts of the diastereomers are listed in Table 21.
Figure 48 - $^6$Li spectrum at -42.7°C using resolution enhancement. Sample is 2F 2-methylbutyllithium in cyclopentane.
Table 21
Relative amounts of the diastereomers expected from a random distribution of the optical isomers of 2-methylbutyllithium.

<table>
<thead>
<tr>
<th>Hexamer</th>
<th>relative amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_6 + S_6$</td>
<td>3.1</td>
</tr>
<tr>
<td>$R_5 S + S_5 R$</td>
<td>18.8</td>
</tr>
<tr>
<td>$R_4 S_2 + S_4 R_2$</td>
<td>46.9</td>
</tr>
<tr>
<td>$R_3 S_3$</td>
<td>31.3</td>
</tr>
</tbody>
</table>

As can be observed in comparing Table 20 with Table 21, despite the poorly resolved $^6$Li spectrum in Figure 47, there is very good agreement between the four $^6$Li peaks produced by 2-methylbutyllithium and the relative intensities of the four different diastereomers expected in this system. It may be assumed that the four peaks in the $^6$Li spectra are due to the presence of the four diastereomeric hexamers.

Variable temperature $^{13}$C spectra of the 2-methylbutyllithium sample are shown in Figure 49. The assignment of the peaks in these spectra are made according to reference 6 and are shown below in Table 22.

In the spectra shown in Figure 49 it may be observed that all five $^{13}$C resonances split as temperature decreases. As temperature descends $C_3$, $C_4$, and $C_5$ split into ten poorly resolved peaks. The chiral carbon, $C_2$, splits into four peaks whose intensities are reminiscent of the $^6$Li spectra.
Figure 49 - Variable temperature $^{13}$C spectra of 2-methylbutyllithium. Sample is 2F 2-methylbutyllithium in cyclopentane.
Table 22
\[^{13}\text{C} \text{ shifts of 2-methylbutyllithium according to reference 10.}\]

\[\begin{array}{c|ccccc}
\text{Carbon} & C^1 & C^2 & C^3 & C^4 & C^5 \\
\hline
C^1 & 23.5 & & & & \\
C^2 & 35.9 & & & & \\
C^3 & 36.6 & & & & \\
C^4 & 11.8 & & & & \\
C^5 & 25.4 & & & & \\
\end{array}\]

of this sample. The number of peaks produced by the \(\alpha\)-carbon is obscured in these spectra by the presence of \(^{13}\text{C}\)-\(\text{Li}\) coupling.

The \(^{13}\text{C}\) spectra, when examined closely, reveal the \(\alpha\)-carbons of 2-methylbutyllithium to show fluxional hexameric coupling of 3.3 Hz as high as \(-20^\circ\text{C}\). A figure revealing this coupling is shown later in this chapter. The observation of this coupling reveals that interaggregate exchange among these hexamers has reached the slow limit by \(-20^\circ\text{C}\). This information contradicts Fraenkel’s earlier report that these hexamers underwent fast interaggregate exchange as low \(-50^\circ\text{C}\) (8). Fraenkel’s interaggregate exchange studies on 2-methylbutyllithium made use of \(^1\text{H NMR}\) and changes in the lineshapes due to this exchange. His conclusions were based upon the idea that all sites in a hexamer were equivalent, therefore, the exchange bringing
about the changes in the $^1$H lineshapes must need be interaggregate. The $^{13}$C spectra shown in Figure 49 revealed 10 different chemical shifts for each of $C^3$, $C^4$, and $C^5$, even though $^6$Li spectra confirm the system to be composed of the four diastereomeric hexamers Fraenkel predicted. This indicates that the alkyl groups within hexamers may occupy non-equivalent sites; therefore, the changes in $^1$H lineshapes he observed did not necessarily require interaggregate exchange. These inconsistencies are discussed later in this chapter.

Shown in Figure 50 are $^{13}$C spectra of the $\alpha$-carbon region of 2-methylbutyllithium at $-42.7^\circ$C. The bottom spectrum in this figure is a normal $^{13}$C spectrum in which $^{13}$C-$^6$Li coupling of 3.3 Hz is revealed. Both the middle spectrum and the top spectrum make use of $^6$Li decoupling and originate from the same FID. The difference between the middle and top spectra is that resolution enhancement was used in the top spectrum.

What looks to be eight different types of $\alpha$-carbons in the middle spectrum is revealed to be ten poorly resolved peaks in the top spectrum. These peaks are labeled P through Y. Immediately the conclusion may be drawn that, although these hexamers are fluxional, they are not randomly fluxional. If these hexamers were randomly fluxional, the maximum number of $\alpha$-carbon peaks observed would be six. The
Figure 50 - $^{13}$C spectra of 2-methylbutyllithium. Sample is 2F 2-methylbutyllithium. Temperature = -42.7°C. The bottom spectrum is normal $^{13}$C, the middle spectrum is $^{13}$C($^6$Li), and the top spectrum is $^{13}$C($^6$Li) using resolution enhancement.

* - indicates a peak which has been folded-in due to the reduced spectral width.
hexamer would produce only one α-carbon signal, as would the combination of the $R_6$ and $S_6$ hexamers. The $R_3S_3$ and the $S_4R_2$ hexamers would together produce two α-carbon resonances in a ratio of 4 to 2. The $R_5S$ and $S_5R$ hexamers would together produce two α-carbon signals in a ratio of 5 to 1.

In order to determine which α-carbons were produced by which hexamers, and thus determine the number of non-equivalent sites within each hexamer, a $^{13}{\text{C}}-^6{\text{Li}}$ HETCOR was run on this 2-methylbutyllithium sample. This spectrum is shown in Figure 51. As might be expected, resolution in this spectrum is very poor and assignment is difficult in viewing the figure. However, use of the interactive display of this spectrum on the VXR-300 computer reveals this experiment to provide a tremendous amount of information. It is shown in this experiment that peaks P, W, and X correlate with $^6{\text{Li}}$ peak XXII. $^{13}{\text{C}}$ peaks Q, R, and V correlate with $^6{\text{Li}}$ peak XXI. $^{13}{\text{C}}$ peaks S, T, and U correlate with $^6{\text{Li}}$ peak XX and $^{13}{\text{C}}$ peak Y correlates with $^6{\text{Li}}$ peak XXIII. This data is summarized in Table 23.

An intensity study was run on the α-carbon region of the $^{13}{\text{C}}$ spectrum in order that the relative amounts of each type of α-carbon on each hexamer could be determined. It was assumed that the α-carbons would all possess similar relaxation rates and NOE effects therefore a normal $^{13}{\text{C}}$ spectrum would be sufficient for an intensity determination.
Figure 51 - $^1$H-$^6$Li HETCOR. The sample is 2F 2-methylbutyllithium in cyclopentane. Temp = -50°C. D1 = 7.5s D3 = 0.15s. D4 = .0236s. PP = 696.0μs.
The resolution enhanced spectrum shown in Figure 48 was used in the intensity determination. Resolution between the peaks is very poor and the intensities are approximate. However, the intensities are fairly consistent with the $^6$Li intensity determination tabulated in Table 20 and the mathematically predicted intensities in Table 21. The result of this study is tabulated in Table 23.

<table>
<thead>
<tr>
<th>$^{13}$C peak</th>
<th>shift (ppm)</th>
<th>intensity</th>
<th>$^6$Li correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>23.96</td>
<td>3.3</td>
<td>XXII</td>
</tr>
<tr>
<td>Q</td>
<td>23.77</td>
<td>3.1</td>
<td>XXI</td>
</tr>
<tr>
<td>R</td>
<td>23.70</td>
<td>12.4</td>
<td>XXI</td>
</tr>
<tr>
<td>S</td>
<td>23.50</td>
<td>12.8</td>
<td>XX</td>
</tr>
<tr>
<td>T</td>
<td>23.46</td>
<td>5.5</td>
<td>XX</td>
</tr>
<tr>
<td>U</td>
<td>23.44</td>
<td>11.8</td>
<td>XX</td>
</tr>
<tr>
<td>V</td>
<td>23.30</td>
<td>30.6</td>
<td>XXI</td>
</tr>
<tr>
<td>W</td>
<td>22.93</td>
<td>13.4</td>
<td>XXII</td>
</tr>
<tr>
<td>X</td>
<td>22.70</td>
<td>3.5</td>
<td>XXII</td>
</tr>
<tr>
<td>Y</td>
<td>22.68</td>
<td>3.1</td>
<td>XXIII</td>
</tr>
</tbody>
</table>

Table 23

$^{13}$C shifts, intensities, and $^6$Li correlations of the $\alpha$-carbon region of 2-methylbutyllithium.

The NMR sample was 2F 2-methylbutyllithium. Intensity study was performed at -42.7°C. $^{13}$C-$^6$Li HETCOR was performed at -50°C.

The non-equivalence observed in specific hexamers may now be addressed. According to the original assignment of the hexamers based on the $^6$Li intensities, $^6$Li peak XXIII is produced by the hexamers $R_6$ and $S_6$. This $^6$Li peak correlated with the $^{13}$C $\alpha$-carbon peak Y. In the $R_6$ hexamer, all sites
are equivalent and enantiomeric with all sites in the $S_6$ hexamer. Thus these hexamers together produce only one $^{13}$C $\alpha$-carbon resonance. Table 21 reveals this hexamer to constitute 3.1% of the total amount of hexamers, therefore, $\alpha$-carbon resonance $Y$ should comprise approximately 3.1% of the total $\alpha$-carbon signal. As shown in Table 23, peak $Y$ constitutes 3.1% of the total $\alpha$-carbon signal.

The $^6$Li peak XXII is produced by the hexamers $R_3S$ and $S_3R$. The consideration of these hexamers may be simplified by considering only one or the other and recognizing that every site in $R_3S$ has an enantiomeric site in $S_3R$. Similar simplifications are used in the explanation of the other hexamers. These simplifications make use of the fact that NMR cannot distinguish between enantiomeric sites such as the $R$ isomers in $R_6$ and the $S$ isomers in $S_6$. Of greater interest is the more complicated hexamers such as $R_3S$ and $S_3R$. In the $R_3S$ hexamers there is more than one chemical shift for the $\alpha$-carbons of the $R$ isomers; however, for each $R$ isomer site in this hexamer, there is an enantiomeric site in the $S_3R$ hexamer which is filled by the enantiomer of $R$, which is $S$. For this reason one may consider only one or the other of the diastereomeric pair, such as $R_3S$, with the realization that the consideration of $S_3R$ would provide no different chemical shifts, but simply double the intensity of all the shifts caused by the $R_3S$ hexamer. Thus the
consideration of only one of the hexamers does not affect the number of $^{13}$C peaks produced, nor the relative intensity among those signals.

The $R_S$ hexamer is shown in Figure 52 using the simplified hexagonal structure used previously to represent the hexamers discussed in chapters 3 and 4. A rigid structure has been ruled out by the observance of coupling consistent with fluxional hexamers; however, it may be observed in viewing Figure 52 that, if the structure were rigid, there would be three types of $R$ groups and one type of $S$ group. One would then expect this hexamer to possess four types of $\alpha$-carbons. Random fluxionality would lead to two types of $\alpha$-carbons, one from each the $R$ and $S$. If this hexamer makes use of the limited fluxionality as discussed in chapters 3 and 4, it would possess three types of $\alpha$-carbons in a ratio of 1:4:1. Considering the fact that the $R_S$ and $S_R$ hexamers should compose 18.8% of the total amount of hexamer, the $\alpha$-carbons from these hexamers should compose 3.1%, 12.6%, and 3.1% of the total amount of $\alpha$-carbon signal. The $^6$Li peak XXII correlates to the $^{13}$C peaks P, W, and X which have an intensity ratio of 3.3:13.4:3.5 respectively. This ratio is in good agreement with the expected ratio considering the poor resolution in the $^{13}$C spectrum.

The $^6$Li peak labeled XX is produced by the lithiums in
Figure 52 - The $R_6S$ hexamer using the simplified representation.
the hexamers whose constitution is \(R_3S_3\). The three different structures available for this composition are shown in Figure 53. For explanation purposes consideration will only be given to the \(R\) isomers in these hexamers, realizing that each \(S\) isomer in these hexamers occupies a site which is enantiomeric with an \(R\) group. Structure A in this figure would possess two types of \(R\) isomers in a 2 to 1 ratio. Structure B possesses only one type of \(R\) isomer and structure C possess three types of \(R\) isomers.

Since these hexamers were shown by \(\text{\^{13}C-\text{\textsuperscript{6}Li}}\) coupling to be fluxional, the rigid structures are not a possibility. Random fluxionality of these hexamers would lead to only one type of \(R\) isomer in these hexamers creating only one \(\alpha\)-carbon signal. This \(R\) isomer would be enantiomeric with the \(S\) isomer in this hexamer and thus the entire hexamer would cause only one type of \(\alpha\)-carbon. Since the \(\text{\textsuperscript{6}Li}\) peak from this hexamer correlated with \(\text{\^{13}C}\) peaks S, T, and U in the \(\text{\^{13}C-\text{\textsuperscript{6}Li}}\) HETCOR, this hexamer is known to not be randomly fluxional.

The limited fluxionality of this hexamer would allow structures A and B in Figure 53 to convert between each other and allow all three \(R\) isomers in structure A to occupy each of the two different sites. Thus structures A and B would together produce only one type of \(R\) isomer which would be enantiomeric with the \(S\) isomer in this hexamer.
Figure 53 - The three possible structures for the $R_3S_3$ hexamers using the simplified representation.
Therefore, only one α-carbon signal should originate from the A and B structures.

The limited fluxionality will not cause exchange between structure C in Figure 53 with either structure A or B. However of the three types of R isomers in this hexamer, the two which are opposite each other will exchange, causing there to be two types of R isomers from this hexamer in a ratio of 2 to 1. As with the other structures, the S isomers of this hexamer occupy positions which are enantiomeric with the R isomers and thus have the same chemical shifts. The total number of $^{13}$C α-carbon shifts from the hexamers of composition $R_3S_3$ is thus 3, one from structures A and B of Figure 53 and the other two from structure C of Figure 53. The two different types of hexamers with this composition do not produce different $^6$Li peaks due to the similarity of these hexamers from the lithiums point of view.

The total amount of hexamer of composition $R_3S_3$, relative to the entire amount of hexamers should be 31.1% as shown in Table 21. This fits well with the integration of the α-carbons from these hexamers relative to the amount of α-carbon signal. Table 23 reveals α-carbons S, T, and U constitute 30.1% of the total α-carbon signal. Of these three types of α-carbons a random distribution of the R and S isomers should result in 40% of the structures being of
type A and B in Figure 53 and 60% of type C. This would result in a total ratio of these three peaks of 2 to 2 to 1, as the α-carbons from structure C are in a 2 to 1 ratio. There is very poor resolution between these three peaks making integration difficult at best, however peaks S, T, and U integrate to a ratio of 2.3 to 1 to 2.1 which is very close to the expected ratio for these three peaks.

The $^6$Li peak XXI is produced by the lithiums in the hexamers whose constitution is $R_4S_2$ or $S_4R_2$. This peak correlated with the $^{13}$C peaks Q, R, and V in the $^{13}$C-$^6$Li HETCOR. The total amount of α-carbon signal from these hexamers should be 46.9% as shown in Table 21. The $^{13}$C α-carbon peaks Q, R, and E, together make up 46.1% of the total α-carbon signal as shown in Table 23.

Figure 54 displays the six possible structures of these two hexamers. If these hexamers were randomly fluxional two signals from the α-carbons of the R isomers would be expected. One of these signals would originate from the $R_4S_2$ hexamer and the other from the $S_4R_2$ hexamer. The S isomers would occupy enantiomeric positions of the R isomers thus making the total number of α-carbon sites from this hexamer, two in a ratio of 2 to 1. Considering the limited fluxionality, structures D and E of Figure 54 are exchanging structures, as are there enantiomers, structures G and H. Henceforth the exchange combination of structures D and E
Figure 54 - The six possible structures for the $R_4S_2$ and $S_4R_7$ hexamers.
will be referred to as DE and the exchange combination of structures G and H will be referred to as GH. This limited fluxionality causes there to be two types of R isomers in the DE structures. In structure F, all of the R isomers are equivalent. The total number of sites the R isomer may occupy in the \( R_4S_2 \) hexamer would then be three.

In the hexamer of composition \( S_4R_2 \), the GH structure would produce one type of R isomer and structure I would produce another. The total number of sites the R isomer may occupy in the \( R_4S_2 \) and \( S_4R_2 \) hexamers is then five. This obviously does not fit with the three observed \( \alpha \)-carbons for this hexamer. Since the other hexamers in this system appear to be undergoing the limited fluxionality described for the hexamers in chapters 3 and 4, and since random fluxionality has been ruled out for this hexamer, it would seem this hexamer must also undergo this same limited fluxionality. However, if this hexamer is undergoing limited fluxionality, the non-equivalence observed in the other systems is not so apparent in this hexamer. Proposed reasons for this will be discussed in the chemical shift correlation section below.

A chemical shift consistency begins to become apparent in considering the \( R_6+S_6 \) and the \( R_6S+S_6R \). Examining the environment from the point of view of the \( R \), it would seem that the presence of the \( S \) isomer shifts the \( \alpha \)-carbon of the
R isomer downfield. Therefore the α-carbons from the R isomer of the pure \( R_6 \) hexamer are the most upfield of the α-carbons. Likewise the α-carbons of the \( S_6 \) are enantiomeric with these α-carbons and thus possess the same chemical shift.

In the \( R_5S \) and the \( S_5R \) hexamers there are three types of R groups. The two types of R isomers on the \( R_5S \) hexamer are part of a hexamer which contains only one S. One of these two types is the unique R isomer which is always opposite the S group, therefore one would expect it to be most like the pure \( R_6 \) hexamer. This unique R, as shown above, should constitute approximately 3.1% of the total amount of α-carbon signal. This is exactly the amount that should originate from the \( R_5+R_6 \) hexamer α-carbons. As may be observed, the \(^{13}C \) α-carbon peak X is 0.02 ppm downfield of the α-carbon peak from the \( R_6 \) hexamer, peak Y. One may also observe that these two peaks are of approximate equal intensity. Therefore it would seem peak X is caused by the α-carbons from the unique R in the \( R_5S \) hexamer, and its enantiomeric site, the unique S in the \( S_5R \) hexamer.

The other type of R isomer in the \( R_5S \) hexamer shown in Figure 52, is the type which is an average between the two R isomers which are ortho the S isomers and those which are meta the S isomers. The α-carbon signal which originates from these four R isomers should have only a small amount of
$S$ influence and thus be shifted only slightly downfield from peak $X$. The intensity of this peak should be four times that of peak $X$. Peak $W$ is the $^{13}C$ peak which is caused by these $\alpha$-carbons as revealed by its intensity and chemical shift.

The last type of $R$ isomer in the $R_5S$ and $S_5R$ hexamers is the $R$ isomer in the $S_5R$ hexamer. This hexamer is the only $R$ isomer in this hexamer and thus would be shifted downfield from the other two types of $R$ isomers. The intensity of this peak should be equal to that of peak $X$ and $1/4$ that of peak $W$. This data fits well with peak $P$, the most downfield of all the $\alpha$-carbon peaks. The enantiomeric site in the $R_5S$ hexamer would have exactly the same chemical shift.

When considering the small differences in the environments of the $R$ isomers of the $R_4S_2$ and $S_4R_2$ hexamers, it may be noticed that there is one relatively large difference in these environments which separates the shifts into two areas of the spectrum. The $R$ isomers of the $S_4R_2$ hexamers should have considerably more influence from the $S$ isomers than the $R$ groups of the $R_4S_2$ hexamers and thus be shifted further downfield according to the trends noticed in the $R_5+S_6$ hexamers and $R_5S+S_5R$ hexamers described above.

Equal amounts of the $S_4R_2$ and the $R_4S_2$ hexamers should be present in the solution with their combined intensity being $46.9\%$ of the total intensity of $\alpha$-carbons. Since there are
only half as many $R$ isomers in the $S_4R_2$ hexamers as in the $R_4S_2$ hexamers this ratio should be divided between the two groups in a 1 to 2 ratio. As explained above the $\alpha$-carbons from the $S_4R_2$ and $R_4S_2$ hexamers are the $^{13}$C peaks Q, R, and V. Of these three peaks Q and R are very close in chemical shift and are shifted approximately 0.5 ppm downfield of peak V. The total intensity of peaks Q and R is 15.5 whereas the intensity of peak V is 30.6. This is an intensity ratio of 1 to 2.0. This would seem to indicate that peaks Q and R are caused by the $R$ isomer $\alpha$-carbons of the $S_4R_2$ hexamer and the enantiomeric site, the $S$ isomer $\alpha$-carbons of the $R_4S_2$ hexamer.

The $R$ isomers of the $S_4R_2$ hexamers are divided into two types, one from structure GH of Figure 54 and the other from structure I of Figure 54. Assuming a random distribution of these two structures, the mathematical distribution of structure GH and structure I should be in a ratio of 4 to 1. The intensities of peaks Q and R as shown in Table 23 are 3.3 and 12.4 respectively. This is in good agreement with the expected intensities from the $R$ isomers of the $S_4R_2$ and the $S$ isomers of the $R_4S_2$ hexamers undergoing limited fluxional exchange.

The $R$ isomers of the $R_4S_2$ hexamers and the $S$ isomers of the $S_4R_2$ hexamers must now be explained. The data indicates that the chemical shifts of the $\alpha$-carbons from all of sites
occupied by the more abundant isomer in each hexamer are too close to be resolved. Considering the R isomer of the $R_4S_2$ hexamer as shown in Figure 54, there are three different environments. Figure 55 displays the local environment of each of these three R isomers with the exchanges these groups undergo. The top two exchange schemes represent exchange structures for the two different types of R isomers in structures D and E of Figure 54. The bottom exchange scheme represents the local environment of the single type of R isomer in the F structure of Figure 54. It may be observed that all of the R isomers in question have a common exchange structure in which it is bordered by one R isomer and one S isomer.

All of the evidence combined for the $R_4S_2$ and $S_4R_2$ hexamers suggests that these three different R isomer $\alpha$-carbons, shown in Figure 55, have the same chemical shift because of similar environments, not because they are exchanging with each other. This is suggested by the fact that the other hexamers examined are consistent with hexamers undergoing the limited fluxional exchange, and by the obvious similarity in environments as shown in Figure 55.

Based on the chemical shift arguments discussed above, it would be expected that the R isomer $\alpha$-carbons of the $R_3S_3$ hexamers would have a chemical shift intermediate between
Figure 55 - The local environments for the three types of R isomers in the $R_4S_7$ hexamers.
the R isomers with the least S isomer influence and the R isomers with the most S isomer influence. The R isomer with the least S isomer influence would be the R isomers of the R₆ hexamer, (α-carbons peak Y), and the R isomer with the most S isomer influence would be the R isomers of the S₃R hexamer (α-carbon peak P). Therefore the chemical shifts for the α-carbons of the R isomers from the R₃S₃ hexamer should be approximately midway between the shifts of peak Y and peak P. This is consistent with the observed α-carbons of the R₃S₃ hexamers, peaks S, T, and U being approximately 0.5 ppm upfield of peak P and approximately 0.8 ppm downfield of peak Y.

In order to verify for certain that the different peaks observed in 2-methylbutyllithium were indeed caused by the presence of different optical isomers, optically pure (R)-2-methylbutyllithium was prepared (14). Figure 56 displays variable temperature ¹³C spectra of (R)-2-methylbutyllithium. It is immediately obvious that the splitting observed in the racemic mixture of 2-methylbutyllithium as shown in Figure 49 is not as apparent in this mixture. A small amount of splitting of the ¹³C peaks may be observed due to the presence of the 0.55% (S)-2-methylbutyllithium. This contaminant generates a small amount of the RS₅ hexamer. This data verifies that the observed splitting in the racemic mixture is caused by the presence of the
Figure 56 - Variable temperature $^{13}$C spectra of (R)-2-methylbutyllithium. Sample is 2F in (R)-2-methylbutyllithium. * - peaks from the hydrocarbon contaminant, 3,6-dimethyloctane.
different diastereomers created by the presence of both optical isomers of 2-methylbutyllithium.

Shown in Figure 57 are $^{13}$C\{$^6$Li\} spectra of the $\alpha$-carbon region of both the racemic 2-methylbutyllithium and the (R)-2-methylbutyllithium. It may be observed in this figure that the chemical shift of the $\alpha$-carbon peak of the (R)-2-methylbutyllithium is identical with peak Y of the racemic mixture. Thus the assignment of peak Y in the racemic mixture as the $\alpha$-carbon of the $R_6 + S_6$ is verified.

Shown in Figure 58 are $^6$Li spectra from both the racemic 2-methylbutyllithium and the (R)-2-methylbutyllithium samples. Instrumental difficulties encountered in the running of (R)-2-methylbutyllithium made for a poorly shaped peak, however, these spectra reveal that the assignment of the lithiums of the $R_6$ and $S_6$ hexamers as $^6$Li peak XXIII was correct.

Exchange processes in 2-methylbutyllithium. It can be concluded from this information that 2-methylbutyllithium is not randomly fluxional at low temperature but undergoes a limited fluxional exchange in which the R and S isomers are not randomly distributed throughout the hexamer. The limited fluxional exchange proposed to occur in lithium tert-butoxide/tert-butyllithium hexamers and the tert-butyllithium/n-alkyllithium hexamers is consistent with the data presented here for 2-methylbutyllithium. This
Figure 57 - The α-carbon region of the $^1$H$^6$Li spectra of (R)-2-methylbutyllithium (top) and racemic 2-methylbutyllithium (bottom). Temp = -42.7°C.

* - indicates a spinning sideband and is also present on the downfield side of this peak.
Figure 58 - $^6$Li spectra of (R)-2-methylbutyllithium (top) and racemic 2-methylbutyllithium (bottom). Temp = $-42.7^\circ$C.
indicates that limited fluxionality is not a process peculiar to hexamers in which there are two types of groups, one of which is much more sterically demanding than the other, but is an exchange process common to pure alkyllithium hexamers in general.

The role of the open faces in the fluxionality of hexamers has in the past been questioned (1)(2). This limited fluxional exchange takes advantage of the open faces to accomplish fluxionality, thus revealing their role in fluxionality and offering the explanation that; indeed, without open faces, the process of fluxionality must proceed by a different mechanism.

Fraenkel in his work on sec-butyllithium (9) discusses the multiple peaks observed in both the $^{13}$C and $^6$Li spectra and assumes them to arise due to the four diastereomeric hexamers that would be produced by this compound. Sec-butyllithium exists as an equilibrium between hexamer and tetramer and therefore the $^6$Li spectra revealed the presence of five peaks (9). One of these peaks was assumed to be caused by the tetramer and the other four caused by the four diastereomeric hexamers. This is very similar to the work on 2-methylbutyllithium discussed here. However, Fraenkel observed only four peaks in the $^{13}$C spectrum at -41°C for C3. The other carbons in this compound did not have sufficient resolution to determine the number of peaks. An
inconsistency develops here between his work on sec-butyllithium and the work discussed here on 2-methylbutyllithium. The present work, while observing ten $^{13}$C peaks for the other carbons, observed only four peaks for the chiral carbon of 2-methylbutyllithium ($C^2$). This was assumed to be a situation peculiar to the chiral carbon in that its environment was determined only by the hexamer of which it was part. The work reported in reference 9 would seem to indicate that sec-butyllithium hexamers undergo a random fluxionality, and environments are sufficiently similar to cause the different isomers in these hexamers to have the same shift at the $C^3$ carbon.

As an example, in randomly fluxional $R_4S_2$ and $S_4R_2$ hexamers, there are two types of alkyl groups. The isomer which makes up four of these alkyl groups is not equivalent with the isomer which makes up two of these alkyl groups. Therefore, if the $R_4S_2$ and $S_4R_2$ hexamers are randomly fluxional, together they should produce two $^{13}$C environments in a ratio of 4 to 2. The difference between these environments may not be sufficient to distinguish them from each other.

The $^{13}$C and $^6$Li spectra displayed in reference 9 are inconsistent in that visual inspection of the four peaks produced by the diastereomeric pairs in each spectrum have intensities which do not seem to correlate with each other.
The $^6\text{Li}$ spectrum displays four hexamer peaks, three of which have approximately equal intensities. The four observable peaks for $C_3$ in the $^{13}C$ spectrum appear to have very different intensities. It would seem that the data in reference 9 is inconclusive, and the nature of the fluxionality of the sec-butyllithium hexamers remains a mystery.

This present work also revealed the error made in the earlier study of 2-methylbutyllithium (8) in that interaggregate exchange was shown to reach the slow limit by $-22.1^\circ\text{C}$. The earlier work proposed fast interaggregate exchange at temperatures as low as $-50^\circ\text{C}$ due to changes in the proton spectra brought about by exchanges of the $\alpha$-carbon between non-equivalent sites (8). This present work reveals the presence of non-equivalent sites within these hexamers, thus showing that intraaggregate exchange would be sufficient to cause the changes manifested in the $^1\text{H}$ lineshapes observed in the earlier study.

The earlier work (8), also quantitated exchange rates for inversion at the $\alpha$-carbons. These exchange rates slowed to $0.05 \text{ s}^{-1}$ by $-30^\circ\text{C}$. This indicates that the exchange causing inversion at the $\alpha$-carbon may be the same process as the limited fluxional exchange.
Synthesis of alkyllithium compounds. The synthesis of both the racemic mixture and optically pure 2-methylbutyllithium was accomplished with a synthetic route very similar to that of tert-butyllithium as described in chapter 2. The starting compound for the synthesis of 2-methylbutyllithium was 2-methyl-1-butanol (Aldrich 99%). The entire synthesis proceeded according to the reactions 33 through 36 below:

\[
\begin{align*}
3\text{ROH} + \text{PBr}_3 & \rightarrow \text{RBr} + \text{P(OH)}_3, & [33] \\
\text{RBr} + \text{Mg} & \rightarrow \text{RMgBr}, & [34] \\
2\text{RMgBr} + \text{HgCl}_2 & \rightarrow \text{R}_2\text{Hg} + \text{BrMgCl}, & [35] \\
\text{R}_2\text{Hg} + 2\text{Li} & \rightarrow 2\text{RLi} + \text{Hg}, & [36]
\end{align*}
\]

In these four reactions R is a 2-methylbutyl group. The synthesis of 1-bromo-2-methylbutane made use of the reaction between an alcohol and a phosphorus trihalide as shown in reaction 33 above (16). The phosphorus trihalide synthesis is preferred over a simple reaction of an alcohol with an hydrogen halide since the alkyl group in this case is subject to rearrangement if the reaction is allowed to proceed by an \(S_{N}1\) mechanism. The \(S_{N}2\) mechanism employed in the alcohol/phosphorus tribromide reaction maintains the proper structure of the 2-methylbutyl group.

All the glassware used in the reaction apparatus was
heated in an oven to 200°C then assembled immediately upon removal from the oven and allowed to cool under an argon flow. The reaction apparatus consisted of a 3000 ml 3-necked flask equipped with a dropping funnel and a mechanical stirrer. An argon inlet was attached to the 3rd neck in order that the reaction be carried out under an inert atmosphere. To the flask was added 185 ml of 2-methyl-1-butanol (1.7 moles) along with 47.4 ml of pyridine. This solution was chilled in an ice bath before any PBr₃ was added. To the dropping funnel was then added 65 ml (0.7 moles) of PBr₃, this was an excess of 0.13 moles. Over a period of two hours the PBr₃ was added dropwise to the 2-methyl-1-butanol solution with the reaction mixture being stirred vigorously throughout this addition. The reaction was evidenced by the evolution of a yellow gas upon each drop addition, along with the formation of an orange precipitate. After the addition of the PBr₃ was complete, the reaction mixture was allowed to warm to room temperature. A distillation apparatus was attached to the flask and the product was distilled at 122°C into a 250 ml flask. The distillate was mixed with 50 mls of petroleum ether and washed with three successive washings using 400 ml each of; (1) a 5% sodium hydroxide solution, (2) a 10% sulfuric acid solution and (3) cold deionized water. The 1-bromo-2-methylbutane/petroleum ether solution was dried
overnight with magnesium sulfate. The following day the solution was filtered and the petroleum ether was roto-evaporated. The remaining liquid was distilled at 122°C. The total amount of product obtained was 154 grams which is a 60% yield according to the amount of 2-methyl-1-butanol used.

The synthetic procedure from 1-bromo-2-methylbutane to the bis(2-methylbutyl)mercury is identical to the procedures used for the conversion of tert-butyl chloride to bis(tert-butyl)mercury. For a full discussion of these procedures, see chapter 2. The bis(2-methylbutyl)mercury was a viscous liquid which was vacuumed distilled at 3 torr and 95 °C. A \textsuperscript{13}C NMR spectrum of the distillate revealed resonances at 55.2 ppm, 37.2 ppm, 36.7 ppm, 26.7 ppm, and 13.6 ppm. These shifts correspond to previously observed shifts of bis(2-methylbutyl)mercury (12). \textsuperscript{199}Hg satellites were observed on either side of the alpha carbon with a $J(\textsuperscript{13}C-\textsuperscript{199}Hg)$ equal to 684 Hz. This coupling value identifies the compound as bis(2-methylbutyl)mercury as opposed to 2-methylbutyl mercuric chloride which would possess a $J(\textsuperscript{13}C-\textsuperscript{199}Hg)$ equal to approximately 1500 Hz (13).

The final step in the synthetic procedure was the lithiation reaction shown in equation 36 above. This was accomplished in a manner identical to the lithiation of bis(tert-butyl)mercury. In the drybox 14.6 grams (0.037
mols) of bis(2-methylbutyl)mercury was placed a reaction vessel with 50 ml of cyclopentane (Aldrich 99%, which had been distilled from LiAlH₄) and 1.5 grams of lithium metal (⁶Li-enriched to 95.5%). The reaction vessel was then removed from the box and placed on the vacuum line where it was again degassed by the freeze-pump-thaw method. This vessel was then flame sealed and shaken on a shaker table for 8 days.

After the 8 day period, the vessel was carried back into the glove box and broken open. The reaction mixture was filtered through a fine frit filter, and a $^{13}$C NMR spectrum was obtained. $^{13}$C chemical shifts at 23.5 ppm, 35.9 ppm, 36.6 ppm, 11.8 ppm, and 25.4 ppm were consistent with previously reported chemical shifts of 2-methylbutyllithium (10). This spectrum also revealed a significant amount of bis(2-methylbutyl)mercury remained unreacted. Due to the unreacted bis(2-methylbutyl)mercury, more lithium metal was needed. A second reaction vessel was prepared and 1 gram of lithium metal was cut and placed into it. The reaction mixture was then transferred via pipette to this reaction vessel. The new reaction vessel was again degassed, flame sealed, and placed on the shaker table. After 7 days the vessel was again carried into the glove box, broken open and a sample prepared for NMR analysis. No unreacted bis(2-methylbutyl)mercury was detected in this solution, therefore
the reaction was determined to be complete.

The reaction mixture was again filtered and then placed in an erlenmeyer flask equipped with a high vacuum stopcock assembly. On the vacuum line the cyclopentane was cryopumped from the reaction mixture leaving behind 5.1 grams (0.065 mols) of a clear viscous liquid which NMR spectra revealed to be the 2-methylbutyllithium. This is an 88% yield according to the amount of mercury compound used in the reaction. The 2-methylbutyllithium was returned to the glove box and transferred via a pipette to a 25 ml vessel equipped with a roto-flow high vacuum stopcock. This was the stock supply of the 2-methylbutyllithium used in this study.

S-(-)-2-methylbutyllithium. Optically pure 2-methyl-1-butanol (Aldrich 99% optical purity) was used as starting material for a synthesis identical to the one described above for the racemic mixture (14). The alcohol was examined by polarimetry for specific rotation as an optical purity test. An observed optical rotation of 5.72° at 24°C was obtained on a Rudolph visual polarimeter equipped with a sodium lamp. This compares with the reported value of -5.90° at 20°C(15) According to equation 37, this translates to a rotation of -5.78° at 24°C.

\[ [\alpha] = 0.03t - 6.50 \]  

[37]
The difference between the observed optical rotation at 24°C of -5.72° and the expected optical rotation of -5.78°, reveals the (S)-2-methylbutanol to contain 0.55% (R)-2-methylbutanol.

Due to the expense of the starting material smaller amounts were used resulting in reduced yields, but the reactions and procedures followed were simply scaled down from the procedures discussed above for the racemic compound.

The synthetic route for (S)-2-methylbutyllithium was identical to that of racemic 2-methylbutyllithium. (S)-2-methylbutanol (Aldrich 99%) was used as the starting product. The initial reaction began with 30.0 grams (0.341 mols) of (S)-2-methylbutanol and concluded with the obtainment of approximately 3 grams of the desired (S)-2-methylbutyllithium.

3,6-Dimethyloctane. At some point along the synthetic route to (R)-2-methylbutyllithium, 3,6-dimethyloctane was produced. The presence of this contaminant was verified by comparison with a commercial sample (Pfaltz & Bauer 99%). The $^{13}$C chemical shifts were determined to be C$^1$ - 11.3 ppm, C$^2$ - 34.0 ppm, C$^3$ - 34.8 ppm, C$^4$ - 29.6 ppm, and C$^5$(Me) - 19.2 ppm (14). This contaminant is a hydrocarbon and thus should not interfere with the exchange processes of 2-methylbutyllithium in a hydrocarbon solvent.
NMR sample preparation. Due to their high reactivity, all of the NMR sample tubes were prepared in the argon-filled drybox discussed in chapter 1. The solvent used in these sample tubes, was a mixture of 92% cyclopentane (Wiley Organics 99.9%) and 8% d\textsuperscript{10}-cyclopentane (MSD isotopes 98.8% D).

In the drybox, appropriate amounts of 2-methylbutyllithium and solvent to obtain a 2F solution were transferred to an NMR tube fitted with a stopcock assembly. This tube and stopcock assembly was then removed from the drybox and placed on the vacuum line. The solution was then degassed using the freeze-pump-thaw method. The tube was then flame sealed and allowed to warm to room temperature overnight.

The syntheses of the \textit{n}-propyllithium and the \textit{n}-butyllithium used in the \textit{n}-propyllithium/\textit{n}-butyllithium mixture are discussed in chapter 4. The mixture was prepared in the argon-filled drybox in a manner similar to mixtures discussed in chapter 4. A 1.55 ml solution containing 0.257 grams of \textit{n}-butyllithium dissolved in the cyclopentane solution was prepared. A second 1.55 ml solution was prepared containing 0.243 grams of \textit{n}-propyllithium in cyclopentane. These two solutions were then mixed in an NMR tube resulting in a tube which was 2.9F in alkyllithium compound and contained an \textit{n}-propyllithium to
$n$-butyllithium ratio of 1.2 to 1. The tube was then fitted with a stopcock assembly and removed from the box. The sample tube was then placed on the vacuum line and degassed using the freeze-pump-thaw method. Lastly the tube was flame-sealed and allowed to warm up overnight.

**NMR Experiments.** This study of 2-methylbutyllithium made use of two NMR spectrometers. One of these is the Varian VXR-300 used in the previous chapters and the other is a Varian Gemini-200 spectrometer. The only experiments discussed in this chapter which were performed on the Gemini-200 were the $^{13}$C spectra shown in Figure 56. The resonance frequency for $^{13}$C at 4.7 Tesla is 50 MHz.

Typical parameters for the one-dimensional $^{13}$C experiments performed on the Gemini-200 were a pulse width of 10 μ-seconds, an acquisition time of 2.9 seconds, no relaxation delay, approximately 10,000 data points, and a spectral width of 5200 Hz. Typically, approximately 2000 transients were sufficient to obtain the desired signal-to-noise ratio.

Typical parameters for the one-dimensional $^{13}$C experiments performed on the Varian VXR-300 using the 10 mm probe were a pulse width of 17 μseconds, an acquisition time of 3 seconds, no relaxation delay, approximately 10,000 data points, and a spectral width of 3000 Hz. Typically, approximately 2000 transients were sufficient to obtain the
desired signal-to-noise. If $^6$Li decoupling was used, the setting of the $^6$Li decoupler was performed as described in the experimental section of chapter 4. The resolution enhancement used in Figure 50 was obtained by setting a resolution enhancement time constant of 0.199 s. and an apodization function time constant of 0.597 s. to define a bell shaped weighting function applied to the FID before Fourier transformation.

The $^6$Li spectra displayed in this chapter were all obtained on the VXR-300 NMR using the 10 mm probe. Typical parameters used to obtain the one-dimensional $^6$Li spectra were, a pulse of 22.0 $\mu$s, an acquisition time of 20 seconds, no relaxation delay, approximately 4000 data points, and a spectral width of 300 Hz. Typically, 4 transients were sufficient to obtain the desired signal-to-noise ratio. The resolution enhancement used in Figure 48 was obtained by setting a resolution enhancement time constant of 1.920 s. and an apodization function time constant of 5.760 s. to define a bell shaped weighting function applied to the FID before Fourier transformation.

The $^{13}$C-$^6$Li HETCOR experiment was performed at $-50^\circ$C. The parameters for the experiment were adjusted as described in reference 17. The $90^\circ$ and $180^\circ$ pulses on the $^{13}$C nuclei required by the pulse sequence were 21.5 $\mu$s and 43 $\mu$s respectively. The delay values for D3 and D4 were
0.15 seconds and 0.0236 seconds respectively, as suggested in reference 9 for the observed coupling. A relaxation delay of 7.5 seconds was used.

The number of transients per increment required to obtain the desired signal-to-noise ratio was 64. The acquisition time for each transient was 1.024 seconds. This resulted in 1024 data points collected for each transient over the 500 Hz spectral width. Before Fourier-transformation, the number of data points was zero-filled to 2048 and line broadening of 0.3 Hz was used to enhance the signal. The resulting data-point density was 0.5 Hz per data point.

The $^6$Li dimension made use of a 90° pulse of 696 \( \mu \)seconds through the decoupler coil. The spectral width in this dimension was 50 Hz. The number of data points in this dimension is determined by the number of increments performed. In this experiment 128 increments were performed. This value was zero-filled to 256 before Fourier-transformation, resulting in a data point density in this dimension of 0.4 Hz per data point. No resolution enhancement or line-broadening were used in this dimension.

The shimming of the NMR sample for this experiment was accomplished through the observed channel as discussed in chapter 3. The spin rate used was 10 Hz. The data was collected in the double precision mode.
Temperature Measurement. The measurement of temperature for these experiments was accomplished with a methanol NMR thermometer as described in chapter 2. The temperature of the $^{13}$C-$^6$Li HETCOR of -50°C is simply the temperature from the digital readout of the variable temperature controller, and the actual temperature is presumably 2 to 5 degrees cooler.
CHAPTER BIBLIOGRAPHY


12. Young, T. C.; Thomas, R. D., University of North Texas, unpublished results.


APPENDIX

PULSE SEQUENCE SOURCE CODE LISTINGS

FORTRAN PROGRAM D2DNMR
SOURCE CODE FOR
PURE ABSORPTION 2DEXSY
WITH AVAILABLE *Li DECOUPLING

PSGLIB Filename: X2DLDA

PULSE SEQUENCE AS DESCRIBED BELOW AND ACCORDING
SPECTROSCOPY AS USED IN THE 2DEXSY PULSE SEQUENCE
PHASE CYCLING EMPLOYED IS AS DESCRIBED BY STATER ET. AL
WITH THE EXCEPTION THAT EXPERIMENTS 12345676 IN THE ORDER
PROPOSED BY STATER ARE PERFORMED IN THE ORDER 1235746 IN
ORDER TO ACHIEVE A MORE RAPID ALTERNATION OF RECEIVER PHASE
WHICH ASSURES BETTER CANCELLATION
*Li DECOUPLING IS AVAILABLE IN THIS PULSE SEQUENCE

PARAMETERS:

MIX: MIXING TIME
KAPPA: VALUE THAT ALLOWS ACCORDIAN SPECTROSCOPY
PHASE: 0 GIVES NON-PHASE-SENSITIVE EXPERIMENT, 16 TRANSIENTS
       MINIMUM CYCLE, 32 WITH CYCLOPS
       (P-TYPE PEAKS)
1,2 GIVES PHASE-SENSITIVE EXPERIMENT, 8 TRANSIENTS
       EACH MINIMUM CYCLE, 16 WITH CYCLOPS

PROCEDURE PULSESEQUENCE;
VAR KAPPA,MIX,PHASE:REAL; IPHASE:INTEGER; DMX : TEXT4;
BEGIN
GETVAL(MIX,'MIX'); GETVAL(PHASE,'PHASE');
GETVAL(DMX,'DMX'); GETVAL(KAPPA,'KAPPA');
MIX:=MIX+KAPPA;
IPHASE:=TRUNC(PHASE+0.5);

"CALCULATE BASIC PHASE CYCLING"
"V10 IS THE 'PSEUDO-TRANSIENT COUNTER' WHICH GOES
 01234... FOR PHASE=0
 02456... FOR PHASE=1
 13579... FOR PHASE=2*
IF IPHASE=0 THEN ASSIGN(CT,V10) ELSE DBL(CT,V10);
IF IPHASE=2 THEN INCR(V10);
HLU(V10,V1); "0011"
DBL(V1,V5); "0022"
HLU(V1,V6); "0001111"
ADD(V5,V6,V1); "00211322003311"
MOD2(V10,V7); "01010101"
HLU(V10,V3); "0011"
HLU(V3,V3); "0001111"
"REVERSE SENSE OF DIAGONAL"
DEL(V7, V8): "##20##"
ADD(V1, V8, V1): ADD(V2, V8, V2): ADD(V3, V8, V3):
"IF ABSORPTION MODE IN BOTH CHANNELS IS DESIRED AFTER THE
FIRST TRANSFORM, THE FOLLOWING LINE CAN BE USED"
"IF IPHASE=2 THEN DEC(i, i):

STATUS(A);
VAR1;
VAR2:
IF (DMX1) ='Y' THEN SP20N
ELSE SP2OFF;
IF (DMX2) ='Y' THEN SP20N
ELSE SP2OFF:
REFPULSE(PW1, NOFL1, 0, 0);
DELAY(D1);
REFPULSE(PW2, NOFL2, 0, 0);
STATUS(C);
IF (DMX3) ='Y' THEN SP20N
ELSE SP2OFF;
DELAY(MIX);
STATUS(D);
IF (DMX4) ='Y' THEN SP20N
ELSE SP2OFF:
REFPULSE(PW3, NOFL1, NOFL2);
MOD4(V4, OPH); "SET RECEIVER"
END;
SOURCE CODE FOR
$^{13}C$-$^{6}Li$-$^{1}H$ HETCOR

PSGLIB Filename: HTCRLD

THE NORMAL HETCOR PULSE SEQUENCE MODIFIED TO ALLOW FOR 6LI DECOUPLING BY USING THE VARIABLE DMX

PROCEDURE PULSESEQUENCE;
VAR J1XH, JNXH, PP, D3, D4, D5: REAL;
DMX, PRESAT, DM, HMULT: TEXT;
RXGATE: BOOLEAN;
BEGIN
  RXGATE := (ROF=0.0);
  IF RXGATE THEN ROF:=0.0; "PHASE SWITCHING TIME"
  "SET THE NEW VARIABLES FROM PARAMETER TABLE"
  GETVAL(PP, 'PP ');
  GETVAL(DM, 'DM ');
  GETVAL(J1XH, 'J1XH ');
  GETVAL(JNXH, 'JNXH ');
  GETVAL(HMULT, 'HMULT ');
  GETVAL(PRESAT, 'PRESAT ');
  GETVAL(DMX, 'DMX ');
  IF (JNXH<>0.0) AND (HMULT[1]<>Y) THEN BEGIN
    HMULT[1] := 'Y';
    PUTVAL(HMULT, 'HMULT ');
    DISPLAYLINET
    'WARNING: HMULT CHANGED TO Y SINCE JNXH IS NOT ZERO
      3,YELLOW,TRUE);
    END;
  "CALCULATE DELAYS"
  IF JNXH<>0.0 THEN
    BEGIN "SET UP FOR 2 & 3 BOND J EXPTS"
      D3:=1.0/(2.0*JNXH); D4:=1.0/(3.0*JNXH);
    END
  ELSE
    BEGIN "SET UP FOR 1 BOND J EXPTS"
      D3:=1.0/(2.0*J1XH); D4:=1.0/(3.0*J1XH);
    END;
    D5:=1.0/(2.0*J1XH);
    PUTVAL(D3, 'D3 ');
    PUTVAL(D4, 'D4 ');
    "SET UP PHASE CYCLING "
    "U1=FIRST PROTON PULSE"
    "U2=FIRST TWO PROTON BIRD PULSES"
    "U3=LAST PROTON BIRD PULSE"
    "U4=FINAL PROTON PULSE"
    "U5,U6= COMPOSITE 13C 180"
    "U7=FINAL 13C PULSE"
    "OPH=RECEIVER"
ASSIGN(ZERO_.V1); ASSIGN(ZERO_.V5);
ASSIGN(THREE_.V5); ASSIGN(ZERO_.V7);
MOD4(CI_.V4);
MOD4(CI_.DPH): "0123 (CHANGE TO 0321 TO P-TYPE SELECTION);"
HLV(CI_.V2); HLV(V2_.V2); "0000111122223333"
IF JN=H=0.0 THEN ADD(TWO_.V2_.V5); "2222333300001111"

"RELAXATION DELAY"
STATUS(A);
VARR;
VARZ;
IF DMX[1]="V" THEN
VARR;
ELSE SP20FF;
IF DMX[1]="V" THEN
BEGIN
DISPLAYLINE( DECOUPLER MUST BE SET AS DM-NNY
.5,RED,TRUE);
OP.:FALSE; "ABORTS ACQUISITION"
RETURN;
END
ELSE
DECLv'LON; "SETS MAXIMUM DHP VALUE"
HDDELAY(D1);
IF RXGATE THEN RCVOFF;

IF PRESAT[1]="V" THEN
BEGIN
RGPULSE(PW,ZERO,ROF1,ROF1);
IF RXGATE THEN RCVOFF;
HDDELAY(0.05);
END;

STATUS(B);
IF DMX[2]="V" THEN
SP20F;
ELSE SP20FF;
RCVOFF; DECPULSE(PP_.V1); IF NOT RXGATE THEN RCVRON;
DELAY(D2/2.0);
IF HMULT[1]="V" THEN
BEGIN "SIMPLE 13C 180"
RGPULSE(PW,VS,ROF1,0.0);
RGPULSE(2.0*PW,VS,0.0,0.0);
RGPULSE(PW,VS,0.0,ROF1);
IF RXGATE THEN RCVOFF;
END
ELSE
BEGIN "BIRD COMPOSITE IS0"
  RCVROFF; DECPULSE(PP, V3); IF NOT RXGATE THEN RCVROFF;
  DELAY(DS-ROF1-PW-1.5*PF);
  RGPULSE(PW, VS, ROF1, 0.0);
  SIMPULSE(2.0*PW, 2.0*PF, VS, V2, 0.0, 0.0);
  RGPULSE(PW, VS, 0.0, ROF1);
  IF RXGATE THEN RCVROFF;
  DELAY(08-ROF1-PW-1.5*PF);
  RCVROFF; DECPULSE(PP, V3); IF NOT RXGATE THEN RCVROFF;
END;
  DELAY(D2/2.0);
  DELAY(D3-ROF1);
  SIMPULSE(PW, PF, MT, V4, ROF1, ROF2);
  DECLVLLOFF;
  DELAY(D4);

"OBSERVE PERIOD"
STATUS(0);
IF DMX[3] = 'Y' THEN
  SP2ON
  ELSE SP2OFF;
  DECPHASE(ZERO);
END;
C 2DNMR EXCHANGE PROGRAMME
C UPDATED BY BRYAN CARLSON 1990
C DAVID STEPHENSON 1985

COMPLEX*16 A(8,8)
DOUBLE PRECISION P(8)
CHARACTER*50 SAMP
CHARACTER*3 CHAR
CHARACTER*50 TTID,FNAME*20,COR*3
DOUBLE PRECISION B(8,8)
CHARACTER AGA*3
COMPLEX*16 CL(8,8)
CHARACTER SUP*3
CHARACTER OPT*3
COMPLEX*16 LAMBDA(8)
COMMON/BCDE/AGA
COMMON/CDEF/JKL

CONTINUE
PRINT*, 'INDICATE INPUT DATA: I FOR INTENSITIES, K FOR RATES'
PRINT*, 'TYPE E FOR ERROR ANALYSIS'
READ(5, '(A3)') OPT
IF(INDEX(OPT,'K').EQ.1) GOTO 602
IF(INDEX(OPT,'I').EQ.1) GOTO 601
IF(INDEX(OPT,'E').EQ.1) GOTO 620
PRINT*, 'TYPE EITHER I,K OR E NITWIT'
PRINT*, '
GOTO 603
CONTINUE
CALL INPUTE
GOTO 621
CONTINUE
PRINT*, '
PRINT*, 'KINETIC TO INTENSITY PROGRAMME  D.S. 1985'
CONTINUE
CALL INPUTK(B,M)
IF(INDEX(AGA,'Y').EQ.1) GOTO 770
PRINT*, 'TYPE X TO SUPPRESS MATRIX PRINTING'
READ(5, '(A3)') SUP
CONTINUE
DO 70 I=1,M
DO 71 J=1,M
A(I,J)=B(I,J)
CONTINUE
CONTINUE
IF(INDEX(SUP,'X').EQ.1) GOTO 751
DO 61 I=1,M
WRITE(6,60)(B(I,J),J=1,M)
60    FORMAT(8(2X,F14.7))
61 CONTINUE
PRINT*, ' ' 
PRINT*, ' ' 
751 CONTINUE
CALL ALLMAT(A,M,CL,LAMBDA)
CALL BLLMAT(A,M,CL,LAMBDA)
IF(INDEX(SUP,'X').EQ.1) GOTO 750
PRINT*, ' ' 
PRINT*, ' DIAGONALISATION MATRIX, A'
PRINT*, ' ' 
DO 41 I=1,M
WRITE(6,40)(REAL(A(I,J)),J=1,M)
40 FORMAT(2X,8(2X,F14.7))
41 CONTINUE
PRINT*, ' ' 
PRINT*, ' INVERSE OF MATRIX A'
PRINT*, ' ' 
DO 42 I=1,M
WRITE(6,43)(REAL(CL(I,J)),J=1,M)
43 FORMAT(8(2X,F14.7))
42 CONTINUE
PRINT*, ' ' 
PRINT*, ' LAMBDA ARRAY -- MATRIX DIAGONAL'
PRINT*, ' ' 
WRITE(6,46)(REAL(LAMBDA(I)),I=1,M)
46 FORMAT(8(2X,F14.7))
750 CONTINUE
CALL MULTYK(M,A,CL,LAMBDA)
608 CONTINUE
PRINT*, ' ' 
PRINT*, ' *AGAIN?*' 
READ(5,'(A3)') AGA
IF(INDEX(AGA,'Y').EQ.1) GOTO 755
IF(INDEX(AGA,'N').EQ.1) GOTO 607
PRINT*, ' TYPE EITHER YES OR NO NITWIT'
GOTO 608
607 CONTINUE
GOTO 600
601 CONTINUE
PRINT*, ' INTENSITIES TO KINETIC RATES D.S. 1985'
KIQ=0
KIR=0
KIP=0
PRINT*, ' DO YOU WANT TO SAVE THE DATA IN A TEXT FILE?' 
PRINT*, ' TYPE EITHER NO OR A TITLE BEGINING WITH A'
PRINT*, ' FOUR LETTER IDENTIFIER'
PRINT*, ' ' 

READ(5, '(A50)') TTID

IF(INDEX(TTID, 'N').EQ.1.AND.INDEX(TTID, 'O').EQ.2) GOTO 436

KIP=33
CONTINUE

IF(KIQ.NE.44.OR.KIR.EQ.55) GOTO 471

PRINT*, 'INPUT NEW HEADING FOR OUTPUT DATA'
READ(5, '(A50)') TTID
CONTINUE

GOTO 473
CONTINUE
KIR=55
CONTINUE

PRINT*, 'INPUT MATRIX SIZE; N FOR NXN'
READ(5, *) M

PRINT*, 'INPUT MATRIX ROW-WISE SEPARATING THE' PRINT*, 'ELEMENTS WITH COMMAS AND TERMINATING'
PRINT*, 'ROWS WITH {RETURN}'
DO 111 I=1, M
READ(5, *) (B(I, J), J=1, M)
CONTINUE

PRINT*, 'INPUT MATRIX'

DO 661 I=1, M
WRITE(6, 660) (B(I, J), J=1, M)
CONTINUE

PRINT*, 'IS THE DATA CORRECT?'
READ(5, '(A3)') COR
IF(INDEX(COR, 'Y').EQ.1) GOTO 431
IF(INDEX(COR, 'N').EQ.1) GOTO 432
PRINT*, 'TYPE EITHER YES OR NO NITWIT'
GOTO 433
CONTINUE

PRINT*, 'INPUT ROW, COLUMN NUMBER OF INCORRECT DATUM POINT'

READ(5, *) I, J
PRINT*, 'INPUT NEW VALUE'
READ(5, *) VALUE
B(I, J) = VALUE
GOTO 434
CONTINUE

IF(KIP.NE.33) GOTO 444
IF(KIQ.EQ.44) GOTO 472
CALL SETINF(2, 0, 80)
CALL OPNFIL(2, RETCOD, 'DATA', 'OKNEW OKOLD WROK.' )
CONTINUE

PRINT*, 'INPUT NAME OF SAMPLE TESTED'
READ(5, '(A50)') SAMP
WRITE(2, 88) SAMP
WRITE(2, 88) TTID
WRITE(2, 491) TTID
WRITE(2, 441) INTENSITY MATRIX
DO 442 I=1,M
WRITE(2, 443) (B(I,J), J=1,M)
443 FORMAT(2X, 8(2X, F12.4))
442 CONTINUE
444 CONTINUE
PRINT*, 'INPUT SITE POPULATIONS'
WRITE(6, 901) ('P', J, ',', J=1, M-1, ', P', M
901 FORMAT(2X, 8(A1, I1, A1, 2X))
READ(5, *) (P(I), I=1, M)
SUM=0.0
SUN=0.0
DO 888 I=1,M
SUN=SUN+ABS(P(I))
888 CONTINUE
DO 889 I=1,M
P(I)=P(I)/SUN
889 CONTINUE
DO 904 I=1,M
DO 905 J=1,M
SUM=SUM+ABS(B(I,J))
905 CONTINUE
904 CONTINUE
PRINT*, 'INPUT NORMALISATION CONSTANT'
READ(5, *) ACA
IF(ACA.GT.0) GOTO 222
SUM=1
ACA=1
222 CONTINUE
DO 906 I=1,M
DO 907 J=1,M
B(I,J)=B(I,J)/SUM*ACA/P(I)
907 CONTINUE
906 CONTINUE
DO 112 I=1,M
DO 113 J=1,M
A(I,J)=B(I,J)
113 CONTINUE
112 CONTINUE
CALL ALLMAT(A, M, CL, LAMBDA)
CALL BLLMAT(A, M, CL, LAMBDA)
PRINT*, 'DIAGONALISATION MATRIX'
PRINT*,
DO 641 I=1,M
WRITE(6,640)(REAL(A(I,J)),J=1,M)
640 FORMAT(2X,8(2X,F14.7))
641 CONTINUE
PRINT*,' INVERSE  MATRIX'
DO 642 I=1,M
WRITE(6,643)(REAL(CL(I,J)),J=1,M)
642 CONTINUE
PRINT*,' LAMBDA  ARRAY'
WRITE(6,646)(REAL(LAMBDA(I)),I=1,M)
IF(KIP.NE.33) GOTO 445
WRITE(2,481)((P(I)*100),I=1,M)
481 FORMAT(//,14X,'POPULATIONS
(PERCENT)'/,2X,8(2X,F12.4))
WRITE(2,446)(REAL(LAMBDA(I)),I=1,M)
446 FORMAT(//,14X,'LAMBDA ARRAY'//,2X,8(2X,F12.4))
445 CONTINUE
646 FORMAT(2X,8(2X,F14.7))
PRINT*,' CALL MULTY(M,A,CL,LAMBDA,KIP)
PRINT*,' * AGAIN? *
KIQ=44
610 CONTINUE
READ(5,'(A3)') CHAR
IF(INDEX(CHAR,'Y').EQ.1) GOTO 107
IF(INDEX(CHAR,'N').EQ.1) GOTO 609
PRINT*,' TYPE EITHER YES OR NO NITWIT'
PRINT*,''
GOTO 610
609 CONTINUE
600 CONTINUE
621 CONTINUE
CALL CLSFIL(2,RETCOD)
END
SUBROUTINE MULTY(M,A,CL,LAMBDA,KIP)
COMPLEX*16 A(8,8),CL(8,8),LAMBDA(8)
DOUBLE PRECISION E(8,8),F(8,8),G(8,8)
PRINT*,' INPUT MIXING TIME'
READ(5,*)TM
DO 10 I=1,M
IF(REAL(LAMBDA(I)).GT.0.0) GOTO 777
PRINT*,'**NEGATIVE VALUE IN LAMBDA ARRAY**'
WRITE(2,778)
WRITE(2,779)
WRITE(2,780)
778 FORMAT(//"****WARNING! NEGATIVE LAMBDA VALUE****"//)
779 FORMAT(/'PROBABLE LARGE ERROR IN OUTPUT DATA!'//)
780 FORMAT(/'USUAL CAUSE MIXING TIME TOO LONG!'//)
PRINT*, 'VALUE ZEROED'
LAMBDA(I)=1E-16
777 CONTINUE
REALL=REAL(LAMBDA(I))
E(I,I)=(ALOG(REALL))/TM
10 CONTINUE
DO 11 I=1,M
DO 12 J=1,M
IF(I.EQ.J) GOTO 12
E(I,J)=0.0
12 CONTINUE
11 CONTINUE
DO 204 I=1,M
DO 205 J=1,M
F(I,J)=0.0
DO 206 K=1,M
F(I,J)=E(I,K)*REAL(CL(K,J))+F(I,J)
206 CONTINUE
205 CONTINUE
204 CONTINUE
DO 104 I=1,M
DO 105 J=1,M
G(I,J)=0.0
DO 106 K=1,M
G(I,J)=REAL(A(I,K))*F(K,J)+G(I,J)
106 CONTINUE
105 CONTINUE
104 CONTINUE
TOT=0.0
IF(KIP.NE.33) GOTO 482
WRITE(2,483) TM
483 FORMAT(//,9X,'MIXING TIME =',2X,F6.3,2X,'SECONDS://'//)
WRITE(2,499)
499 FORMAT(14X,'KINETIC MATRIX'/)
482 CONTINUE
DO 300 I=1,M
WRITE(6,301)(G(I,J),J=1,M)
IF(KIP.NE.33) GOTO 497
WRITE(2,498)(G(I,K),K=1,M)
497 CONTINUE
301 FORMAT(2X,F6.3,2X,F14.7))
498 FORMAT(2X,F6.3,2X,F12.4))
300 CONTINUE
IF(KIP.NE.33) GOTO 476
SUBROUTINE ALLMAT(A,M,CL,LAMBDA)
C ALLMAT DIAGONALIZES THE NT BY NT DIMENSIONAL A MATRIX. THE
C EIGENVECTORS ARE OVERWRITTEN ON THE ORIGINAL MATRIX. THE
C THE EIGENVECTOR MATRIX IS CALCULATED AS THE CL MATRIX. THE
C EIGENVALUES ARE CONTAINED IN THE ONE DIMENSIONAL LAMBDA ARRAY.
IMPLICIT REAL*8(A-H,O-Z)
INTEGER R,RP1,RP2
DIMENSION IINT(8)
COMPLEX*16 A(8,8),HL(8,8),LAMBDA(8),MULT(8),SHIFT(4),
1TEMP,SIN,COS,TEMP1,TEMP2,TRACE,H(8,8),CL(8,8),
2CR(8,8),EIG(8)
COMMON/TEM/HL
COMMON/TALIS/IINT,TRACE,NCAL
COMMON/EIVEC/CR,H,EIG
COMMON/ROUND/EPS
C
N=M
TRACE=(0.0,0.0)
DO 61 I = 1,N
61 TRACE=TRACE+ A(I,I)
NCAL=N
IF(N.NE.1)GO TO 1
LAMBDA(1)=A(1,1)
A(l,l)=(l.0,0.0)
CL(1,1)=(1.0,0.0)
GO TO 37
1 ICOUNT=0
SHIFT(1)=(0.0,0.0)
IF(N.NE.2)GO TO 4
2 TEMP=(A(1,1)+A(2,2)+CDSQRT((A(l, 1)+A(2 ,2))**2-14.*(A(2,2)*A(1,1)-A(2,l)*A(l,2))))/2.
IF(DABS(DREAL(TEMP)).GT.1.OE-12)  GOTO 3
IF(DABS(DIMAG(TEMP)).GT.1.0E-12)  GOTO 3
LAMBDA(M)=SHIFT(1)
LAMBDA(M-l)=A(1,1)+A(2,2)+SHIFT(1)
GO TO 37
3 LAMBDA(M)=TEMP+SHIFT(1)
LAMBDA(M-1)=(A(2,2)*A(1,1)-A(2,1)*A(1,2))/(LAMBDA(M)-SHIFT(1))
1ISHIFT(1)
GO TO 37
C
C REDUCE MATRIX A TO HESSENBURG FORM
4 NM2=N-2
   DO 15 R=1,NM2
   RP1=R+1
   RP2=R+2
   ABIG=0.
   IINT(R)=RP1
   DO 5 I=RP1,N
      ABSSQ=DREAL(A(I,R))**2+DIMAG(A(I,R))**2
      IF(ABSSQ.LE.ABIG)GOTO 5
      IINT(R)=I
      ABIG=ABSSQ
   5 CONTINUE
   INTER=IINT(R)
   IF(DABS(ABIG).LT.1.0E-14) GOTO 15
   IF(INTER.EQ.RP1)GO TO 8
   DO 6 I=R,N
      TEMP=A(RP1,I)
      A(RP1,I)=A(INTER,I)
   6 A(INTER,I)=TEMP
   DO 7 1=1,N
      TEMP=A(I,RP1)
      A(I,RP1)=A(I,INTER)
   7 A(I,INTER)=TEMP
   DO 9 I=RP2,N
      MULT(I)=A(I,R)/A(RP1,R)
   9 A(I,R)=MULT(I)
   DO 10 I=RP2,N
      DO 10 J=RP2,N
         TEMP=TEMP+A(I,J)*MULT(J)
      10 A(I,RP1)=A(I,RP1)+TEMP-MULT(I)*A(RP1,RP1)
   DO 144 I=RP2,N
      DO 14 J=RP2,N
         A(I,J)=A(I,J)-MULT(I)*A(RP1,J)
   144 CONTINUE
   15 CONTINUE

C CALCULATE EPSILON

EPS=0.
   DO 16 I=1,N
16 EPS=EPS+CDABS(A(I,I))
   DO 18 I=2,N
      SUM=0.
      IM1=I-1
      DO 17 J=IM1,N
17 EPS=EPS+CDABS(A(I,J))
   18 CONTINUE
17 SUM=SUM+CDABS(A(I, J))
18 IF(SUM.GT.EPS)EPS=SUM
    EPS=DSQRT(DFLOAT(N))*EPS*1.0E-12
    IF(DABS(EPS).LT.1.0E-12)EPS=1.0E-12
    DO 199 I=1,N
    DO 19 J=1,N
19 H(I, J)=A(I, J)
199 CONTINUE
20 IF(N.NE.1)GO TO 21
    LAMBDA(M)=A(1,1)+SHIFT(1)
    GO TO 37
21 IF(N.EQ.2)GO TO 2
22 MN1=M-N+1
23 IF(DABS(DREAL(A(N,N))).GT.1.0E-12.OR.DABS(DIMAG(A(N,N))).GT.1.0E-12)IF(DABS(DREAL(A(N,N-l))/A(N,N)))+DABS(DIMAG(A(N,N-l))/A(N,N)))-1.E-9)24,24,23
24 LAMBDA(MN1)=A(N,N)+SHIFT(1)
    ICOUNT=0
    N=N-1
    GO TO 21
C
C DETERMINE SHIFT
C
25 SHIFT(2)=(A(N-1,N-1)+A(N,N)+CDSQRT((A(N-1,N-1)+A(N,N))**2-4.*(A(N,N)*A(N-1,N-1)-A(N,N-l)*A(N-l,N))))/2.
26 IF(DABS(DREAL(SHIFT(2))).GT.1.0E-12.OR.DABS(DIMAG(SHIFT(2))).GT.1.0E-12)GOTO 26
27 SHIFT(3)=(A(N,N)*A(N-l,N-l)-A(N,N-l)*A(N-l,N))/SHIFT(2)
28 IF(CDABS(SHIFT(2)-A(N,N)).LT.CDABS(SHIFT(3)-A(N,N)))GO TO 28
    INDEX=3
    GO TO 29
29 INDEX=2
29 IF(CDABS(A(N-1,N-2)).GE.EPS)GO TO 30
    LAMBDA(MN1)=SHIFT(2)+SHIFT(1)
    LAMBDA(MN1+1)=SHIFT(3)+SHIFT(1)
    ICOUNT=0
    N=N-2
    GO TO 20
30 SHIFT(1)=SHIFT(1)+SHIFT(INDEX)
DO 31 I=1,N
   A(I,I)=A(I,I)-SHIFT(INDEX)
C
C PERFORM GIVENS ROTATIONS, QR ITERATES
C
IF (ICOUNT.LE.10) GO TO 32
NCAL=M-N
GO TO 37
32 NM1=N-1
   TEMP1=A(1,1)
   TEMP2=A(2,1)
   DO 36 R=1,NM1
      RP1=R+1
      RHO=DSQRT(DREAL(TEMPI)**2+DIMAG(TEMPI)**2+
           1DREAL(TEMP2)**2+DIMAG(TEMP2)**2)
      IF (DABS(RHO).LT.1.OE-12) GOTO 201
      COS=TEMPl/RHO
      SIN=TEMP2/RHO
      INDEX=MAX0(R-1,1)
      DO 33 I=INDEX,N
         TEMP=DCONJG(COS)*A(R,I)+CONJG(SIN)*A(RP1,I)
         A(RP1,I)=-SIN*A(R,I)+COS*A(RP1,I)
      33 A(R,I)=TEMP
   201 TEMPI = A(RP1,RP1)
   TEMP2=A(R+2,R+1)
   IF (DABS(RHO).LT.1.OE-12) GOTO 36
   DO 34 I=1,R
      TEMP=COS*A(I,R)+SIN*A(I,RP1)
      A(I,RP1)=-DCONJG(SIN)*A(I,R)+CONJG(COS)*A(I,RP1)
   34 A(I,R)=TEMP
   INDEX=MIN0(R+2,N)
   DO 35 I=RP1,INDEX
      A(I,RP1)=DCONJG(COS)*A(I,RP1)
   35 CONTINUE
   ICOUNT=ICOUNT+1
   GO TO 22
37 RETURN
END
SUBROUTINE BLLMAT(A,M,CL,LAMBDA)
IMPLICIT REAL*8(A-H,0-Z)
COMPLEX*16 A(8,8),HL(8,8),LAMBDA(8),VECT(8),MULT(8),TEMP,
TRACE,SUMEIG,H(8,8),EIG(8),CR(8,8),CL(8,8)
LOGICAL TWICE,INTH(55)
DIMENSION IINT(8)
COMMON/TEM/HL
COMMON/TALIS/IINT,TRACE,NCAL
COMMON/EIVEC/CR,H,EIG
COMMON/ROUND/EPS
C
C       CALCULATE VECTORS
C
IF(NCAL.EQ.0)GO TO 57
NCALM = NCAL - 1
DO 68 I = 1,NCALM
   IP1 = I + 1
   DO 68 J=IP1,NCAL
      IF(CDABS(LAMBDA(I))-CDABS(LAMBDA(J)).LE.1.OE-12)GOTO68
      TEMP = LAMBDA(I)
      LAMBDA(I) = LAMBDA(J)
      LAMBDA(J) = TEMP
   CONTINUE
68 CONTINUE
DO 70 I = 1,NCALM
   IP1= I+1
   DO 71 J = IP1,NCAL
      IF(CDABS(LAMBDA(I)-LAMBDA(J))-3.0E-07*CDABS(LAMBDA(I)).GT.1.OE-12)GOTO 71
      LAMBDA(I) = LAMBDA(I) - (3.0E-07)*LAMBDA(I)
   CONTINUE
71 CONTINUE
70 CONTINUE
N=M
NM1=N-1
IF(N.NE.2)GO TO 38
EPS=DMAX1(CDABS(LAMBDA(1)),CDABS(LAMBDA(2)))*1.E-8
IF(DABS(EPS).LT.1.OE-12)EPS=1.OE-12
H(1,1)=A(1,1)
H(1,2)=A(1,2)
H(2,1)=A(2,1)
H(2,2)=A(2,2)
38 DO 56 L=1,NCAL
   DO 40 1=1,N
      DO 39 J=1,N
         39 HL(I,J)=H(I,J)
      END
      DO 44 I=1,NM1
         MULT(I)=(0.0,0.0)
         INTH(I)=.FALSE.
         IP1=I+1
         IF(CDABS(HL(IP1,I)).LE.CDABS(HL(I,I)))*.LE.CDABS(HL(I,I)))GO TO 42
         INTH(I)=.TRUE.
DO 41 J=I,N
    TEMP=HL(I+1,J)
    HL(I+1,J)=HL(I,J)
 41  HL(I,J)=TEMP

IF(DABS(DREAL(HL(I,I))).LE.1.OE-12.AND.DABS(DIMAG(HL(I,I))).LE.1.E-12)GOTO 44
    MULT(I)=-HL(I+1,I)/HL(I,I)
    DO 43 J=IP1,N
      HL(I+1,J)=HL(I+1,J)+MULT(I)*HL(I,J)
 43  CONTINUE
    DO 45 I=1,N
    45 VECT(I)=(1.0,0.0)
    TWICE=.FALSE.
IF(DABS(DREAL(HL(N,N))).LE.1.OE-12.AND.DABS(DIMAG(HL(N,N))).LE.1.E-12)HL(N,N)=DCMPLX(EPS,0.0D0)
    VECT(N)=VECT(N)/HL(N,N)
    DO 48 I=1,NM1
      K=N-I
      DO 47 J=K,NM1
        VECT(K)=VECT(K)-HL(K,J+1)*VECT(J+1)
      47  CONTINUE
      IF(DABS(DREAL(HL(K,K))).LE.1.OE-12.AND.DABS(DIMAG(HL(K,K))).LE.1.E-12)HL(K,K)=DCMPLX(EPS,0.0D0)
      VECT(K)=VECT(K)/HL(K,K)
    48  VECT(K)=VECT(K)/SSS
    SSS = 0.
    DO 1001 I = 1,N
      SSS = SSS + (DREAL(VECT(I)))**2 + (DIMAG(VECT(I)))**2
1001  SSS = DSQRT(SSS)
    DO 50 I = 1,N
      VECT(I) = VECT(I)/SSS
      IF(TWICE)GO TO 52
      DO 51 I=1,NM1
        IF(.NOT.INTH(I))GO TO 51
        TEMP=VECT(I)
        IF(.NOT.INTH(I))GO TO 51
        TEMP=VECT(I)
        VECT(I)=VECT(I+1)
        VECT(I+1)=TEMP
      51  VECT(I+1)=VECT(I+1)+MULT(I)*VECT(I)
      TWICE=.TRUE.
      GO TO 46
      IF(N.EQ.2)GO TO 55
      NM2=N-2
      DO 54 I=1,NM2
        N1I=N-1-I
        NI1=N-I+1
        DO 53 J=NI1,N
        VECT(J)=H(J,N1I)*VECT(N1I+1)+VECT(J)
 53  VECT(J)=H(J,N1I)*VECT(N1I+1)+VECT(J)
INDEX = IINT(N1I)
TEMP = VECT(N1I + 1)
VECT(N1I + 1) = VECT(INDEX)
54 VECT(INDEX) = TEMP
55 DO 56 I = 1, N
56 A(I, L) = VECT(I)
   IF (NCAL .NE. N) GO TO 64
   CALL NVRT(A, CL, N)
   SUMEIG = (0.0, 0.0)
   DO 59 I = 1, NCAL
59 SUMEIG = SUMEIG + LAMBDA(I)
   GO TO 57
64 NCALP = NCAL + 1
   WRITE(6, 65) NCALP
65 FORMAT (' CONVERGENCE FAILURE IN CALCULATION OF NO.
   I2, 28H EIGENVALUE - RUN TERMINATED')
   STOP
57 RETURN
END
SUBROUTINE NVRT(Q, QNV, N)
C
C NVRT INVERTS THE EIGENVECTOR MATRIX GENERATED BY ALLMAT
C
IMPLICIT REAL*8(A-H, O-Z)
COMPLEX*16 TFR, QNV(8, 8)
COMPLEX*16 QQNV(8, 8), TEMP(8, 8), P(8), Q(8, 8)
COMMON/TEM/TEMP
IF(N .NE. 1) GO TO 1
QNV(1, 1) = 1./Q(1, 1)
GO TO 120
1 DO 410 I = 1, N
   DO 410 J = 1, N
      TEMP(I, J) = Q(I, J)
410 QQNV(I, J) = DCMPLX(0.D0, 0.D0)
   DO 11 I = 1, N
11 QQNV(I, I) = DCMPLX(1.D0, 0.D0)
   K = 1
92 I = K
   L = K
9 S = CDABS(TEMP(I, K))
   T = CDABS(TEMP(L, K))
   IF(S .GT. 1.0E-08) GOTO 20
   GOTO 10
20 L = I
10 IF (I - N) 30, 40, 30
30 I = I + 1
   GO TO 9
40 IF (L - K) 50, 60, 50
50 J = K
6 TFR = TEMP(K, J)
TEMP(K,J)=TEMP(L,J)
TEMP(L,J)=TFR
IF (J-N) 8,7,8
8 J=J+1
GO TO 6
7 DO 69 IN=1,N
   TFR=QQNV(K,IN)
   QQNV(K,IN)=QQNV(L,IN)
69 QQNV(L,IN)=TFR
60 I=K+1
71 TFR=TEMP(I,K)/TEMP(K,K)
    TEMP(I,K)=DCMPLX(0.D0,0.D0)
    J=K+1
3 TEMP(I,J)=TEMP(I,J)-TFR*TEMP(K,J)
    IF (J-N) 5,4,5
5 J=J+1
GO TO 3
4 DO 39 IN=1,N
39 QQNV(I,IN)=QQNV(I,IN)-TFR*QQNV(K,IN)
    IF (I-N) 70,80,70
70 I=I+1
GO TO 71
80 IF (K-N+1) 90,91,90
90 K=K+1
GO TO 92
91 DO 750 IN=1,N
750 QNV(N,IN)=QQNV(N,IN)/TEMP(N,N)
    I=N-1
99 J=I+1
DO 751 IN=1,N
751 P(IN)=DCMPLX(0.D0,0.D0)
102 DO 752 IN=1,N
752 P(IN)=P(IN)+TEMP(I,J)*QNV(J,IN)
    IF (J-N) 100,101,100
100 J=J+1
GO TO 102
101 DO 753 IN=1,N
753 QNV(I,IN)=(QQNV(I,IN)-P(IN))/TEMP(I,I)
    IF (I-1) 110,120,110
110 I=I-1
GO TO 99
120 RETURN
END

SUBROUTINE MULTYK(M,A,CL,LAMBDA)
CHARACTER AGA*3
DIMENSION CONST(8)
COMPLEX*16 A(8,8),CL(8,8),LAMBDA(8)
CHARACTER Q*3
CHARACTER SUP*3
DOUBLE PRECISION E(8,8),F(8,8),G(8,8)
COMMON/DAVE/P(8)
COMMON/ABCD/SUP
COMMON/BCDE/AGA

612 CONTINUE
PRINT*, 'INPUT TWO CHARACTERS: TYPE H FOR HELP'
READ(5,'(A3)') Q
IF(INDEX(Q,'H').NE.1) GOTO 611
PRINT*, 'CHARACTER 1: MATRIX NORMALISATION'
PRINT*, 'Q  NO NORMALISATION'
PRINT*, 'N ELEMENT(1,1)-TOP LEFT- EQUALS 100'
PRINT*, 'DEFAULT SUM OF ALL ELEMENTS EQUALS 100'
PRINT*, 'CHARACTER 2: R ALLOWS CYCLING TO INPUT OF MIXING TIME'
PRINT*, 'E OUTPUTS EXPONENTIAL CONSTANTS'
PRINT*, 'DEFAULT NORMAL RUNNING'
PRINT*, 'NOTE: INPUT OF NEGATIVE MIXING TIME BREAKS OUT OF LOOP CAUSED BY INPUT OF R'
PRINT*, 'MIXING TIME'
PRINT*, 'INPUT MIXING TIME'
READ(5,*) TM
IF(TM.LT.0.0) GOTO 1996
DO 10 I=1,M
E(I,I)=EXP(TM*REAL(LAMBDA(I)))
10 CONTINUE
DO 11 I=1,M
DO 12 J=1,M
IF(I.EQ.J) GOTO 12
E(I,J)=0.0
12 CONTINUE
11 CONTINUE
DO 204 I=1,M
DO 205 J=1,M
F(I,J)=0.0
206 CONTINUE
205 CONTINUE
204 CONTINUE
DO 104 I=1,M
DO 105 J=1,M
G(I,J)=0.0
106 CONTINUE
105 CONTINUE
104 CONTINUE
DO 501 I=1,M
DO 502 J=1,M
G(I,J)=G(I,J)*P(I)
502 CONTINUE
501 CONTINUE
TOT=0.0
DO 302 I=1,M
DO 303 J=1,M
TOT=TOT+G(I,J)
303 CONTINUE
302 CONTINUE
IF(INDEX(Q,'Q').EQ.1) GOTO 701
IF(INDEX(Q,'N').EQ.1) GOTO 701
DO 304 I=1,M
DO 305 J=1,M
G(I,J)=G(I,J)/TOT
305 CONTINUE
304 CONTINUE
701 CONTINUE
IF(INDEX(Q,'N').NE.1) GOTO 719
PJK1=G(1,1)
DO 729 I=1,M
DO 739 J=1,M
G(I,J)=G(I,J)/PJK1
739 CONTINUE
729 CONTINUE
719 CONTINUE
DO 300 I=1,M
WRITE(6,301)(G(I,J)*100,J=1,M)
301 FORMAT(2X,8(2X,F14.7))
300 CONTINUE
IF(INDEX(Q,'R').EQ.2) GOTO 700
IF(INDEX(Q,'E').NE.2) GOTO 1996
DO 1992 I=1,M
DO 1991 J=1,M
WRITE(6,1994) ' ELEMENT ',I,',',J
1994 FORMAT(A9,I1,A1,I1)
DO 1990 K=1,M
CONST(K)=REAL(A(I,K))*REAL(CL(K,J))*P(I)
1990 CONTINUE
WRITE(6,1993)(CONST(K),K=1,M)
1993 FORMAT(8(2X,F14.7))
1991 CONTINUE
1992 CONTINUE
1996 CONTINUE
RETURN
END
SUBROUTINE INPUTK(B,M)
CHARACTER AGA*3
CHARACTER SUP*3
DOUBLE PRECISION B(8,8)
REAL R(8)
COMMON/DAVE/P(8)
COMMON/BCDE/AGA
COMMON/ABCD/SUP
COMMON/CDEF/JKL
IF(INDEX(AGA,'Y').EQ.1) GOTO 752
PRINT*, 'INPUT NUMBER OF SITES'
READ(5,*) N
PRINT*, 'INPUT SITE POPULATIONS'
WRITE(6,27) ('P',J,',',J=1,N-1), 'P', N
27 FORMAT(2X,8(A1,I1,A1,2X))
READ(5,*) (P(I),I=1,N)
SUN=0.0
DO 818 I=1,N
SUN=P(I)+SUN
818 CONTINUE
DO 828 I=1,N
P(I)=P(I)/SUN
828 CONTINUE
752 CONTINUE
IF(INDEX(AGA,'Y').EQ.1) N=M
DO 13 I=1,N-1
PRINT*, 'INPUT RATE CONSTANTS'
WRITE(6,12) ('K',I,J,',',J=I+1,N-1), 'K', I, J
12 FORMAT(2X,8(A1,2I1,A1,2X))
READ(5,*)(B(I,J),J=I+1,N)
13 CONTINUE
DO 101 I=1,N-1
DO 102 J=I+1,N
B(J,I)=B(I,J)*P(I)/P(J)
102 CONTINUE
101 CONTINUE
PRINT*,
PRINT*, 'INPUT RELAXATION RATES'
WRITE(6,14) ('R',J,',',J=1,N-1), 'R', N
14 FORMAT(2X,8(A1,I1,A1,2X))
READ(5,*) (R(J),J=1,N)
DO 23 I=1,N
B(I,I)=0.0
DO 24 J=1,N
IF (I.EQ.J) GOTO24
B(I,I)=B(I,I)-B(I,J)
24 CONTINUE
23 CONTINUE
DO 25 I=1,N
B(I,I)=-R(I)+B(I,I)
25 CONTINUE
M=N
JKL=N
RETURN
END
SUBROUTINE INPUTE
DOUBLE PRECISION B(8,8), BB(8,8)
DOUBLE PRECISION P(8)
COMPLEX*16 A(8,8)
COMPLEX*16 CL(8,8)
COMPLEX*16 LAMBDA(8)
DOUBLE PRECISION E(8,8)
DOUBLE PRECISION GE(8,8), EK(36,36)
DOUBLE PRECISION G(8,8)

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PRINT*, '2D NMR ERROR ANALYSIS  D.S. 1985'
PRINT*,
KER=0
IER=0
PRINT*, 'INPUT MATRIX SIZE; N FOR NXN'
READ(5,*)M
PRINT*, 'INPUT MATRIX ROW-WISE SEPARATING THE '
PRINT*, 'ELEMENTS WITH COMMAS AND TERMINATING'
PRINT*, 'ROWS WITH {RETURN}'
DO 111 1=1,M
READ(5,*) (BB(I,J), J=1,M)
CONTINUE
PRINT*, ' INPUT MATRIX'
PRINT*,
DO 61 1=1,M
WRITE(6,60) (BB(I,J), J=1,M)
60     FORMAT(2X,8(2X,F14.7))
61    CONTINUE
PRINT*, ' INPUT SITE POPULATIONS'
WRITE(6,901) ('P', J, ',', ',', J=1,M-1), 'P', M
901   FORMAT(2X,8(A1,II,A1,2X))
READ(5,*) (P(I), I=1,M)
1100 CONTINUE
IF (IER.EQ.0) GOTO 1102
BB(IER,KER)=BB(IER,KER)*102/100
IF (IER.EQ.KER) GOTO 1301
BB(KER,IER)=BB(KER,IER)*102/100
1301 CONTINUE
SUN=0.0
DO 601 I=1,M
SUN=SUN+P(I)
601 CONTINUE
SUN=SUN/P(I)
602 CONTINUE
DO 902 I=1,M
DO 903 J=1,M
B(I,J)=BB(I,J)/P(I)
903 CONTINUE
902 CONTINUE
SUM=0.0
DO 904 I=1,M
DO 905 J=1,M
SUM=SUM+BB(I,J)
905 CONTINUE
904 CONTINUE
DO 906 I=1,M
DO 907 J=1,M
B(I,J)=B(I,J)/SUM
907 CONTINUE
906 CONTINUE
DO 112 I=1,M
DO 113 J=1,M
A(I,J)=B(I,J)
113 CONTINUE
112 CONTINUE
CALL ALLMAT(A,M,CL,LAMBDA)
CALL BLIMAT(A,M,CL,LAMBDA)
IF(IER.NE.0) GOTO 1211
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
DO 41 I=1,M
WRITE(6,40)(REAL(A(I,J)),J=1,M)
40 FORMAT(2X,8(2X,F14.7))
41 CONTINUE
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
DO 42 I=1,M
WRITE(6,43)(REAL(CL(I,J)),J=1,M)
43 FORMAT(2X,8(2X,F14.7))
42 CONTINUE
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
PRINT*,' ',
WRITE(6,46)(REAL(LAMBDA(I)),I=1,M)
46 FORMAT(2X,8(2X,F14.7))
1211 CONTINUE
CALL MULTYE(M,A,CL,LAMBDA,E,G,IER,KER,LST,TM)
CALL ERROR(M,BB,G,GE,IER,JER,KER,LER,LST,EK)
IF(LST.EQ.99) GOTO 1101
GOTO 1100
1101 CONTINUE
RETURN
SUBROUTINE ERROR(M,BB,G,GE,IER,KER,LER,LST,EK)
DOUBLE PRECISION BB(8,8),EK(36,36),TEK(36,36),EJ(36,36)
DOUBLE PRECISION GE(8,8),G(8,8)
DOUBLE PRECISION UK(36,36),VK(36,36)
IF(IER.EQ.0) GOTO 10
BB(IER,KER)=BB(IER,KER)*100/102
IF(IER.EQ.KER) GOTO 99
99 CONTINUE
10 CONTINUE
IF(IER.NE.0) GOTO 20
DO 30 I=1,M
DO 40 J=1,M
GE(I,J)=G(I,J)
40 CONTINUE
30 CONTINUE
DO 29 I=1,36
DO 39 J=1,36
EK(I,J)=0.0
39 CONTINUE
29 CONTINUE
IER=1
KER=1
LER=0
JER=0
GOTO 190
20 CONTINUE
AER=BB(IER,KER)*2/100
KER=KER+1
IF(KER.LE.M) GOTO 200
IER=IER+1
KER=IER
200 CONTINUE
JER=JER+1
DO 50 I=1,M
DO 60 J=I+1,M
LER=LER+1
EK(LER,JER)=(G(I,J)-GE(I,J))/AER
60 CONTINUE
50 CONTINUE
LER=0
IF((IER.LE.M).AND.(KER.LE.M)) GOTO 190
JI=(M*M+M)/2
JK=(M*M-M)/2
DO 9 I=1,JK
DO 19 J=1,JI
TEK(I,J)=0.0
UK(I,J)=0.0
VK(I,J)=0.0
19 CONTINUE
CONTINUE
DO 70 I=1,JK
DO 80 J=1,JI
TEK(J, I) = EK(I, J)
CONTINUE
70 CONTINUE
PRINT*, 'INPUT INTENSITY ERRORS'
DO 100 I=1,M
WRITE(6, 90) ('I', I, J, ',', J=I, M)
90 FORMAT (2X, 36 (A1, 2I1, A1, 2X))
CONTINUE
READ(5, *) (EJ(1, 1), I=1, JI)
DO 120 I=1, JI
DO 130 J=1, JK
UK(I, J) = EJ(I, I) * TEK(I, J) * EJ(I, I)
130 CONTINUE
120 CONTINUE
PRINT*,
DO 140 I=1, JK
DO 150 J=1, JK
VK(I, J) = 0.0
DO 160 K=1, JI
VK(I, J) = EK(I, K) * UK(K, J) + VK(I, J)
160 CONTINUE
150 CONTINUE
140 CONTINUE
WRITE (6, 180) (VK(I, J), J=1, JK)
180 FORMAT (2X, 12 (F14.7))
CONTINUE
PRINT*,
PRINT*, 'RATE CONSTANT ERRORS'
PRINT*,
WRITE (6, 159) (SQRT(VK(I, I)), I=1, JK)
159 FORMAT (2X, 8 (F14.7))
LST=99
190 CONTINUE
RETURN
END
SUBROUTINE MULTYE(M, A, CL, LAMBDA, E, G, IER, KER, LST, TM)
COMPLEX*16 A(8, 8), CL(8, 8), LAMBDA(8)
DOUBLE PRECISION E(8, 8), F(8, 8)
DOUBLE PRECISION G(8, 8)
IF (IER .NE. 0) GOTO 7777
PRINT*, 'INPUT MIXING TIME'
READ(5, *) TM
7777 CONTINUE
DO 10 I=1, M
IF (REAL(LAMBDA(I)) .GT. 0.0) GOTO 777
PRINT*, '**NEGATIVE VALUE IN LAMBDA ARRAY**'
PRINT*, 'VALUE ZEROED'
LAMBDA(I)=1E-16
777 CONTINUE
REAL=(REAL(LAMBDA(I)))
E(I,I)=(ALOG(REAL))/TM
10 CONTINUE
DO 11 I=1,M
DO 12 J=1,M
IF(I.EQ.J) GOTO 12
E(I,J)=0.0
12 CONTINUE
11 CONTINUE
DO 204 I=1,M
DO 205 J=1,M
F(I,J)=0.0
DO 206 K=1,M
F(I,J)=E(I,K)*REAL(CL(K,J))+F(I,J)
206 CONTINUE
205 CONTINUE
204 CONTINUE
DO 104 I=1,M
DO 105 J=1,M
G(I,J)=0.0
DO 106 K=1,M
G(I,J)=REAL(A(I,K))*F(K,J)+G(I,J)
106 CONTINUE
105 CONTINUE
104 CONTINUE
IF(IER.NE.0) GOTO 1501
DO 300 I=1,M
WRITE(6,301)(G(I,J),J=1,M)
301 FORMAT(2X,8(2X,F14.7))
300 CONTINUE
1501 CONTINUE
RETURN
END


Books


