A CARBON-13 AND LITHIUM-6 NMR STUDY OF ALKYLLITHIUM COMPOUNDS

THESIS

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MASTER OF SCIENCE

By

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A variable temperature $^{13}$C and $^{6}$Li NMR study has been conducted for $^{6}$Li-enriched ethyl-, n-propyl-, isopropyl-, n-butyl-, isobutyl-, t-butyl-, isopentyl-, 2-ethylbutyl-, and n-hexyl lithium in cyclopentane. Significant differences in the $^{13}$C NMR parameters are observed as a function of the alkyl group and temperature. These changes are compared to the $^{6}$Li spectra and explained in terms of the aggregates present. $^{13}$C-$^{6}$Li coupling is readily observed in both the $^{13}$C and $^{6}$Li spectra of compounds which contain branching at either the alpha or beta carbons of the alkyl group. This coupling has been used to identify the aggregates present in solution and to identify the fluxional behavior of these aggregates.
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CHAPTER I
INTRODUCTION

Due to their unique combination of structure, reactivity, and solubility, alkyllithium compounds are used routinely in organic and organometallic synthesis (1,2). Despite this wide use, the nature of alkyllithium compounds in solution is still not well understood. It has long been known that alkyllithiums form polymeric aggregates in solution, but the detailed nature of this association has remained one of the outstanding problems of organometallic chemistry for many years (3).

NMR spectroscopy has played a prominent role in the study of this association and has provided information concerning the structure and fluxionality of these aggregates in solution (4,5,6,7). Recently, Fraenkel et al. (8,9) have demonstrated the usefulness of $^{13}$C and $^6$Li NMR spectroscopy in the study of n-alkyllithiums in hydrocarbon solution. The observation of $^{13}$C-$^6$Li scalar coupling in the low temperature $^{13}$C spectra of $^{13}$C- and $^6$Li-enriched n-propyllithium provided the first direct evidence for aggregation states higher than six for any alkyllithium compound. This was also the first observation of carbon-lithium coupling in any straight-chain alkyllithium in
hydrocarbon solvent. This coupling provided information
concerning the fluxional behavior of these higher aggregates.

In order to explore the use of this technique in the
study of alkyllithium-hydrocarbon solutions, several $^6$Li-
enriched alkyllithium compounds have been prepared in
hydrocarbon solvent and studied by $^{13}\text{C}$ and $^6\text{Li}$ NMR spectroscopy.

As an introduction to this work, some fundamental
aspects of the solution behavior of alkyllithiums will be
discussed briefly. Several excellent reviews on this
subject have appeared in the literature (3,4,5,6,7), and
the reader is referred to these articles for a more de-
tailed discussion.

Both colligative and NMR data have been used to
establish the aggregation states of a number of alkyl-
lithium compounds in solution (Table I). A number of
factors have been shown to influence the degree of aggrega-
tion. The extent of aggregation is strongly dependent
upon the steric requirements of the alkyl group with more
branching at the alpha carbon resulting in smaller aggrega-
gates. For example, both ethyllithium (10) and n-butyl-
lithium (11) exist mainly as hexamers in cyclohexane while
sec-butyllithium (12) and t-butyllithium (10) are tetra-
meric in the same solvent. The menthyl group (2-isopropyl-
5-methylcyclohexane) is so bulky that menthyllithium exists
**TABLE I**

**DEGREE OF ASSOCIATION OF ALKYLLITHIUM COMPOUNDS IN SOLUTION**

<table>
<thead>
<tr>
<th>R-Group</th>
<th>Paraffins, e.g. Cyclohexane or Cyclopentane</th>
<th>Solvent Aromatics, e.g. Benzene</th>
<th>Basic Solvents, e.g. Et₂O, THF or Et₃N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl (a)</td>
<td>6</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>n-Propyl (b)</td>
<td>6</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>&gt;6 below -20°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butyl</td>
<td>6 (c)</td>
<td>6 (c)</td>
<td>4 (d)</td>
</tr>
<tr>
<td></td>
<td>&gt;6 below -20°C(e)</td>
<td></td>
<td>&lt;4 below -70°C(f)</td>
</tr>
<tr>
<td>n-Pentyl (g)</td>
<td>...</td>
<td>6</td>
<td>...</td>
</tr>
<tr>
<td>n-Octyl (g)</td>
<td>...</td>
<td>6</td>
<td>...</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>4</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>&gt;4 above 0.02 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethylsilylmethyl (a)</td>
<td>6</td>
<td>4</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>&gt;4 above 0.06 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sec-Butyl (h)</td>
<td>4</td>
<td>4</td>
<td>...</td>
</tr>
<tr>
<td>t-Butyl (a)</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Menthol (i)</td>
<td>2</td>
<td>2</td>
<td>...</td>
</tr>
</tbody>
</table>

(a) Reference 10  (b) Reference 9  (c) Reference 11  
(d) Reference 14  (e) Reference 15  (f) Reference 17  
(g) Reference 18  (h) Reference 12  (i) Reference 13
only as a dimer (13). This trend clearly indicates the reduced steric hindrance in the smaller aggregates. For alkyllithiums with intermediate steric bulk in the alkyl group (e.g., isopropyllithium and trimethylsilylmethyl-lithium), a solvent and concentration dependent equilibrium between tetramers and hexamers exists (10). All experimental evidence indicates that tetramers are the highest aggregate formed in basic solvents such as Et2O, THF, or Et3N (10,14,17).

Temperature can also affect the degree of association of alkyllithiums in solution. In hydrocarbon solvent, the aggregation states of n-propyl- (8,9), n-butyl- (15), and 2-methylbutyllithium (16) are reported to increase with decreasing temperature while the aggregation state of n-butyl-lithium in THF decreases with decreasing temperature (17). These changes in aggregation state with changes in experimental conditions suggest the existence of two or more aggregates in equilibrium as well as demonstrating the small difference in energies of the aggregates.

The structure of the alkyllithium tetramer and hexamer (Figure 1) originally proposed by Brown (19), have since been shown to exist in the solid state as well. X-ray crystallographic studies have provided the structures of methyl- (20,21), ethyl- (22,23), cyclohexyl- (24), and trimethylsilyllithium (25,26). Both methyllithium and
Fig. 1--Alkyl lithium hexamer and tetramer. Stipled spheres represent lithium atoms; blank spheres represent alpha carbons of alkyl groups.
ethyllithium are tetrameric in the solid state while cyclohexyllithium and trimethylsilyllithium are hexameric.

In each of the aggregates, a group IV atom interacts with three lithium atoms and vice versa. The tetramer consists of an inner tetrahedral framework of lithium atoms with an alkyl group sitting over each of the four triangular faces. In the hexamer, the lithium atoms have a configuration similar to the chair conformation of cyclohexane which can also be viewed as a distorted octahedron. Each alkyl group sits over one of the eight triangular faces with the two larger and transoid faces remaining empty. The point group symmetry of the hexamer is ideally $D_{3d}$ while that of the tetramer is $T_D$.

The interaction of the alkyl group with the three lithium atoms is usually described (4) in terms of a localized electron deficient bridge bond involving a hybrid orbital of the alkyl group with orbitals from three lithium atoms. Streitwieser et al. (27) have proposed a completely ionic model for the bonding in methyllithium where the tetramer consists of interpenetrating tetrahedra of methyl anions and lithium cations. A description of these and other bonding models can be found in an excellent review by Wardell (3).

NMR spectroscopy has been particularly useful in the identification of both the structure and fluxional behavior of several alkyllithium aggregates in solution.
In coordinating solvents, $^{13}\text{C}$-enriched tetrameric methyl-
lithium (28) and n-butyllithium (29) both exhibit $^{13}\text{C}-$
$^7\text{Li}$ scalar coupling at low temperatures (Table II). In
both compounds, the lithium atoms were found to be coupled
with the three nearest carbon atoms in the tetramer but
not with the more distant lithium. This indicates that

\begin{center}
\textbf{TABLE II}
\end{center}

$^{13}\text{C}-^7\text{Li}$ COUPLING CONSTANTS FOR
ALKYLLITHIUM COMPOUNDS

<table>
<thead>
<tr>
<th>R-Group</th>
<th>Solvent</th>
<th>Temperature</th>
<th>$J^{13\text{C}-^7\text{Li}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl*</td>
<td>THF, Et$_2$O, Et$_3$N</td>
<td>-60°C</td>
<td>14.5-15 Hz</td>
</tr>
<tr>
<td>n-Butyl**</td>
<td>Et$_2$O</td>
<td>-70°C</td>
<td>14</td>
</tr>
<tr>
<td>t-Butyl**</td>
<td>Cyclohexane</td>
<td>Room temperature</td>
<td>11</td>
</tr>
<tr>
<td>t-Butyl**</td>
<td>Toluene</td>
<td>Room temperature</td>
<td>10</td>
</tr>
<tr>
<td>t-Butyl***</td>
<td>Benzene</td>
<td>Room temperature</td>
<td>10.7</td>
</tr>
</tbody>
</table>

*Reference 18 **Reference 29 ***Reference 30

the solvated tetramers undergo slow intraaggregate carbon-
lithium bond exchange at low temperature. At temper-
atures above -60°C, this coupling disappears which is
indicative of rapid interaggregate exchange.

In hydrocarbon solvents, $^{13}\text{C}$-enriched t-butyllithium
exhibits $^{13}\text{C}-^7\text{Li}$ coupling in the $^{13}\text{C}$ spectrum of the alpha
carbon (29,30). Line intensity ratios indicate that each carbon atom of the tetramer is interacting with all four lithium atoms through rapid intraaggregate carbon-lithium bond exchange. This is the only case where $^{13}\text{C}-^{7}\text{Li}$ coupling had been observed in hydrocarbon solvents.

In contrast, the $^{13}\text{C}$ resonance for the alpha carbon of n-alkyllithiums in hydrocarbon solution exhibit only broad unresolved resonances at low temperature and no $^{13}\text{C}-^{7}\text{Li}$ coupling is observed (8,29,31). This has been attributed to a combination of rapid intermolecular carbon-lithium bond exchange and quadrupole-induced relaxation of the $^{7}\text{Li}$ nucleus (31). At high temperatures, rapid intermolecular exchange decouples $^{13}\text{C}$ from $^{7}\text{Li}$. At low temperatures, when this exchange has slowed, quadrupole-induced relaxation becomes fast enough to cause decoupling. This has recently been confirmed by Fraenkel et al. (8) for n-propyllithium in cyclopentane. A sample of n-propyllithium enriched with $^{13}\text{C}$ at the alpha carbon was prepared using both natural abundant and $^{6}\text{Li}$-enriched lithium metal. The $^{6}\text{Li}$ nucleus has the smallest quadrupole moment known (32) and relaxation is inefficient for this nucleus (33). Fraenkel did not observe $^{13}\text{C}-^{7}\text{Li}$ coupling in the non-enriched n-propyllithium sample but did observe $^{13}\text{C}-^{6}\text{Li}$ coupling at low temperature in the enriched sample. Furthermore, at higher field strength (67.9 MHz vs. 22.0 MHz for $^{13}\text{C}$), Fraenkel observed five
peaks in both the $^{13}$C and $^6$Li spectra (9). From the $^{13}$C-$^6$Li coupling he was able to assign the five peaks to a hexamer, an octamer, and three different nonamers. Intraaggregate bond exchange occurs within each of these aggregates and is still rapid on the NMR time scale at -93°C. This provided the first direct evidence for these higher aggregates. The similarity of the low temperature $^6$Li spectra of n-butyllithium (15) with that of n-propyllithium suggests that higher aggregates can also exist for other n-alkyllithiums in hydrocarbon solution.

The usefulness, as shown by Fraenkel, of enriching alkyllithium compounds with $^6$Li suggested that a study of isotopically enriched alkyllithium compounds could provide useful information about the types of aggregates present in hydrocarbon solution and about the fluxionality of these aggregates. To this end, several straight- and branched-chain alkyllithium compounds, isotopically enriched with $^6$Li, have been prepared in cyclopentane and have been studied using $^{13}$C and $^6$Li NMR spectroscopy. The results of this study are summarized below. While this work was in progress, Seebach et al. (17) have reported the results of a $^{13}$C NMR study of a series of $^{13}$C- and $^6$Li-enriched organolithium compounds in basic solvents.
CHAPTER BIBLIOGRAPHY


CHAPTER II

EXPERIMENTAL

Synthesis of Compounds

Dialkylmercury Compounds

Due to their high toxicity, all dialkylmercury compounds were handled in an efficient fume hood. Moreover, all glassware that came in contact with these compounds was rinsed in concentrated nitric acid prior to further cleaning.

The general methods used in the synthesis of the dialkylmercury compounds are from procedures compiled by Nesmeyanov (1). The dialkylmercury compounds were prepared by the reaction of mercuric chloride with the appropriate Grignard reagent in ethyl ether. This interaction involves the following reactions:

$$\text{HgCl}_2 + \text{RMgX} \rightarrow \text{RHgX} + \text{MgX}_2 \quad (1)$$

$$\text{RHgX} + \text{RMgX} \rightarrow \text{RHgR} + \text{MgX}_2 \quad (2)$$

$$\text{RHgR} + \text{HgCl}_2 \rightarrow 2 \text{RHgCl} \quad (3)$$

The reactions can yield the alkylmercuryhalide (Equations 1 and 3) as well as the dialkylmercury compound (Equation 2) with the major product dependent upon reaction conditions.
Due to the poor ether solubility of the alkylmercuryhalide, the second reaction is hampered and this decreases the yield of the dialkylmercury compound. In order to obtain the dialkylmercury compound in good yield it is necessary to use mechanical stirring, prolonged reaction times, and an excess of the Grignard reagent (2).

Because all of the dialkylmercury compounds were prepared in a similar fashion, only the synthesis of di-n-butylmercury and the previously unreported bis(2-ethylbutyl)mercury will be described in detail. The individual synthetic references, along with some physical properties, for the dialkylmercury compounds prepared in this study are given in Table III.

**Di-n-butylmercury.**-- In a 3-liter, 3-neck flask fitted with a condenser, mechanical stirrer, and dropping funnel was placed 36.5 g (1.5 mole) of Mg turnings along with 500 ml of ethyl ether that had been freshly distilled from LiAlH₄. A small amount of n-butylchloride was added to the flask followed by approximately 2 ml of 1,2-dibromoethane to initiate the reaction. The remainder of the n-butylchloride (139 g, 1.5 mole) was added dropwise at a rate sufficient to maintain a steady reflux of ether. The addition was complete after one hour and the mixture was stirred for an additional twenty minutes until the reaction stopped.
### TABLE III

**PHYSICAL PROPERTIES AND SYNTHETIC REFERENCES OF DIALKYL MERCURY COMPOUNDS**

<table>
<thead>
<tr>
<th>R-Group</th>
<th>Boiling Point</th>
<th>Melting Point</th>
<th>Density</th>
<th>Synthetic Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl*</td>
<td>97-98/125 mm</td>
<td>...</td>
<td>2.4237</td>
<td>2</td>
</tr>
<tr>
<td>n-Propyl*</td>
<td>82-84/19 mm</td>
<td>...</td>
<td>2.0208</td>
<td>2</td>
</tr>
<tr>
<td>Isopropyl*</td>
<td>63/10 mm</td>
<td>...</td>
<td>2.0024</td>
<td>2</td>
</tr>
<tr>
<td>n-Butyl*</td>
<td>120-123/23 mm</td>
<td>...</td>
<td>1.7779</td>
<td>2</td>
</tr>
<tr>
<td>Isobutyl*</td>
<td>86/10 mm</td>
<td>...</td>
<td>1.7678</td>
<td>3</td>
</tr>
<tr>
<td>t-Butyl*</td>
<td>...</td>
<td>78-82/5 mm**</td>
<td>...</td>
<td>4</td>
</tr>
<tr>
<td>Isopentyl*</td>
<td>125/10 mm</td>
<td>...</td>
<td>1.6397</td>
<td>3</td>
</tr>
<tr>
<td>n-Hexyl*</td>
<td>158/10 mm</td>
<td>...</td>
<td>1.5361</td>
<td>3</td>
</tr>
<tr>
<td>2-Ethylbutyl</td>
<td>112/5 mm</td>
<td>...</td>
<td>...</td>
<td>***</td>
</tr>
</tbody>
</table>

* Collected from synthetic references and reference 1.

** Sublimes.

*** See Text.
The Grignard reagent was decanted through large diameter Tygon tubing into a 3-liter, 3-neck flask fitted with a mechanical stirrer, reflux condenser and Soxhlet extractor. Mercuric chloride (136 g, 0.5 mole) was placed in an extraction thimble and the thimble was placed in the extractor. Approximately 500 ml of additional ether was added to the flask and the mixture was heated to reflux with constant stirring. A large amount of white precipitate appeared within one hour. The extraction was allowed to continue for approximately twenty hours.

After the reaction mixture had cooled, approximately 600 ml of distilled water were cautiously added to destroy any remaining Grignard reagent and to dissolve the magnesium salts. The mixture cleanly separated into 2 layers and both layers were transferred into a 200 ml separatory funnel and separated. The water layer was extracted with several portions of ether. The ether layers were combined, washed with water, and dried over anhydrous MgSO$_4$.

Most of the ether was removed on a rotary evaporator and the remaining liquid was vacuum distilled twice. The final product was a clear colorless liquid.

**Bis(2-ethylbutyl)mercury.**-- Mercuric chloride (67.9 g, 0.25 mole) was reacted with the Grignard (prepared from 0.61 mole of Mg turnings and 0.61 mole of 3-(bromomethyl) pentane in 400 ml of ether) for 45 hours using the procedure
described above. The crude product was isolated as described above and vacuum distilled twice. The final product was a clear colorless liquid. Anal. Calcd for C$_{12}$H$_{26}$Hg: C, 38.86; H, 7.07. Found: C, 37.00; H, 7.20.

All of the dialkylmercury compounds were identified using either $^{13}$C or $^{199}$Hg NMR (5,6,7,8). The $^{13}$C chemical shifts for the dialkylmercury compounds prepared in this study are given in Table IV. Because these compounds are subject to slow decomposition by either heat or light (9), all compounds were protected from light and stored in a refrigerator until further use.

**Alkylithium Compounds**

Because alkylithium compounds are extremely air-sensitive, all manipulations involving the synthesis and handling of these compounds were carried out on a vacuum line (10$^{-5}$ torr or less) or in an argon filled drybox. All solvents were dried over LiAlH$_4$ and degassed prior to further use.

The drybox was manufactured by the S. Blickman Company and was equipped with a home built purification system designed to remove water and oxygen from the box atmosphere.

The purification system consists of a 40 cm x 14 cm copper column which houses alternating layers of type 5A molecular sieves (Fisher Scientific) and Alpha De-Ox
<table>
<thead>
<tr>
<th>R-Group</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-6</th>
<th>NMR Reference</th>
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(a) In d$_6$-benzene at 22.5 MHz.

(b) In ppm based on d$_6$-benzene=128.0 ppm.

(c) $J_{^{199}Hg-^{13}C}$ in Hz.

(d) Not observed.
oxygen removal catalyst (Alpha Products). A blower continuously circulates the box atmosphere through the column which is external to the box but part of a closed system. The column is regenerated by passing a 5/95 percent hydrogen-argon mixture through the column while heating to 250°C. The utility of this type of column has been described elsewhere (10,11).

While the purity of the box atmosphere has not been determined accurately, it was judged to be acceptable after observing that freshly cut lithium metal remained shiny during all manipulations and that the bare filament of a twenty-five watt light bulb would burn for over six hours in the box (12). The column was regenerated prior to each use of the box in order to insure the best possible atmosphere.

The alkyllithium compounds were prepared by the cleavage of the corresponding dialkylmercury compound with excess $^6$Li metal in cyclopentane (13).

$$\frac{n}{2} \text{RHgR} + n^6\text{Li} \rightarrow (R^6\text{Li})_n + \frac{n}{2} \text{Hg}$$

This reaction, while being slow to reach completion, has the advantage of producing alkyllithium compounds free of halide contamination which could interfere with the NMR studies. Because all of the alkyllithium compounds were prepared in the same fashion, only the preparation of n-butyllithium will be described in detail.
n-Butyllithium.— Approximately 6.9 g (0.02 mole) of di-n-butylmercury were degassed on the vacuum line until there was no more gas evolution (8 freeze-pump-thaw cycles). Lithium chips were freshly cut from lithium rod (94.5 per cent $^6$Li, Oak Ridge National Laboratory) in the drybox and placed in a specially constructed reaction vessel equipped with two 14/20 taper joints and a break seal. A minimum two-fold excess of $^6$Li metal was used and the metal chips were cut as small as possible to increase the surface area. The mercury compound was transferred, via pastuer pipette, into the reaction vessel. The vessel was evacuated on the vacuum line and the di-n-butylmercury was degassed again. Approximately 22 ml of dry, degassed cyclopentane were distilled into the reaction vessel from a calibrated vessel. The reaction vessel was sealed off, wrapped in aluminum foil and placed on a shaker table. Within one day the surface of the lithium metal had become dark and pitted and within one week the mixture contained a large amount of finely divided metal. In all of the preparations, the reaction vessel was allowed to shake a minimum of two weeks before any NMR samples were prepared.

Preparation of NMR Samples

In the drybox, the appropriate reaction vessel was opened at the break seal. Several ml of the solution
were transferred to a fine frit sintered glass Buchner funnel that had been equipped with a sidearm and a 24/40 standard taper joint. The funnel was stoppered and the solution was quickly filtered into another vessel using back pressure supplied by a rubber bulb attached to the sidearm of the funnel. Approximately 2 ml of the filtered solution were immediately transferred, via pastuer pipette, into an 8 mm NMR tube equipped with a standard taper joint. This was degassed on the vacuum line and sealed. All samples were stored in liquid nitrogen until NMR spectra could be obtained.

Unless otherwise noted, all samples are 2M (based on monomer) in alkyllithium compound assuming complete conversion of the dialkyldimethylmercury compound.

NMR Spectra

Prior to running any NMR spectra, the top of the 8 mm NMR tube was wrapped with enough Teflon tape to make it fit snugly into a 10 mm NMR tube. A small amount of either deuterated methylene chloride (13C spectra) or a one molar solution of LiClO4 in deuterated acetone (6Li spectra) was placed in the 10 mm tube to act as an external reference and an internal lock. The 8 mm tube was then inserted into the 10 mm tube and the top of this assembly was wrapped with Parafilm.
Both $^{13}\text{C}$ and $^{6}\text{Li}$ NMR spectra were obtained on a JEOL JNM-FX90Q FT spectrometer using the optional NM-MVKIT1 tunable module and 10 mm tunable insert. Both $^{13}\text{C}$ and $^{6}\text{Li}$ spectra were run with simultaneous proton decoupling.

Low temperatures were obtained by liquid nitrogen boil off controlled with a JEOL JNM-VT-3B temperature controller. The temperature of the sample was determined by securing an ethanol thermometer in a 10 mm NMR tube which contained cyclopentane. This tube was placed in the probe and the thermometer was allowed to equilibrate for a minimum of ten minutes at each temperature setting. The thermometer was then quickly withdrawn from the probe and read. The sample tube was then placed in the probe and allowed to equilibrate for a minimum of ten minutes before running any spectra. After each experiment, the thermometer was again placed in the probe to determine if the temperature had changed. No variation in the temperature was ever observed and the reported temperatures are believed to be accurate within one degree Celcius.

$^{13}\text{C NMR Spectra}$

$^{13}\text{C}$ NMR spectra were obtained at 22.5316 MHz with 1000 90° pulses (30° for t-butyllithium) repeated every 3 seconds. An 8K transform was carried out over a spectral width of 1400 Hz. The 3 second repetition rate was
used to partially suppress the resonance from cyclopentane which has a $T_1$ relaxation time of 29.2 seconds at 30°C (14). Deuterated methylene chloride was used as an external reference and an internal lock. All $^{13}\text{C}$ chemical shifts were assigned relative to cyclopentane (25.8 ppm).

$^{6}\text{Li NMR Spectra}$

$^{6}\text{Li}$ NMR spectra were obtained at 13.186211 MHz with 20-60 50° pulses. Repetition rates varied from 60 seconds at ambient temperature to 32 seconds at the low temperature limit. An 8K transform was carried out over a spectral width of 250 Hz. $^{6}\text{Li}$ chemical shifts were assigned relative to one molar LiClO$_4$ in deuterated acetone. This solution also served as an internal $^{7}\text{Li}$ lock. Use of the $^{7}\text{Li}$ lock was necessary due to the close proximity of the $^{6}\text{Li}$ and $^{2}\text{H}$ resonances.
CHAPTER BIBLIOGRAPHY


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CHAPTER III

RESULTS AND DISCUSSION

Fraenkel's assignment of an octamer and several nonamers from the $^{13}\text{C}-^{6}\text{Li}$ coupling observed in cyclopentane solutions of $^{6}\text{Li}$-enriched n-propyllithium (1) suggested that $^{6}\text{Li}$-enrichment could prove useful in the NMR study of other alkyllithiums. Thus, a $^{13}\text{C}$ and $^{6}\text{Li}$ NMR study of cyclopentane solutions of various straight- and branched-chain alkyllithium compounds enriched with $^{6}\text{Li}$ has been conducted. The results of this study are summarized below. A complete listing of the $^{13}\text{C}$ and $^{6}\text{Li}$ chemical shifts for the compounds studied can be found in the Appendix.

Straight-Chain Compounds

The study of the alkyllithium compounds was begun by measuring the $^{13}\text{C}$ and $^{6}\text{Li}$ NMR spectra of $^{6}\text{Li}$-enriched n-propyl-, ethyl-, n-butyl-, and n-hexyllithium in cyclopentane as a function of temperature. It was of interest to see how the length of the alkyl group would affect the equilibria between the various aggregation states and the $^{13}\text{C}-^{6}\text{Li}$ coupling.
While the study of n-propyllithium was essentially a repetition of Fraenkel's work, several important changes were made. First, the alkyllithium compounds prepared in this study were not isotopically enriched with $^{13}$C. Therefore, the study of n-propyllithium was necessary in order to determine if this lack of $^{13}$C-enrichment would severely limit the sensitivity of the $^{13}$C NMR experiments. Secondly, in order to increase the sensitivity, all compounds were prepared as 2M solutions unless otherwise noted. Finally, all compounds were prepared from the corresponding dialkylmercury compound rather than from the alkylhalide. This eliminated any possibility of halide contamination.

**n-Propyllithium**

The variable temperature $^{13}$C spectra of the alpha carbon of n-propyllithium are shown in Figure 2. A single peak (16.1 ppm) is present at 30°C. As the temperature is lowered, two new peaks appear downfield and gain in intensity at the expense of the original peak. At the low temperature limit these three peaks appear at 15.6, 17.3, and 18.4 ppm. Using Fraenkel's assignments (1), the upfield, center, and downfield peaks are assigned to the hexamer, octamer, and nonamer, respectively. The spectra from this work agree qualitatively with the spectra obtained by Fraenkel at 22.0 MHz (2). However, the relative
Fig. 2--Variable temperature $^{13}$C NMR spectra of the alpha carbon of 2 M n-propyllithium in cyclopentane.
magnitudes of the peaks are different. The reason for this difference in magnitudes is the over three-fold increase in concentration (2M based on monomer vs. 0.6M) which shifts the equilibria toward the higher aggregates. The equilibrium constants have not been determined due to overlapping peaks, but the change in the spectra are consistent with this argument. For example, at low temperature, the downfield nonamer peak is the largest peak in this work, while the hexamer peak is the largest in Fraenkel's work.

The $^{13}$C-$^6$Li coupling observed by Fraenkel at 22.0 MHz is not readily observable in these spectra. With the use of resolution enhancement (subtraction of an exponentially weighted FID from a non-weighted FID) coupling is observed (Figure 3). The observed coupling is approximately 3.3 Hz for the hexamer and 2.5 Hz for the octamer. These values agree well with the values of 3.35 Hz and 2.5 Hz obtained by Fraenkel. The three different nonamers observed by Fraenkel at 67.9 MHz are not resolved at this field strength and, therefore, coupling is not resolved for the nonamer.

The variable temperature $^6$Li spectra of n-propyllithium (Figure 4) confirm the existence of at least three different aggregation states in solution. At 30°C a single peak is present at 1.94 ppm downfield from the LiClO$_4$
Fig. 3--(a) Enhanced and (b) non-enhanced $^{13}$C NMR spectra of the alpha carbon of n-propyllithium at $-82^\circ$C.
Fig. 4--Variable temperature $^6$Li NMR spectra of 2 M n-propyllithium in cyclopentane.
reference. As the temperature is lowered, the peaks corresponding to the octamer and nonamer appear upfield from this peak. At -80°C the hexamer, octamer and nonamer have chemical shifts of 1.87, 1.80, and 1.72 ppm, respectively. The three different nonamers should be observable in the $^6$Li spectra at this field strength and, in fact, two very small unresolved peaks are seen at 1.65 ppm.

**Ethyl-, n-Butyl-, and n-Hexyllithium**

The results obtained for the other n-alkyllithiums are very similar to those obtained for n-propyllithium. The $^{13}$C resonance of the alpha carbons of ethyl-, n-butyl-, and n-hexyllithium all appear as a single peak at 30°C. At low temperature, the single resonance of each compound has split into three peaks (Figure 5) which are presumably due to a hexamer, an octamer, and at least one type of nonamer. In the case of n-butyllithium and n-hexyllithium, the three peaks are somewhat obscured by a signal from another carbon atom in the molecule that falls in this region of the spectrum. However, the low temperature $^6$Li spectra of these compounds (Figure 6) clearly indicate the presence of the three aggregates. The minor peaks observed in the low temperature $^6$Li spectra of n-propyllithium are not seen in the spectra of the other n-alkyllithiums and so it is not clear whether more than three aggregation states are present.
Fig. 5--Low temperature $^{13}$C NMR spectra of the alpha carbon of ethyl-, n-butyl-, and n-hexyllithium in cyclopentane. Asterisk indicates a solvent impurity.
Thus, ethyl-, n-butyl-, and n-hexyllithium all exist in at least three different aggregation states at low temperature in hydrocarbon solution. Based on the similarity between the spectra of these compounds and the spectra of n-propyllithium, the three aggregation states are believed to be a hexamer, an octamer, and at least one nonamer.

Even with resolution enhancement, there is no evidence for $^{13}\text{C} - ^{6}\text{Li}$ coupling in these three compounds. Evidently, some type of interaggregate exchange process is still rapid, relative to the $^{13}\text{C} - ^{6}\text{Li}$ coupling, in solutions of these compounds at low temperature. This is puzzling because one might expect, based on steric arguments, that interaggregate exchange would be slower for n-butyllithium and n-hexyllithium than for n-propyllithium. A very small $^{13}\text{C} - ^{6}\text{Li}$ coupling constant could also explain the lack of splitting. However, it would be difficult to rationalize why n-propyllithium would have an unusually large coupling constant.

An increase in the length of the alkyl group does produce one clear trend which is apparent in the $^{6}\text{Li}$ spectra. Although accurate integration values are impossible due to peak overlap, it is clear that longer alkyl groups shift the equilibria toward the smaller aggregates (Figure 6). The higher aggregation states are favored when
Fig. 6--Low temperature $^6$Li NMR spectra of ethyl-, n-butyl-, and n-hexyllithium in cyclopentane.
the alkyl group is small (e.g., ethyllithium), while the hexamer is favored when the alkyl group is long (e.g., n-hexyllithium). This trend is expected based on the greater steric hindrance encountered in the higher aggregates.

Branched-Chain Compounds

Although the spectra of the straight-chain compounds are nearly identical, the introduction of branching at the alpha or beta carbon introduces significant changes. Both the number and type of aggregates present in solution change, and $^{13}$C-$^6$Li coupling is readily observable.

Isopropyllithium

The variable temperature $^{13}$C NMR spectra of the alpha carbon of isopropyllithium are shown in Figure 7. At 30°C peaks are seen at 6.2 and 10.3 ppm with the upfield resonance predominating. As the temperature is lowered, the downfield peak grows in intensity at the expense of the other and by 0°C it has become the dominant peak. The relative areas of the peaks remain constant below -15°C, which indicates that interaggregate exchange has slowed to the point where equilibrium is not reached during the time required for the experiment (approximately one hour).

Isopropyllithium has been shown (3) to be mainly tetrameric below 0.02 m in hydrocarbon solution, with an
Fig. 7--Variable temperature $^{13}$C NMR spectra of the alpha carbon of 2 M isopropyllithium in cyclopentane.
equilibrium occurring between tetramers and hexamers at higher concentrations. Therefore, the upfield resonance, which predominates at high temperature, represents the tetramer. This assignment is consistent with the straight-chain compounds in which the higher aggregates appear downfield.

As the temperature is lowered, the hexamer peak splits into a multiplet with nine to eleven lines of equal spacing appearing above the noise, and the tetramer splits into seven lines. The observed splittings for the hexamer and tetramer are 3.29 Hz and 6.1 Hz respectively.

The most direct interpretation of the hexamer multiplet is that each carbon is interacting with six equivalent lithium atoms through rapid intraaggregate carbon-lithium bond exchange. This would give a thirteen line multiplet where two lines are lost in the noise. If the hexamer were undergoing slow intraaggregate exchange, with each carbon atom interacting with three lithium atoms, only a seven line pattern would be observed.

Thus, as proposed for the n-propyllithium hexamer (1), the observed splitting of 3.29 Hz for the isopropyllithium hexamer represents the average of the three nearest neighbor 
$^{13}\text{C}-^6\text{Li}$ couplings with the three couplings to the more distant lithium atoms. In general, this observed splitting is given by:
where $J$ is the one bond coupling, $J'$ is the long range coupling, and $n$ is the aggregation number. Assuming that the long range coupling is negligible for the isopropyl lithium hexamer, then the three nearest neighbor couplings would be 6.58 Hz. Within experimental error, this is the same coupling observed for the n-propyllithium hexamer in cyclopentane (1).

Rapid intraaggregate exchange in a tetrameric species would produce a nine line multiplet from the interaction of each carbon with four equivalent lithium atoms. The seven line multiplet observed for the isopropyllithium tetramer suggests, in fact, that intramolecular exchange is sufficiently slow on the NMR time scale such that each carbon is interacting with only the three lithium atoms adjacent to it in the tetramer. Thus, the observed $^{13}\text{C}-^{6}\text{Li}$ coupling of 6.1 Hz represents the near neighbor coupling. Translated to $^{13}\text{C}-^{7}\text{Li}$ coupling, this value would be 16 Hz, which is not much different from the values observed for methyllithium (4) and n-butyllithium (5) in ether, 14.7 and 15 Hz respectively. These are known to be couplings in slowly exchanging tetrameric etherates.

Further support for these interpretations comes from the ratio of line intensities observed in the two
multiplets. Table V shows the calculated and observed line intensities (relative to the center of the multiplet) for both the hexamer and tetramer of isopropyl-lithium. The calculated line intensities for a fast exchanging hexamer and slow exchanging tetramer correspond well to the observed line intensities of the hexamer and tetramer respectively.

It is also interesting to note that coupling is observed in the hexamer at higher temperatures than in the tetramer (see Figure 7). One would expect coupling to be seen first in the aggregate with the larger coupling constant. One explanation for this discrepancy could be that interaggregate exchange between tetramers, or between tetramers and some intermediate (in low concentration), occurs at a much faster rate than interaggregate exchange between hexamers. This would require that a lower temperature be reached in order to slow the exchange and observe coupling.

Another possible explanation is that the isopropyl-lithium tetramer is in a transition between fast and slow intraaggregate exchange in the +30°C to -15°C temperature range and that, during this transition, coupling is obscured. This would mean that at 0°C, interaggregate exchange between hexamer and tetramer has slowed sufficiently to allow the observation of coupling in the
TABLE V
CALCULATED AND OBSERVED LINE INTENSITIES
FOR THE ISOPROPYLLITHIUM HEXAMER AND TETRAMER*

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<td>Observed</td>
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</table>

*Ratio of line intensities relative to the center of the multiplet.
hexamer while coupling in the tetramer is still obscured because of the fast to slow intraaggregate exchange transition. This explanation is consistent with the variable temperature $^{13}$C spectra of the t-butyllithium tetramer described in a later section.

The variable temperature $^6$Li spectra of isopropyl-lithium (Figure 8) confirm the existence of the two aggregation states. Due to the much smaller chemical shift range of the $^6$Li nucleus, the interaggregate exchange process that is slow enough to allow the observation of both aggregates at 30°C in the $^{13}$C spectrum is still rapid enough to average the $^6$Li chemical shifts. This results in the single peak at 1.25 ppm and, based on the $^{13}$C data, is primarily due to the tetramer. As the temperature is lowered, the exchange is slowed further and two peaks are observed. At -85°C the two peaks have chemical shifts of 1.10 and 1.02 ppm.

The two $^6$Li peaks have unambiguously been assigned on the basis of $^{13}$C satellites which are observed at the base of the $^6$Li peaks (Figure 9). At -15°C a pair of satellites symmetrically flank the downfield peak and are separated by 3.29 Hz. Thus, in contrast to the n-alkyl-lithiums, the higher aggregate appears downfield. The $^{13}$C satellites from the tetramer are very broad at this temperature. This is probably due to their being
Fig. 8--Variable temperature $^6\text{Li}$ NMR spectra of 2 M isopropyllithium in cyclopentane.
Fig. 9—$^{13}$C satellites in $^6$Li NMR spectrum of isopropyllithium at -15°C.
broadened by the same exchange process which prevents the observation of coupling in the $^{13}$C spectra of the tetramer. They sharpen somewhat at lower temperatures, but never become as sharp as the hexamer satellites. This lends support to the notion that the tetramer is in a transition from rapid to slow intraaggregate exchange.

Details about the relative energies of the two aggregates can be obtained using the $^{13}$C peak areas at the different temperatures. The concentration of the hexamer and tetramer at the various temperatures are given in Table VI along with the equilibrium constants and free energies defined by the following equilibrium. As previously mentioned, at temperatures below 258 K the exchange has become so slow that equilibrium is not reached during the time of the experiment. Therefore, no equilibrium constants or free energies can be calculated below 258 K.

If $\Delta H$ and $\Delta S$ are independent of temperature, a plot of $\ln K_{eq}$ versus $1/T$ for temperatures above 258 K should produce a straight line with a slope equal to $-\Delta H/R$ and a y-intercept of $\Delta S/R$. A linear least squares fit of the data ($r=0.9977$) gives a $\Delta H$ value of $-6.16 \pm 0.04$ Kcal/mole of hexamer ($-1.03 \pm 0.007$ Kcal/mole of monomer), and a $\Delta S$ value of $-21.5 \pm 0.6$ eu/mole of hexamer ($-3.58 \pm 0.1$ eu/mole of monomer). The negative value of $\Delta S$ is
### TABLE VI

EQUILIBRIUM CONSTANTS AND $\Delta G$ VALUES FOR THE ISOPROPYLLITHIUM EQUILIBRIUM

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<th>$T ; ^\circ K$</th>
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<tr>
<td>188</td>
<td>1.0</td>
<td>0.49</td>
<td>0.22</td>
<td>0.17</td>
</tr>
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</table>

(a) From $^{13}$C spectra.
(b) Based on a total monomer concentration of 2M.
(c) Defined by $3/2 (RLi)_4 + (RLi)_6$.
(d) See text.
consistent with a system which is proceeding to a smaller number of particles with no solvent interaction.

The significance in the change in energy becomes apparent when one considers the total number of bonding interactions involved in Equation 6. The fact that there are eighteen carbon-lithium bonding interactions on each side of the equation indicates that the average carbon-lithium bond interaction is stronger in the hexamer than in the tetramer. This is in spite of the greater steric interactions in the hexamer. The stronger carbon-lithium bond in the hexamer is in complete agreement with the \(^{13}\text{C}-\text{\textsuperscript{6}Li}\) coupling of 6.6 Hz and 6.1 Hz in the hexamer and tetramer respectively. This is also consistent with PRDDO molecular orbital calculations (6) that suggest greater C-Li charge separation and greater Li 2p character in the bonds of the tetramer. The difference in coupling is also consistent with a change in hybridization on the alpha carbon. The one bond carbon-hydrogen couplings for the hexamer and tetramer have been measured at 100 Hz and 104 Hz respectively.

**t-Butyllithium**

Adding additional branching at the alpha carbon destroys the tetramer-hexamer equilibrium observed for isopropyllithium. Only one resonance is observed in the \(^{13}\text{C}\) spectrum at all temperatures (Figure 10). Apparently,
Fig. 10--Variable temperature $^{13}$C NMR spectra of the alpha carbon of 1 M t-butyllithium in cyclopentane.
the t-butyl group is so bulky that formation of any aggregate higher than the tetramer is energetically unfavorable even at low temperature. This is consistent with colligative data (3) which has shown that t-butyllithium exists as a tetramer.

The most striking feature of these spectra is that coupling is observable at all temperatures. This indicates that the bulky t-butyl group hinders any interaggregate exchange process. A seven line multiplet (10.7 ppm) is seen at 30°C with a splitting of 4.15 Hz. As the temperature is lowered, the coupling pattern becomes complex and by -20°C a new seven line multiplet appears with a splitting of 5.45 Hz.

This is the first direct observation of the transition from rapid to slow intraaggregate exchange. The seven line multiplet observed at 30°C is due to the interaction of each carbon with the four lithium atoms of the tetramer. This would produce a nine line pattern with two of the lines lost in the noise. As the temperature is lowered, intraaggregate exchange is slowed and by -20°C each carbon is interacting with only the three adjacent lithium atoms. This would produce the seven line multiplet which is observed. The observed line intensities agree well with those calculated for fast and slow intramolecular exchange (Table VII).
Hartwell and Brown (7) had inferred from studies of the exchange between trimethylsilylmethyllithium and t-butyllithium, that t-butyllithium undergoes the transition from rapid to slow intraaggregate exchange at these temperatures. The fast exchange limit has been observed in the $^{13}$C NMR spectra (5,8). However, this work provides the first direct observation of that transition.

The variable temperature $^6$Li spectra of t-butyllithium are shown in Figure 11. As expected, a single large peak is present at $30^\circ$C (1.19 ppm) and remains sharp as
Fig. 11—Variable temperature $^6$Li NMR spectra of 1 M $t$-butyllithium in cyclopentane.
the temperature is lowered. In addition to this large peak are several much smaller peaks present in the spectra. Figure 12 shows the baseline portion of the $^6$Li spectra at several temperatures. At 30°C, four small peaks are seen downfield from the LiClO$_4$ reference. The two peaks which symmetrically flank the $^6$Li resonance are the $^{13}$C satellites present under the condition of fast intraaggregate exchange. These peaks are, as expected, separated by 4.15 Hz. As the temperature is lowered, these satellites broaden and become difficult to see. By -40°C they have reappeared with a separation of 5.45 Hz which indicates that intramolecular exchange has slowed.

The broad peak which appears at 0.39 ppm in the room temperature spectra is due to alkoxide impurity. This was verified by exposing a sample of t-butyllithium to air and observing the corresponding increase in the intensity of the peak. Alkoxide groups can replace alkyl groups in alkyllithium aggregates (9). Assuming that the t-butoxide group occupies one face of a t-butyllithium tetramer, one would expect that under conditions of slow intraaggregate exchange that there would be one chemical shift for the three lithium atoms adjacent to the t-butoxide group and one chemical shift for the more distant lithium atoms. This is exactly what is observed. As the temperature is lowered, the broad peak sharpens and a smaller peak
Fig. 12—Enlarged baseline of the variable temperature $^6$Li NMR spectra of 1 M t-butyllithium in cyclopentane.
appears downfield at 0.88 ppm. These two peaks also occur in the expected three to one ratio. The alkoxide impurity is present in a relative concentration of 2.5 per cent which means that 10 per cent of the tetramers contain a t-butoxide group.

The small peak which appears at 1.28 ppm is more difficult to explain. As the temperature is lowered, this peak broadens and dissapears only to reappear again 1.1 Hz further downfield. This peak persisted in samples of t-butyllithium purified by sublimation.

One could speculate on the existence of dimers in small concentration. The dimer of n-butyllithium, which is present at low temperatures in coordinating solvent, is known (10) to appear downfield from the corresponding tetramer. It would, however, be difficult to explain the change in chemical shift that occurs during the transition of the tetramer from fast to slow intraaggregate exchange. Another possibility is that isobutene has been eliminated and LiH formed, giving rise to the small peak. These possibilities have not been investigated further.

It is interesting to speculate on the magnitude of any long range coupling in the t-butyllithium tetramer. The coupling constant of 5.45 Hz observed in the slow exchange limit would, in order to satisfy the 4.15 Hz splitting observed in the fast exchange limit, require that the
Clark et al. (11) have predicted from INDO molecular orbital calculations that long range coupling in the methyl lithium tetramer should be on the order of 0.04 to 0.5 Hz. Thus, if there is any long range coupling, an additional pair of $^{13}\text{C}$ satellites should flank the $^6\text{Li}$ resonance at low temperature with a separation of 0.25 Hz. In fact, small shoulders separated by 0.24 Hz are seen on the $^6\text{Li}$ peak at -60°C but are not seen at -82°C. Therefore, it is not clear whether the shoulders are due to long range coupling or whether exchange has not completely slowed at -60°C, resulting in some residual coupling to the back lithium.

**Isobutyllithium**

In order to investigate the effect of branching at the beta carbon, $^6\text{Li}$-enriched isobutyllithium was studied. The aggregation state of this compound had not previously been reported. The variable temperature $^{13}\text{C}$ spectra of the alpha carbon are shown in Figure 13. Only one resonance is seen for this carbon even at low temperatures. No coupling is observed at 30°C, indicating that interaggregate exchange is still rapid on the NMR time scale. However, by -20°C this exchange has slowed and the peak splits into more than nine lines with a separation of 3.11 Hz. As the temperature is lowered further, this splitting persists and by -70°C the multiplet has begun to broaden.
Fig. 13--Variable temperature $^{13}\text{C}$ NMR spectra of the alpha carbon of 2 M isobutyllithium in cyclopentane. Asterisk indicates a spinning sideband of the cyclopentane resonance.
At temperatures below -70º C the compound precipitated from solution.

The observation of more than nine lines rules out a slowly exchanging aggregate and a rapidly exchanging tetramer. Therefore, isobutyl lithium exists only as a hexamer at these concentrations and is undergoing rapid intraaggregate exchange. The observed splitting of 3.11 Hz would correspond to a $^{13}$C-6Li coupling constant of 6.22 Hz. The possibility that the compound exists as a rapidly exchanging octamer or nonamer cannot be ruled out on the basis of line intensities but is considered to be highly unlikely. Even in compounds where higher aggregates have been observed, these higher aggregates are only present in any significant amount at low temperatures and are always in equilibrium with a hexamer.

The 6Li spectra of isobutyl lithium serve to verify the existence of only a single aggregation state at this concentration. A single resonance is observed throughout the entire temperature range and even at -70ºC (Figure 14), there is no evidence for any other aggregates.

The $^{13}$C-6Li coupling observed in the $^{13}$C spectra is also evident in the 6Li spectra. Satellites appear at the base of the lithium peak and are separated by 3.11 Hz. However, these satellites have become broad at -70ºC, just as the $^{13}$C multiplet did. This broadening is
Fig. 14--$^6\text{Li}$ NMR spectrum of 2 M isobutyllithium in cyclopentane at $-70^\circ\text{C}$. 
probably due to the precipitation of the compound which occurred at temperatures just below -70°C.

Thus, the placement of the branching at the beta carbon destroys the tetramer-hexamer equilibrium of isopropyllithium, with now only hexamers present. This clearly illustrates how sensitive the aggregates are to steric bulk in the alkyl group.

2-Ethylbutyllithium

The results obtained for the previously unreported 2-ethylbutyllithium are essentially the same as those obtained for isobutyllithium. Only one resonance is seen for the alpha carbon at all temperatures (Figure 15). At 27°C no coupling is observed but, by 0°C, an eleven line multiplet appears with an observed splitting of 3.1 Hz.

The same arguments that were used to identify the isobutyllithium hexamer apply here and therefore, 2-ethylbutyllithium has been assigned as a hexamer undergoing rapid intraaggregate exchange at this concentration. The observed splitting of 3.1 Hz is the exchange averaged coupling and would correspond to a $^{13}$C-$^6$Li coupling constant of 6.2 Hz. The fact that 2-ethylbutyllithium exists as a hexamer indicates that the preferred aggregation state of an alkyl lithium compound is much less sensitive
Fig. 15--Variable temperature $^{13}\text{C}$ NMR spectra of the alpha carbon of 2 M 2-ethylbutyllithium in cyclopentane.
to the length of the branching than to the position of branching in the alkyl group.

One difference between the isobutyllithium and 2-ethylbutyllithium hexamers is the temperature at which coupling is observed. The splitting observed for 2-ethylbutyllithium at approximately 14°C is not observed for isobutyllithium until approximately -10°C. This is indicative of a higher energy pathway for interaggregate exchange in 2-ethylbutyllithium and is clearly the result of the increased steric bulk of the alkyl group.

If the increased steric bulk of the 2-ethylbutyl group results in a slowing of interaggregate exchange, it would also be expected to slow intraaggregate exchange. The change in the coupling pattern for 2-ethylbutyllithium below -20°C could be the result of a transition from rapid to slow intraaggregate exchange similar to that observed for the t-butyllithium tetramer. However, the slow exchange limit is not observed at the lowest temperature and it is not clear whether this transition is actually occurring. The $^{13}$C satellites in the $^6$Li spectra are broad and remain ill-defined throughout the entire temperature range and are of no help in determining what occurs at low temperature.
Isopentyllithium

Branching at the alpha or beta carbon produced results that were drastically different from those obtained for the straight-chain alkylolithiums. Branching at the gamma carbon, however, produces results almost identical to those of the n-alkylolithiums. Both the $^{13}$C spectrum (alpha carbon) and $^6$Li spectrum of isopentyllithium at $-87^\circ$C are shown in Figure 16. At least three unresolved peaks are observed in both the $^{13}$C and $^6$Li spectra. Evidently, isopentyllithium exists in an equilibrium between hexamer, octamer, and nonamer at low temperature. A comparison of the low temperature $^{13}$C spectra with those of the straight-chain alkylolithiums (Figures 2 and 5) shows that the equilibrium is shifted toward the hexamer to a greater extent.

Therefore, while branching at the gamma position produces enough steric interaction to shift the equilibrium toward the hexamer, it does not produce enough strain to prevent the formation of the higher aggregates. One can see again how sensitive the aggregates are to minor changes in the steric bulk of the alkyl group.

As with the straight-chain compounds, no $^{13}$C-$^6$Li coupling is observed over the temperature range studied. In every case where coupling is not observed, aggregation states higher than six are present. This implies that
Fig. 16--$^{13}$C (alpha carbon) and $^6$Li NMR spectra of 2 M isopentyllithium in cyclopentane at -75°C.
some type of rapid interaggregate exchange process operates when these aggregates are present in solution.

**Summary and Conclusions**

A variable temperature $^{13}$C and $^6$Li NMR study of cyclopentane solutions of various straight- and branched-chain alkyl lithium compounds has been conducted. Both the type of aggregates present in solution and the exchange properties of these aggregates has been shown to be extremely sensitive to the extent and position of branching in the alkyl group.

This study confirms the original observation by Fraenkel (1,2) of multiple aggregation states in the low temperature $^{13}$C and $^6$Li NMR spectra of $n$-propyllithium. Similar peaks have also been observed for ethyl-, $n$-butyl-, $n$-hexyl-, and isopentyllithium. Based on the similarity of the spectra, these compounds are also believed to exist in solution as a hexamer, an octamer, and at least one type of nonamer. Thus, the existence of aggregation states higher than six appears to be a general phenomenon in compounds which have no branching in the alkyl group at either the alpha or beta carbons.

With the exception of $n$-propyllithium, no $^{13}$C-$^6$Li coupling has been observed in any of the compounds which form the higher aggregates. This suggests that
interaaggregate exchange is still rapid for these compounds at low temperature. Branching at the alpha or beta carbon of the alkyl group prevents the formation of aggregation states higher than six and slows interaggregate exchange enough to allow the observation of $^{13}\text{C}-^6\text{Li}$ coupling.

This coupling (Table VIII) has been used to identify the aggregation states of isobutyllithium and 2-ethylbutyllithium. It has also been used to identify the fluxional behavior of all the aggregates for which this coupling has been observed.

The magnitude of this coupling alone is useful in studying these systems. Although coupling has been observed for a rather limited number of compounds, they do include primary, secondary and tertiary carbons bonded to lithium. The observed coupling ranges from 2.22-6.1 Hz. All of the larger couplings (greater than 4.5 Hz) correspond to non-fluxional aggregates. Of the fluxional aggregates, the tetramer is 4.15 Hz, the hexamers 3.1-3.3 Hz, and the octamer 2.5 Hz. It thus seems likely that the magnitude of $J_{\text{obs}}$ is first, a measure of the presence or absence of fluxional behavior and, for the fluxional aggregates, is a direct measure of the aggregation state present. This is due to the nearly constant value for $J_{^{13}\text{C}-^6\text{Li}}$. The total range of this quantity
### TABLE VIII

$^{13}$C-$^6$Li COUPLING CONSTANTS OF ALKYL-LITHIUM COMPOUNDS IN CYCLOPENTANE

<table>
<thead>
<tr>
<th>R-Group</th>
<th>n(a)</th>
<th>$J_{obs}$(b)</th>
<th>$1_J^{(13}$C-$^6$Li)(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propyl</td>
<td>6</td>
<td>3.3</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.5</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2.2(d)</td>
<td>6.7</td>
</tr>
<tr>
<td>Isobutyl</td>
<td>6</td>
<td>3.11</td>
<td>6.22</td>
</tr>
<tr>
<td>2-Ethylbutyl</td>
<td>6</td>
<td>3.1</td>
<td>6.2</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>4</td>
<td>6.1</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3.3</td>
<td>6.6</td>
</tr>
<tr>
<td>t-Butyl</td>
<td>4 (30°C)</td>
<td>4.15</td>
<td>5.53</td>
</tr>
<tr>
<td></td>
<td>4 (-60°C)</td>
<td>5.45</td>
<td>5.45</td>
</tr>
</tbody>
</table>

(a) Aggregation number.
(b) Observed peak separation in Hz from $^{13}$C spectra. Separation quoted to nearest 0.01 Hz were also observed as $^{13}$C satellites in the $^6$Li spectra.
(c) In Hz, calculated from $J_{obs} = [3J + (n-3)J']/n$ assuming $J'=0$.
(d) From reference 1.
is 5.45-6.7 Hz. If t-butyllithium is excluded, the total range is only 6.1-6.7 Hz.

Despite the very narrow range of values for the coupling, the coupling is sensitive to subtle differences in the bonding in the aggregates. Unlike the constant $J(\text{\textsuperscript{13}C-\text{\textsuperscript{6}Li}})$ observed for the hexamer, octamer, and nonamer of n-propyllithium, the values of $J$ for the tetramer and hexamer of isopropyllithium are different and suggest differences in the bonding of the two types of aggregates. The similar values of $J$ for the higher aggregates ($n=6, 8, 9$) suggest that bonding in these higher aggregates is similar, even though the structures of the octamers and nonamers remain unknown.

The coupling observed in the $\text{\textsuperscript{13}C}$ spectra of these compounds has also been observed in the $\text{\textsuperscript{6}Li}$ spectra. This has unambiguously tied the $\text{\textsuperscript{13}C}$ and $\text{\textsuperscript{6}Li}$ spectra together, and has been used to assign the $\text{\textsuperscript{6}Li}$ hexamer and tetramer peaks of isopropyllithium. An additional advantage of the observation of coupling in the $\text{\textsuperscript{6}Li}$ spectra is the greater accuracy of the coupling constants due to greater resolution (more data points per spectral width).

Finally, it has been shown that the costly and time consuming procedure of $\text{\textsuperscript{13}C}$-enrichment used by other investigators is not necessary in order to obtain useful information from the $\text{\textsuperscript{13}C}$ spectra. $\text{\textsuperscript{6}Li}$-enrichment is necessary
in order to eliminate the broad lines caused by quadrupolar relaxation of the \( ^7\)Li nucleus. However, \( ^6\)Li-enrichment is relatively easy and very inexpensive. Therefore, \(^{13}\)C and \(^6\)Li NMR spectroscopy can be an extremely useful tool in the study of alkyllithium compounds and may be applicable to a large range of other organolithium compounds as well.
CHAPTER BIBLIOGRAPHY


APPENDIX

$^{13}\text{C}$ AND $^{6}\text{Li}$ CHEMICAL SHIFTS OF
ALKYLLITHIUM COMPOUNDS
### TABLE IX

$^{13}$C CHEMICAL SHIFTS OF ALKYL-LITHIUM COMPOUNDS IN CYCLOPENTANE (a), (b)

<table>
<thead>
<tr>
<th>R-Group</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>C-5</th>
<th>C-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl (c)</td>
<td>0.33</td>
<td>10.7</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>n-Propyl (d)</td>
<td>16.1</td>
<td>22.4</td>
<td>22.3</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Isopropyl (d)</td>
<td>6.2</td>
<td>22.9</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butyl (d)</td>
<td>11.7</td>
<td>30.9</td>
<td>31.5</td>
<td>13.0</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Isobutyl (d)</td>
<td>27.4</td>
<td>29.3</td>
<td>29.3</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>t-Butyl (h)</td>
<td>10.7</td>
<td>32.6</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Isopentyl (d)</td>
<td>8.2</td>
<td>34.7</td>
<td>38.8</td>
<td>21.5</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>n-Hexyl (d)</td>
<td>12.3</td>
<td>29.1</td>
<td>37.9</td>
<td>22.8</td>
<td>31.6</td>
<td>13.8</td>
</tr>
<tr>
<td>2-Ethylbutyl (d)</td>
<td>19.2</td>
<td>42.1</td>
<td>31.5</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

(a) Room Temperature.
(b) In ppm based on cyclopentane=25.8 ppm.
(c) 0.3 M based on monomer.
(d) 2 M based on monomer.
(e) Tetramer
(f) Hexamer
(g) Observed as a single peak.
(h) 1 M based on monomer.
### TABLE X

*6Li CHEMICAL SHIFTS OF ALKYL LITHIUM COMPOUNDS IN CYCLOPENTANE (a)*

<table>
<thead>
<tr>
<th>R-Group</th>
<th>Temperature, °C</th>
<th>6Li Chemical Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl (b)</td>
<td>30</td>
<td>1.78 (c) 1.90</td>
</tr>
<tr>
<td></td>
<td>-85</td>
<td>1.72 (d) 1.63 (e)</td>
</tr>
<tr>
<td>n-Propyl (f)</td>
<td>30</td>
<td>1.87 (c) 1.94</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>1.80 (d) 1.72 (e)</td>
</tr>
<tr>
<td>Isopropyl (f)</td>
<td>30</td>
<td>1.10 (c) 1.25</td>
</tr>
<tr>
<td></td>
<td>-85</td>
<td>1.02 (g)</td>
</tr>
<tr>
<td>n-Butyl (f)</td>
<td>30</td>
<td>1.90 (c) 2.06</td>
</tr>
<tr>
<td></td>
<td>-82</td>
<td>1.87 (d) 1.77 (e)</td>
</tr>
<tr>
<td>Isobutyl (f)</td>
<td>30</td>
<td>1.92 (c)</td>
</tr>
<tr>
<td></td>
<td>-70</td>
<td>1.71 (g)</td>
</tr>
<tr>
<td>t-Butyl (h)</td>
<td>30</td>
<td>1.07 (c) 0.86 (g)</td>
</tr>
<tr>
<td></td>
<td>-85</td>
<td>0.86 (g)</td>
</tr>
<tr>
<td>Isopentyl (f)</td>
<td>27</td>
<td>1.90 (c) 2.01</td>
</tr>
<tr>
<td></td>
<td>-75</td>
<td>1.85 (d) 1.76 (e)</td>
</tr>
<tr>
<td>n-Hexyl (f)</td>
<td>30</td>
<td>1.90 (c) 2.00</td>
</tr>
<tr>
<td></td>
<td>-80</td>
<td>1.88 (d) 1.71 (e)</td>
</tr>
<tr>
<td>2-Ethylbutyl (f)</td>
<td>27</td>
<td>1.94 (c) 1.76 (e)</td>
</tr>
<tr>
<td></td>
<td>-87</td>
<td></td>
</tr>
</tbody>
</table>

(a) In ppm based on 1 M LiClO₄ = 0.00 ppm (external reference). No correction has been made for differences in the bulk magnetic susceptibility of the sample and reference.

(b) 0.3 M based on monomer.  
(c) hexamer  
(d) octamer  
(f) 2 M based on monomer.  
(g) tetramer  
(h) 1 M based on monomer.
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