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Study of the Temperature Dependent Dynamic Behavior of Benzylic Lithium Compounds by Nuclear Magnetic Resonance

Dissertation
Presented in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in the Graduate School of the Ohio State University

By
Kevin V. Martin, B.S., M.S.

The Ohio State University
1995

Dissertation Committee:  
Gideon Fraenkel  
Matthew Platz  
John S. Swenton  
Richard Reuning

Approved by  
Gideon Fraenkel  
Adviser  
Department of Chemistry
To my loving wife Joanna
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VITA

November 15, 1963 ............................................................. born - Brooklyn, New York

June, 1983 - August, 1983 ................................................ Research technician trainee
Exxon Research and Engineering Co.
Linden, New Jersey

August, 1985 - May, 1986 ................................................ NMR technician
E. I. DuPont De Nemours and Co.
Wilmington, Delaware

June, 1986 ............................................................................. B.S. in Chemistry
Department of Chemistry
University of Delaware
Newark, Delaware

September, 1986 - September, 1994............................... Teaching or Research Assistant
Department of Chemistry
The Ohio State University
Columbus, Ohio

June, 1989.............................................................................. M.S. in Chemistry
Department of Chemistry
The Ohio State University
Columbus, Ohio

PUBLICATION

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Introduction

Organolithium compounds have proven to be extremely useful and versatile reagents in organic synthesis. It has been shown that their reactivity is dependent upon their structure in solution. Therefore, a study of the structure of organolithium compounds is an important area of investigation in physical organic chemistry.

Calculations have shown that the carbon lithium bond in organolithium compounds is mostly ionic. Both Streitwieser and Schleyer have used theoretical calculations to show that this important bond is between eighty to ninety percent ionic. The small covalent character allows organolithium compounds to be soluble in hydrocarbon solvents. At the same time the mostly ionic character explains why slight changes in solvent polarity or the addition of various ligands lead to differences in the reactivity and structure of organolithium compounds.

Despite the great difficulty in handling organolithiums due to their air and thermal sensitivity, X-ray crystallography has been used to determine the solid state structure of a great many organolithium reagents. Both methyl- and ethylithium crystallized from hydrocarbon solvents have been determined to be tetramers. The lithium atoms are arranged in a tetrahedral fashion with a single alkyl group on each face of the tetramer. This places each carbon atom near three lithium atoms (see figure 1).
On the other hand both cyclohexyl- and (tetramethylcyclopropyl)methylolithium form hexameric aggregates under donor free conditions (see figure 1). In these cases the lithium atoms are arranged on the corners of an octahedron with one alkyl group on each face; each anionic carbon is associated with three lithium atoms.

When methyllithium complexes with tetramethylethylenediamine (TMEDA), it forms a cubic tetramer in which the lithium and carbon atoms assume alternate positions on the points of the cube. Each lithium is also coordinated to one nitrogen on the TMEDA. It is been shown in many cases that lithium prefers to be coordinated to four electron donating species.

Bicyclobutylithium is a dimer in the presence of TMEDA (see figure 2). In this case the lithium atoms are coordinated to both carbanionic sites and bis-chelated to the TMEDA. It has been shown that α-lithiated 2,6-dimethylpyridine also crystallizes as a dimer in the presence of TMEDA (see figure 2). The aggregate is an eight membered ring with the lithium atoms coordinated to the nitrogen of one pyridine unit, the α-carbon of the other unit, and bis-chelated to the TMEDA.
Benzyl lithium crystallizes as a polymer in the presence of 1,4-diazabicyclo(2.2.2)octane (DABCO). The lithium is coordinated to two nitrogen atoms on two different DABCO molecules and the benzyllic carbanion in a $\eta^3$ manner (see figure 3). The lithium is extremely close to all three carbon atoms. Allyllithium also forms a polymer when it is complexed with TMEDA (see figure 4). The lithium is coordinated to the two TMEDA nitrogen atoms and the terminal carbon atoms of two different allyl groups. On the other hand allyllithium forms a monomer when complexed tridentately with pentamethyldiethylenetriamine (PMDTA).

Figure 2$^5$. Crystal structures of bicyclobutyl lithium (left) $\alpha$-lithiated 2,6-dimethylpyridine (right) complexed with TMEDA.

Figure 3$^5$. Bonding of benzyl lithium in a polymeric crystal.
Phenyllithium crystallizes in three different structures depending on the chelating agent. When diethyl ether is used, it forms a tetrameric etherate. When either TMEDA or PMDTA are added as ligands, a dimer or monomer are formed respectively. In each case the total coordination number of the lithium is three, but the number of carbon atoms coordinated to lithium decreases from three to two to one.

Organolithium compounds can crystallize in a wide variety of different structures. The structure and aggregation are dependent not only on the carbanion but also the solvent and ligand. While the X-ray crystal structure provides clues to the solution structures and aggregation of organolithium compounds, it does not prove what they are. It is therefore necessary to use other tools available to chemists to determine the nature of organolithium compounds in solution.

One method is cryoscopy of organolithium solutions. A solution of t-butyllithium in tetrahydrofuran was found to be a monomer at -108 °C. A solution of s-butyllithium in tetrahydrofuran has an aggregation number of 1.12; this corresponds to a ratio of 88% monomer and 12% dimer. Under similar conditions n-butyllithium consists of a mixture of 39% tetramer and 61% dimer.

Nuclear magnetic resonance (NMR) has been widely used to determine the aggregation of organolithium compounds in solution. The method is based on the existence of scalar coupling between $^{13}$C and directly bonded lithium seen in a number of organolithium compounds.
at low temperatures (ca. 150 K). While $^7\text{Li}$ is the major (98%) naturally occurring isotope, in
general it cannot be used for this purpose since it relaxes too quickly via the electric quadrupole
interaction. However $^6\text{Li}$ relaxes quite slowly so $^1J(^{13}\text{C}, ^6\text{Li})$ is often observed. The multiplicity of
the resonance for $^{13}\text{C}$ directly bonded to $^6\text{Li}$ can thus be used to determine the
number of $^6\text{Li}$ atoms bonded to that $^{13}\text{C}$ atom. The mode of aggregation can then be identified
from this information (see figure 5).

**MONOMER**

$^{13}\text{C}^6\text{Li}$

$\text{C}^6\text{Li}$

**DIMER**

$^{13}\text{C}^6\text{Li}_2$

**TETRAMER**

$^{13}\text{C}^6\text{Li}_3$

Figure 5. Expected $^{13}\text{C}$ multiplicities of organolithium aggregates.
The Fraenkel group has used this effect to measure the aggregation state of many organolithium complexes. One of the earliest studies\(^7\) showed that s-butyllithium in pentane is a mixture of hexamers and tetramers. The same group has shown that propyllithium in cyclopentane is a mixture of hexamers, octamers and three kinds of nonamers\(^8\).

The aggregation of neopentylolithium depends on the solvent, temperature, and ligand\(^9\). In diethyl ether solution neopentylolithium only forms dimers. A one to one mixture of neopentylolithium and diethyl ether in toluene forms a mixture of tetramers and dimers. In tetrahydrofuran a mixture of dimers and monomers is observed. The dimer:monomer ratio decreases as the temperature goes down. While the addition of TMEDA to a tetrahydrofuran solution does not give rise to the exclusive formation of monomers, the addition of a triamine such as PMDTA will do so.

After studying the \(^{13}\text{C}\) NMR spectra of thirteen different lithiated species, Seebach\(^10\) observed that the \((^{13}\text{C}, \, ^6\text{Li})\) coupling constant could be divided into three categories: 17 Hz. for monomers; 8-9 Hz. for dimers; and no detectable \((^{13}\text{C}, \, ^6\text{Li})\) coupling for contact ion pairs. In a study\(^3\) of the \((^{13}\text{C}, \, ^6\text{Li})\) coupling constants of nearly thirty organolithium compounds, Bauer and Schleyer came to the empirical conclusion that \(J \approx 17/n\) (where \(n\) is the aggregation number). This formula applies to a wide variety of \((\text{RLi})_n\) aggregates with different hybridized carbons (i.e. alkyl, vinyl, to acetylenic) and is independent of the solvation or complexation to either ether or amine ligands. This stands in contrast for what has been observed for the coupling of other NMR active isotopes. Both quantum mechanical calculations\(^11\) and empirical observations\(^12\) show that the coupling constant between two atoms depends on the hybridization of the atoms. Ramsey\(^11a\) showed that the Hamiltonian for nuclear spin-spin coupling can be broken into four interactions: 1) Fermi contact; 2) orbital dipole; 3) nuclear spin dipole; and 4) electron spin dipole. Ramsey\(^11a\) and others\(^12\) have shown that the Fermi contact term makes up approximately ninety percent of the total coupling.
Using this information Grant with Karplus and Litchman derived the following relationship:

\[ {^1}J(^{13}C, ^1H) \propto \gamma_{C\gamma H}(\Delta)(N)^{2}(\alpha)^{2}(Z)^{3} \]  \hspace{1cm} (1)

where the \( \gamma \)'s are the gyromagnetic ratios, \( \Delta \) is the average excitation energy, \( N \) is the bond normalization constant, \( \alpha \) is a parameter of the molecular orbital (which is a combination of the two atomic orbitals) that is directly proportional to the degree of "s" character, and \( Z \) represents the effective nuclear charge. Since \( \Delta, N, \) and \( Z \) are dependent on the degree of covalency between the two atoms, they remain fairly constant for all carbon hydrogen bonds. The \( {^1}J(^{13}C, ^1H) \) therefore depends solely on the degree of s-character associated with the carbon atomic orbital because the s-character for the hydrogen atomic orbital remains constant.

In a similar fashion the \( {^1}J(^{13}C, ^6Li) \) coupling constant should also depend on the "s" character of the carbon atom. The \( {^1}J(^{13}C, ^6Li) \) should therefore vary among different organic moieties, but this has been shown to be untrue. Recently Bauer proposed an explanation for this enigma: "on going from aliphatic to acetylenic organolithium compounds, the s-character for the C, Li bond increases in the same way as is found for C, H bonds. However, whereas the covalency of a C, H bond is virtually independent of the C-hybridization, the covalent character of the C, Li bond decreases on going from aliphatic to acetylenic species. The product (s-character \( \times \) covalent bond order) is approximately constant for C, Li bonds, which explains the observed insensitivity of \( {^1}J(^{13}C, ^6Li) \) on carbon hybridization."

Soon after this Reich observed that the \( {^{12}}J(^{13}C, ^6Li) \) coupling constant for organolithium monomers that are stabilized by either silicon or sulfur is approximately 7 Hz. The silicon and sulfur affect the carbon atomic orbital in a different manner than do changes in hybridization. Thus the \( {^{12}}J(^{13}C, ^6Li) \) coupling constant is affected by changes in the type of carbanion which gives rise to a continuum in the values of \( {^{12}}J(^{13}C, ^6Li) \) coupling constants.

Nuclear magnetic resonance has been used in other ways to study the bonding in compounds. Fraenkel found a linear relationship between \(^1\)H shift and electron density for aromatic compounds. In a similar fashion Spiescke and Schneider then correlated \(^{13}\)C shift
with electron density for aromatic compounds. O'Brien, Hart, and Russell\textsuperscript{19} were able to extend this correlation to all \( \text{sp}^2 \) carbons in planar, conjugated systems. They derived the following equation:

\[
\delta^{(13\text{C})}_{\text{average}} = 289.5 - 156.3 \times \rho_{\text{average}}
\]  

(2)

where \( \rho_{\text{average}} \) is the average \( \pi \) electron density. This equation can only be used for planar, unbridged, all-carbon \( \pi \) systems with hydrogen substituents. The average chemical shift must be adjusted when alkyl substituents are added. Fraenkel and Tokuhiro\textsuperscript{20} have explained these effects using Ramsey's theory for chemical shifts.

Nuclear magnetic resonance line shape analysis has been used to study both inter- and intra-molecular motion in organolithium compounds. The fluxional exchange\textsuperscript{21} of tert-butyllithium aggregates was studied by observing the changes in the splitting patterns due to the \((^{13}\text{C}, ^6\text{Li})\) coupling. Subramanian\textsuperscript{22} used this same method to study the carbon lithium bond exchange between monomers of 2,4,6-tri-tert-butylphenyllithium.

Geckle\textsuperscript{23} used line shape analysis to study the barrier to rotation about the ring benzyl carbon in substituted benzyllithium compounds. Winchester\textsuperscript{24} and Cabral\textsuperscript{25} have measured the barrier to rotation within allylic moieties using this method (see figure 6). In a similar fashion Subramanian\textsuperscript{22} measured the rate of rotation around the carbon lithium bond in monomeric 2,4,6-trimethylphenyllithium complexed to PMDTA.
Figure 6. Summary of the activation parameters for reorientation of ions within the pendent ligand of [1-[[bis(2-methoxyethyl)amino]methyl]dimethylsilyl]allyl]lithium.
In systems which may be regarded as contact ion pairs, $^{13}$C-$^6$Li coupling has not been observed; hence siting of the lithium and the dynamics of carbon lithium bond exchange cannot be directly investigated. However, the observation of the NMR of complexed ligands has established that several organolithium ion pairs exist as unique single structures at low temperature. At approximately 150 K these structures are dynamically frozen relative to the NMR time scale. Signal averaging effects seen in the $^{13}$C resonances of these compounds have been interpreted to demonstrate the dynamics of reorientation of ions within the ion pairs.

Winchester$^{24}$ studied the rotational behavior of PMDTA in a complex with [1-(trimethylsilyl)allyl]lithium and TMEDA in a complex with exo,exo-[1,3-bis(trimethylsilyl)allyl]lithium. Cabral$^{25}$ studied the reorientation of TMEDA in a complex with (1,1,3,3-tetramethylallyl)lithium and the rotation of the pendent ligand of [1-[[[bis(2-methoxyethyl)amino]methyl]dimethylsilyl]allyl]lithium (see figure 6). Reorientation of ions within ion pairs was shown to be surprisingly slow with a negligible entropy of activation. The enthalpy of activation of all these motions was found to be approximately seven kcal/mole for the reorientation of the ligand.

The purpose of this thesis is to study the nature of bonding within an organolithium compound and the dynamic behavior of the bonding between the anionic carbon and the lithium cation. The nature of the ionic character in conjugated systems will be investigated. Through the use of NMR line shape analysis, the dynamics of carbon lithium exchange and both ion and ligand reorientation in complexed organolithium compounds will be uncovered.
Results and Discussion

The proposed area of study was to see whether or not the effects observed for allylic lithium compounds are general. This would be accomplished by making a series of benzylic lithium compounds and then measure the activation barriers for the various motions that should be observed. Benzylic lithium compounds with either an external or pendant ligand would be studied.

The first compound studied was (α-trimethylsilyl)benzyllithium complexed first with tetramethylene diamine (TMEDA) 1 and then (bis-(2-methoxyethyl))methylamine 2. The synthesis of these two compounds is in figure 7.

The chemical shift data (see figure 8) indicate that the negative charge is delocalized over the aromatic ring. At lower temperatures the ortho and meta resonances each split into 1:1 doublets. The shifts for the TMEDA resonances of 1 became broad, but never separated into two different peaks. A DEPT experiment was carried out for 2 (see figure 9) in order to confirm the assignments of the chemical shifts for both this compound and other compounds that were studied subsequently.
Figure 7. Synthesis of (α-trimethylsilyl)benzyl lithium.
Figure 8. $^{13}$C NMR spectra of compound 1 in diethyl ether-$d_{10}$ at 250 K.
Figure 9. $^{13}$C NMR DEPT of compound 2 in THF-$d_8$ at 303 K. Shift and multiplicity's of DEPT are marked on compound.
Since it was not possible to study the dynamic behavior of the above compounds, a benzylic lithium with a pendant ligand was the next target compound. Its synthesis is depicted below.

![Chemical reaction diagram](image)

**Figure 10.** Synthesis of benzyllithium, 3, with a pendant ligand.

The NMR data for 3 at 230 K (figure 11) show that the charge is delocalized over the conjugated system. As evidenced by the large downfield of the ortho and para carbon chemical shifts, the negative charge is heavily located on these carbons. It is assumed that the compound assumes the indicated folded structure that is analogous to what was seen by Cabral\textsuperscript{25b}. 
Figure 11. $^{13}$C NMR of 3 in THF-d$_8$ at 230 K.
At 230 K the meta and ortho carbons have each give rise to equal doublets. As the temperature increases, the meta and meta' resonances progressively coalesce and then average to one peak. The ortho and ortho' lines behave in the same way though over a larger temperature range due to the fact that there is a larger difference in their chemical shifts. While the shifts for the ligand broadened at lower temperatures, they did not separate into different peaks at 220 K. Compound 3 was not soluble in THF at lower temperatures, so it was not possible to study the ligand in this system.

The benzylic carbon resonance showed some unexpected temperature dependence. The benzyllithium is supposed to be an ion pair, and certainly no covalency between carbon and lithium with associated "s" character would be expected. At 295 K the benzyl $^{13}$C resonance is indeed a sharp singlet with a width of 3 Hz. However on cooling to 250 K the resonance progressively decoalesces into an equally spaced 1:1:1:1 quartet with a splitting of 7.4 Hz. This implies that there is a real coupling between the $^{13}$C and $^{7}$Li ($I=3/2$). To confirm this hypothesis the compound was then made with butyllithium that was prepared with lithium that was enriched (96%) in $^{6}$Li. The benzyl $^{13}$C resonance was a singlet at 295 K with a width of 2 Hz. The peak decoalesced to a 1:1:1 triplet by 250 K with a splitting of 2.8 Hz. The ratio of the two coupling constants, 2.6, agrees with the ratio of the gyromagnetic constants, 2.641, for the two isotopes of lithium. To confirm that the multiplets were due to coupling to lithium, the $^{6}$Li resonance was decoupled at 250 K; the $^{13}$C was then a sharp singlet with a width of 2.6 Hz. These results establish detectable covalence to the interaction between the benzyl carbon and lithium; further quantum mechanic studies would be needed to establish the degree of covalency.

All of this temperature dependent behavior reflects dynamic phenomena. These can be investigated by the use of line shape analysis. Both the meta-meta' and ortho-ortho' averaging are most likely due to rotation around the ipso-benzyl partial bond. The resulting exchange of shifts is written in the following manner:

$$AB \leftrightarrow BA$$ (3)
The NMR line shape can be calculated as an uncoupled two site, equally populated, 1/2 spin exchanging system at equilibrium. The density matrix method of calculating NMR line shapes as described by Kaplan and Fraenkel\textsuperscript{27} can be used to calculate the rates of exchange at the various temperatures. The density matrix equation to be used is given in equation 4.

\[
\begin{bmatrix}
  i2\pi(\Delta\nu_x) - T^{-1} - k & k \\
  k & i2\pi(\Delta\nu_y) - T^{-1} - k
\end{bmatrix}
\begin{bmatrix}
  \rho_1 \\
  \rho_2
\end{bmatrix} = iC
\begin{bmatrix}
  1 \\
  1
\end{bmatrix}
\] (4)

where \(\Delta\nu's\) are the relative shifts in the rotating frame at the two sites in hertz, \(T^{-1}\) is the line width at slow exchange, \(k\) is the first order rate constant, and \(C\) is an arbitrary proportionality constant. All but the rate constants are known. By using the measured values for the \(\Delta\nu's\) and \(T^{-1}\), and trial values for \(k\) the equations are solved as a function of frequency, \(v\), for

\[
\Delta\nu_i = v - \nu_i
\] (5)

the unknown elements of the density matrix \(\rho_1\) and \(\rho_2\) as defined in equations 6 and 7.

\[
\rho_1 = \langle \alpha | \rho^1 | \beta \rangle
\] (6)

\[
\rho_2 = \langle \alpha | \rho^2 | \beta \rangle
\] (7)

The NMR absorption is then calculated from equation 8.

\[
\text{Abs}(v) = -\text{Im}(\rho_1 + \rho_2)
\] (8)

The rate constants were then adjusted in order to match the calculated line shapes to the experimental spectra. The fitted lineshapes are shown in figures 12 and 13.
Figure 12. $^{13}$C NMR lineshapes for meta carbons of 3 in THF: left) experimental spectra at different temperatures; right) line shapes calculated with rate constants to match spectra.
Figure 12. Continued from previous page.
Figure 13. $^{13}$C NMR lineshapes for ortho carbons of 3 in THF: left) experimental spectra at different temperatures; right) line shapes calculated with rate constants to match spectra.
Figure 13. Continued from the previous page.
The line shapes are due to rotation about the ipso benzyl bond. The activation parameters can be calculated by the use of the Eyring equation.

\[ k = \frac{k_B T}{h} e^{-\frac{-\Delta G^*}{RT}} \]

(9)

where \( k \) is the rate constant, \( T \) is the temperature, \( k_B \) is Boltzman's constant \((1.381 \times 10^{-23} \text{ J/K})\), \( h \) is Planck's constant \((6.626 \times 10^{-34} \text{ J-s})\), \( R \) is the gas constant \((1.987 \text{ cal/mole-K})\), and \( \Delta G^* \) is the energy of activation. After substituting for \( \Delta G^* \), and some rearranging, the Eyring equation becomes:

\[ \ln \left( \frac{k}{T} \right) = \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R} \left( \frac{1}{T} \right) \]

(10)

where \( \Delta S^* \) is the entropy of activation, and \( \Delta H^* \) is the enthalpy of activation. A plot of \( \ln (k/T) \) vs. \( 1/T \) yields a slope of \( -\Delta H^*/R \) and an intercept of \( \ln(k_B/T) + \Delta S^*/R \). The plots for the data in figure 2 and 3 are shown in tables 1 and 2 and figures 14 and 15 respectively.
Table 1. Signal averaging for the meta carbons of compound 3.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>1/T</th>
<th>k s⁻¹</th>
<th>ln(k/T)</th>
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<tr>
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<td>0.00435</td>
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<td>-4.34</td>
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<tr>
<td>240</td>
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<td>-3.56</td>
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<tr>
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<td>28</td>
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<tr>
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Line Width 2.0 Hz.
Chemical Shifts 9182 Hz., 8863 Hz.
Concentration 0.073 M

**Regression Output**

Constant 30.27
Std Err of Y Est. 0.28
R Squared 0.98
No. of Observations 8.00
Degrees of Freedom 6.00

Slope -8062.29
Std Err of Slope 427.26

**Activation Parameters**

Entropy of Activation 11.2 eu
Enthalpy of Activation 16.0 kcal/mole
Table 2. Signal averaging for the ortho carbons of compound 3.

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<th>k s⁻¹</th>
<th>ln(k/T)</th>
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<td>1600</td>
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<tr>
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<td>0.00328</td>
<td>20000</td>
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<td>40000</td>
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Line Width 2.0 Hz.
Chemical Shifts 9182 Hz., 8863 Hz.
Concentration 0.073 M

Regression Output

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<tr>
<td>R Squared</td>
<td>0.99</td>
</tr>
<tr>
<td>No. of Observations</td>
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</tr>
<tr>
<td>Degrees of Freedom</td>
<td>9.00</td>
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</table>

Slope -8130.22
Std Err of Slope 329.15

Activation Parameters

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<th>Entropy of Activation</th>
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</thead>
<tbody>
<tr>
<td>Enthalpy of Activation</td>
<td>16.2 kcal/mole</td>
</tr>
</tbody>
</table>
Figure 14. Eyring plot for the signal averaging of the meta carbons of compound 3.
Figure 15. Eyring plot for the signal averaging of the ortho carbons of compound 3.

The numbers for the entropy (12 eu) and enthalpy (16 kcal/mole) are similar to those seen by Cabral\textsuperscript{250} for the exo-endo exchange seen for in the allylic system. These numbers are consistent for rotation around a partial double bond.

The more interesting effect observed is the coupling between the benzylic carbon and the \(^{6}\text{Li}\) lithium (the \(^{7}\text{Li}\) was studied because it relaxes slower than \(^{7}\text{Li}\)). The benzylic resonance shows a triplet at low temperatures (240 K) and a singlet at high temperatures.
(305 K). The coupling between the two atoms is averaged when the lithium is exchanged between monomers because the $^6\text{Li}$ on the $^{13}\text{C}$ may not have the same spin state as $^6\text{Li}^*$. The exchange step and associated spin states are given in equation 11.

$$^{13}\text{C}^6\text{Li}^* + ^{12}\text{C}^6\text{Li} \xrightarrow{k_2} ^{13}\text{C}^6\text{Li} + ^{12}\text{C}^6\text{Li}^*$$

$\phi \alpha l \ m \ \alpha m \ l$

$\phi \beta l \ m \ \beta m \ l$

where $\phi$ is the spin product function, $\alpha$ and $\beta$ are the spin states of $^{13}\text{C}$, and $l$ and $m$ are the spin states of $^6\text{Li}$. The elements of the density matrix needed to calculate the $^{13}\text{C}$ line shape are diagonal in lithium and off diagonal ($\Delta m = \pm 1$) in $^{13}\text{C}$. The density matrix equation to be used is given in equation 12.

$$
\begin{bmatrix}
12\pi(\Delta \nu - J) - T^{-1} - \frac{2}{3}k & \frac{1}{3}k & 1 - \frac{k}{3} & \frac{1}{3}k \\
\frac{1}{3}k & i2\pi(\Delta \nu) - T^{-1} - \frac{2}{3}k & \frac{1}{3}k & 1 - \frac{k}{3} \\
\frac{1}{3}k & \frac{1}{3}k & i2\pi(\Delta \nu + J) - T^{-1} - \frac{2}{3}k & 1 - \frac{k}{3} \\
\frac{1}{3}k & 1 - \frac{k}{3} & i2\pi(\Delta \nu + J) - T^{-1} - \frac{2}{3}k & 1 - \frac{k}{3}
\end{bmatrix}
\begin{bmatrix}
\rho_1 \\
\rho_2 \\
\rho_3 \\
\rho_4
\end{bmatrix} = iC
\begin{bmatrix}
1 \\
1 \\
1 \\
1
\end{bmatrix}
$$

(12)

where $\Delta \nu$ is the frequency in the rotating frame, $J$ is the $^{13}\text{C}, ^6\text{Li}$ coupling constant, $k$ is the first order rate constant, $T^{-1}$ is the line width and C is an arbitrary proportionality constant. All but the rate constants are known. By using the measured value for $\Delta \nu$ and $T^{-1}$, and trial values for $k$ the equations are solved as a function of frequency, $\nu$, for

$$\Delta \nu_i = \nu - \nu_i$$

(13)

the unknown elements of the density matrix are defined as follows:

$$\rho_1 = \rho_{\beta-\alpha-}$$

(14)

$$\rho_2 = \rho_{\beta\alpha\alpha0}$$

(15)

$$\rho_3 = \rho_{\beta+,\alpha+}$$

(16)
The NMR absorption is then calculated from equation 17.

\[ \text{Abs}(v) = -\text{Im} \ (\rho_1 + \rho_2 + \rho_3) \quad (17) \]

The rate constants were then adjusted in order to match the calculated line shapes to the experimental spectra. The fitted lineshapes are shown in figure 16.

The rate constants were then plotted using the Eyring equation. The results are shown in table 3 and figure 17. It would be expected that the exchange of the lithium atoms between monomers would be bimolecular; the large entropy of activation (-34.4 eu) indicates that this is true. The small enthalpy of activation (5.6 kcal/mole) show that the carbon lithium bond is not very strong. While this type of exchange has been previously studied (see introduction), this is the first case where a delocalized anion has displayed \(^{13}\text{C}, ^{6}\text{Li}\) coupling.

In an attempt to determine the location of the lithium, a nuclear Overhauser experiment was performed on compound 3. This was done by irradiating the protons and measuring the enhancement of the lithium signal. A summary of the results is shown in figure 18. As expected the lithium is closest to the ligand and benzylic carbons. Also the lithium is closer to the silyl methyl carbons than the aromatic carbons. This experiment supports the view that the lithium is above the plane of the aromatic ring.
Figure 16. $^{13}$C NMR lineshapes for benzylic carbon of 3 in THF: left) experimental spectra at different temperatures; right) line shapes calculated with rate constants to match spectra.
Figure 16. Continued from the previous page.
Table 3. Signal averaging for the benzyl carbon resonance of compound 3.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>1/T</th>
<th>k (s⁻¹)</th>
<th>ln(k/T)</th>
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</thead>
<tbody>
<tr>
<td>240</td>
<td>0.00417</td>
<td>3.0</td>
<td>-4.38</td>
</tr>
<tr>
<td>250</td>
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<tr>
<td>255</td>
<td>0.00392</td>
<td>5.6</td>
<td>-3.82</td>
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<tr>
<td>260</td>
<td>0.00385</td>
<td>10.5</td>
<td>-3.21</td>
</tr>
<tr>
<td>265</td>
<td>0.00377</td>
<td>11.5</td>
<td>-3.14</td>
</tr>
<tr>
<td>270</td>
<td>0.00370</td>
<td>12.8</td>
<td>-3.05</td>
</tr>
<tr>
<td>280</td>
<td>0.00357</td>
<td>18.0</td>
<td>-2.74</td>
</tr>
<tr>
<td>285</td>
<td>0.00351</td>
<td>25.0</td>
<td>-2.43</td>
</tr>
<tr>
<td>294</td>
<td>0.00340</td>
<td>35.0</td>
<td>-2.13</td>
</tr>
<tr>
<td>300</td>
<td>0.00333</td>
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</tr>
<tr>
<td>305</td>
<td>0.00328</td>
<td>43.0</td>
<td>-1.96</td>
</tr>
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</table>

Line Width 2.0 Hz.
Chemical Shift 2768 Hz.
Coupling Constant 2.8 Hz.
Concentration 0.075 M

Regression Output

Constant 7.32
Std Err of Y Est 0.12
R Squared 0.98
No. of Observations 11.00
Degrees of Freedom 9.00
Slope -2799.32
Std Err of Slope 128.18

Activation Parameters

Entropy of Activation -34.4 eu
Enthalpy of Activation 5.6 kcal/mole
Figure 17. Eyring plot for the benzyl carbon resonance of compound 3.
Figure 18. Summary of the $\{^1H,^6Li\}$ NOE experiment of compound 3.

At the lowest temperature studied (220 K), the resonances for the ligand carbons and the silyl methyl groups of compound 3 broadened, but never separated into distinct doublets. It was not possible to study this compound at lower temperatures because it came out of solution at 200 K. It was hoped that by adding an alkyl substituent to the aromatic ring, the new compound would be more soluble. The group could not have a $\alpha$ hydrogen as this would be nearly as acidic as the benzylic hydrogen next to the silyl group. It was decided that a tert-butyl group would be an appropriate substituent to add. The synthesis of the new benzylic lithium compound is shown in figure 19.
Figure 19. Synthesis of compound 4.

The $^{13}$C NMR data (figure 20) for compound 4 at 180 K is similar to the low temperature spectrum of compound 3; but at this lower temperature the silyl methyl carbons are split into a doublet, and two of the ligand carbons (NCH$_2$ and OCH$_3$) are also split into doublets. The resonance for the other ligand carbon (OCH$_2$) broadened at lower temperatures, but never separated into two peaks. The resonance for the carbon connecting the ligand to the silyl group remained a sharp line throughout the temperatures studied.
Figure 20. $^{13}$C NMR of compound 4 in THF-d$_8$ at 180 K.
At 210 K, the ortho carbons give rise to an equal doublet. As the temperature increases, the ortho and ortho' resonances progressively coalesce and then average to one peak. The meta and meta' lines behave in a similar fashion over a smaller temperature range. Since the line shape analysis of the ortho and meta carbons gave essentially the same results for compound 3, only the ortho resonance was analyzed for compound 4. Equations 3 to 8 were once again used to calculate the line shapes; the fitted line shapes are given in figure 21.

The rate constants (table 4) were plotted using the Eyring equation (figure 22). The numbers for the entropy of activation (6.6 eu) and enthalpy of activation (14.0 kcal/mole) are similar to those seen for compound 3. These numbers agree with those observed by others. Geckle\textsuperscript{23} had measured an entropy of activation (5.2 eu) and enthalpy of activation (18.5 kcal/mole) for rotation around the ipso benzyl bond of a similar carbanion with two alpha alkyl groups and TMEDA as the ligand. Cabral\textsuperscript{25b} measured an entropy of activation (12 eu) and an enthalpy of activation (16.4 kcal/mole) for (1-silylallyl)lithium with the same pendant ligand as compounds 3 and 4.

At 180 K, the $^{13}$C resonance for the silyl methyl carbons give rise to a broad doublet. As the temperature increases, the silyl lines progressively coalesce and then give rise to a sharp singlet. The NMR line shape can also be calculated as an uncoupled two site, equally populated, 1/2 spin exchanging system at equilibrium. Equations 3 to 8 can be used to calculate the line shapes. Because the exchange does not slow down sufficiently at the lowest temperature (180 K) at which high resolution spectra could be obtained, the relative shifts had to be estimated by placing them a little outside of the observed splitting. The fitted line shapes are shown in figure 23.
Figure 21. $^{13}$C NMR lineshapes for the ortho carbons of 4 in THF: left) experimental spectra at different temperatures; right) line shapes calculated with rate constants to match spectra.
Figure 21. Continued from previous page.
Table 4. Signal averaging for the ortho carbons of compound 4.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>1/T</th>
<th>k</th>
<th>ln(k/T)</th>
</tr>
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<tbody>
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<td>-3.40</td>
</tr>
<tr>
<td>220</td>
<td>0.00455</td>
<td>8</td>
<td>-3.31</td>
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Line Width: 2.0 Hz.
Chemical Shifts: 9145 Hz., 8817 Hz.
Concentration: 0.073 M

Regression Output

- Constant: 25.33
- Std Err of Y Est: 0.74
- R Squared: 0.96
- No. of Observations: 11.00
- Degrees of Freedom: 9.00
- Slope: -6336.89
- Std Err of Slope: 450.13

Activation Parameters

- Entropy of Activation: 6.6 eu
- Enthalpy of Activation: 14.0 kcal/mole
Figure 22. Eyring plot for the signal averaging of the ortho carbons of compound 4.
(The starred point was removed from the regression analysis.)
Figure 23. $^{13}$C NMR lineshapes for the silyl carbons of 4 in THF: left) experimental spectra at different temperatures; right) line shapes calculated with rate constants to match spectra.
Figure 23. Continued from previous page.
Table 5. Signal averaging for the silyl methyl carbons of compound 4.

<table>
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<tr>
<th>Temperature (K)</th>
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Line Width 2.0 Hz.
Chemical Shifts 85 Hz., -157 Hz.
Concentration 0.073 M

Regression Output

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</table>

Slope -3233.64
Std Err of Slope 47.61

Activation Parameters

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Entropy of Activation</td>
<td>-14.6 eu</td>
</tr>
<tr>
<td>Enthalpy of Activation</td>
<td>6.4 kcal/mole</td>
</tr>
</tbody>
</table>
Figure 24. Eyring plot for the signal averaging of the silyl carbons of compound 4.
The rate constants (table 5) were plotted using the Eyring equation (figure 24). The numbers for the entropy of activation (-14.6 eu) and enthalpy of activation (6.4 kcal/mole) are similar to those seen by Cabral\textsuperscript{25b} for the rotation of the ligand around the allylic moiety. Two of the ligand carbon shifts vary with temperature. At temperatures down to 250 K, the resonances for the ligand carbons give rise to sharp singlets. At lower temperatures the resonances progressively de-coalesce. At 180 K the resonances for the NCH\textsubscript{2} and OCH\text subscripts{3} carbons give rise to two broad doublets that overlap slightly. Since the peaks overlap, the resulting exchange has to be written in the following manner:

\[
\text{ABCD} \rightleftharpoons \text{BADC} \tag{18}
\]

The NMR line shape can be calculated as an uncoupled four site, equally populated, 1/2 spin exchanging system at equilibrium. The intensities of the methoxy peaks were increased by 20\% relative to the NCH\textsubscript{2} peaks due to the increased NOE effect of the extra hydrogen. The density matrix equation that was used is given in equation 19.

\[
\begin{bmatrix}
i2\pi(\Delta\nu_w) - T^{-1} - k_1 & k_1 & 0 & 0 \\
k_1 & i2\pi(\Delta\nu_x) - T^{-1} - k_1 & 0 & 0 \\
0 & 0 & i2\pi(\Delta\nu_y) - T^{-1} - k_2 & k_2 \\
0 & 0 & k_2 & i2\pi(\Delta\nu_z) - T^{-1} - k_2
\end{bmatrix}
\]

\[
\begin{bmatrix}
\rho_1 \\
\rho_2 \\
\rho_3 \\
\rho_4
\end{bmatrix}
\ast
\begin{bmatrix}
1 \\
1 \\
1 \\
1
\end{bmatrix}
= iC
\]

where the variables are the same as those defined for equation 4. The equations are solved as a function of frequency, \(\nu\), where
\[ \Delta v_i = v - v_i \]  

and the unknown elements of the density matrix \( \rho_1 \) to \( \rho_4 \) are defined in equations 21 to 24.

\[ \rho_1 = \langle \alpha | \rho^1 | \beta \rangle \]  
\[ \rho_2 = \langle \alpha | \rho^2 | \beta \rangle \]  
\[ \rho_3 = \langle \alpha | \rho^3 | \beta \rangle \]  
\[ \rho_4 = \langle \alpha | \rho^4 | \beta \rangle \]

The NMR absorption is then calculated from equation 25.

\[ \text{Abs}(\nu) = -\text{Im}(\rho_1 + \rho_2 + \rho_3 + \rho_4) \]

Because the rate of exchange is still slightly fast at 180 K, and the middle peaks overlap slightly, the relative shifts were taken from a 125 MHz $^{13}$C NMR spectrum. The rate constants were then adjusted in order to match the calculated line shapes to the experimental spectra. The two rate constants, \( k_1 \) and \( k_2 \), should be the same at a given temperature, but it was not possible to calculate proper line shapes with this conditions. Therefore, the line shapes were calculated with different rate constants. The fitted lineshapes are shown in figure 25.

The Eyring plot for these data (table 6) is shown in figure 26. The average entropy of activation (-13.0 eu) and enthalpy of activation (6.7 kcal/mole) are similar to those for the averaging of the silyl methyl carbons and those seen by Cabral$^{25b}$ for the exchange of the same ligand around the allylic moiety. At this point it can be safe to assume that these line shape changes are due to rotation of the lithium bound to the ligand around the benzyl-silyl bond.
<table>
<thead>
<tr>
<th>T (K)</th>
<th>Experimental Spectrum</th>
<th>Calculated Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td><img src="image1" alt="Experimental Spectrum" /></td>
<td><img src="image2" alt="Calculated Spectrum" /></td>
</tr>
<tr>
<td></td>
<td>OCH$_3$ NCH$_2$</td>
<td>$k_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(OCH$_3$) s$^{-1}$</td>
</tr>
<tr>
<td>250</td>
<td><img src="image3" alt="Experimental Spectrum" /></td>
<td><img src="image4" alt="Calculated Spectrum" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30000</td>
</tr>
<tr>
<td>240</td>
<td><img src="image5" alt="Experimental Spectrum" /></td>
<td><img src="image6" alt="Calculated Spectrum" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>14000</td>
</tr>
<tr>
<td>230</td>
<td><img src="image7" alt="Experimental Spectrum" /></td>
<td><img src="image8" alt="Calculated Spectrum" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9000</td>
</tr>
<tr>
<td>220</td>
<td><img src="image9" alt="Experimental Spectrum" /></td>
<td><img src="image10" alt="Calculated Spectrum" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4800</td>
</tr>
<tr>
<td>210</td>
<td><img src="image11" alt="Experimental Spectrum" /></td>
<td><img src="image12" alt="Calculated Spectrum" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2300</td>
</tr>
<tr>
<td>200</td>
<td><img src="image13" alt="Experimental Spectrum" /></td>
<td><img src="image14" alt="Calculated Spectrum" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td>850</td>
</tr>
</tbody>
</table>

Figure 25. $^{13}$C NMR lineshapes for the ligand carbons of compound 4 in THF: left) experimental spectra at different temperatures; right) line shapes calculated with rate constants to match spectra.
Figure 25. Continued from previous page.
Table 6. Signal averaging for the ligand carbons of compound 4.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>1/T</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>ln($k_1/T$)</th>
<th>$k_2$ (s$^{-1}$)</th>
<th>ln($k_2/T$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.00556</td>
<td>70</td>
<td>-0.94</td>
<td>110</td>
<td>-0.49</td>
</tr>
<tr>
<td>185</td>
<td>0.00541</td>
<td>150</td>
<td>-0.21</td>
<td>200</td>
<td>0.08</td>
</tr>
<tr>
<td>190</td>
<td>0.00528</td>
<td>210</td>
<td>0.10</td>
<td>320</td>
<td>0.52</td>
</tr>
<tr>
<td>195</td>
<td>0.00513</td>
<td>560</td>
<td>1.05</td>
<td>730</td>
<td>1.32</td>
</tr>
<tr>
<td>200</td>
<td>0.00500</td>
<td>850</td>
<td>1.45</td>
<td>1100</td>
<td>1.70</td>
</tr>
<tr>
<td>210</td>
<td>0.00476</td>
<td>2300</td>
<td>2.39</td>
<td>2600</td>
<td>2.52</td>
</tr>
<tr>
<td>220</td>
<td>0.00455</td>
<td>4800</td>
<td>3.08</td>
<td>5500</td>
<td>3.22</td>
</tr>
<tr>
<td>230</td>
<td>0.00435</td>
<td>9000</td>
<td>3.67</td>
<td>8800</td>
<td>3.64</td>
</tr>
<tr>
<td>240</td>
<td>0.00417</td>
<td>14000</td>
<td>4.07</td>
<td>12000</td>
<td>3.91</td>
</tr>
<tr>
<td>250</td>
<td>0.00400</td>
<td>30000</td>
<td>4.79</td>
<td>15000</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Line Width: 2.0 Hz. 2.0 Hz.
Chemical Shifts: 4456 Hz. 4304 Hz. 4340 Hz. 4163 Hz.
Concentration: 0.073 M 0.073 M

Regression Output:

<table>
<thead>
<tr>
<th></th>
<th>OCH$_3$</th>
<th>NCH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>19.37</td>
<td>16.80</td>
</tr>
<tr>
<td>Std Err of Y Est</td>
<td>0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>R Squared</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>No. of Observations</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>8.00</td>
<td>8.00</td>
</tr>
<tr>
<td>Slope</td>
<td>-3817.72</td>
<td>-3060.44</td>
</tr>
<tr>
<td>Std Err of Slope</td>
<td>127.09</td>
<td>180.97</td>
</tr>
</tbody>
</table>

Activation Parameters:

<table>
<thead>
<tr>
<th></th>
<th>OCH$_3$</th>
<th>NCH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entropy of Activation</td>
<td>-10.5 eu</td>
<td>-15.6 eu</td>
</tr>
<tr>
<td>Enthalpy of Activation</td>
<td>7.2 kcal/mole</td>
<td>6.1 kcal/mole</td>
</tr>
</tbody>
</table>
Figure 26. Eyring plot for the signal averaging of the ligand carbons, OCH$_3$ ($k_1$) and NCH$_2$ ($k_2$), of compound 4 in THF.
The resonance of the benzylic carbon of compound 4 showed the same temperature dependence as compound 3. At 255 K the line is split into a sharp 1:1:1 triplet with \( J = 3.4 \text{ Hz} \). As the temperature increases the lines progressively coalesce until the resonance is a sharp singlet at 320 K as a result of the mutual exchange of lithiums between benzyl carbons.

Equations 11 to 17 were used to calculate the line shapes. The fitted line shapes are shown in figure 27.

The rate constants (table 7) were then plotted using the Eyring equation (figure 28). The numbers for the entropy (-20.5) and enthalpy (10.8 kcal/mole) of activation are similar to those seen for compound 3. The large entropy of activation is indicative of a bimolecular reaction, but a concentration study is needed to prove this. Compound 4 was then prepared at three different concentrations. As expected the rate constants for ortho, ligand, and silyl methyl exchanges did not show a dependence on concentration. The rate constants for the benzylic carbon resonance, however, did depend on concentration. This is shown in figures 29 and 30 and table 8.
Figure 27. $^{13}$C NMR line shapes for the benzylic carbon resonance of 4 in THF: left) experimental spectra at different temperatures; right) line shapes calculated with rate constants to match spectra.
Figure 27. Continued from previous page.
Table 7. Signal averaging for the benzylic carbon resonance of compound 4.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k (s⁻¹)</th>
<th>1/T</th>
<th>ln (k/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.2</td>
<td>0.00400</td>
<td>-7.42</td>
</tr>
<tr>
<td>260</td>
<td>0.3</td>
<td>0.00385</td>
<td>-6.76</td>
</tr>
<tr>
<td>265</td>
<td>0.8</td>
<td>0.00377</td>
<td>-5.80</td>
</tr>
<tr>
<td>270</td>
<td>1.0</td>
<td>0.00370</td>
<td>-5.60</td>
</tr>
<tr>
<td>285</td>
<td>1.3</td>
<td>0.00351</td>
<td>-5.39</td>
</tr>
<tr>
<td>298</td>
<td>8.0</td>
<td>0.00336</td>
<td>-3.62</td>
</tr>
<tr>
<td>305</td>
<td>8.6</td>
<td>0.00328</td>
<td>-3.57</td>
</tr>
<tr>
<td>310</td>
<td>13.0</td>
<td>0.00323</td>
<td>-3.17</td>
</tr>
<tr>
<td>315</td>
<td>16.0</td>
<td>0.00317</td>
<td>-2.98</td>
</tr>
<tr>
<td>320</td>
<td>26.0</td>
<td>0.00313</td>
<td>-2.51</td>
</tr>
</tbody>
</table>

Line Width 3.5 Hz.
Chemical Shift 2586 Hz.
Coupling Constant 3.4 Hz.
Concentration 0.038 M

Regression Output:
- Constant: 14.34
- Std Err of Y Est: 0.31
- R Squared: 0.97
- No. of Observations: 10.00
- Degrees of Freedom: 8.00
- Slope: -5435.79
- Std Err of Slope: 328.20

Activation Parameters
- Entropy of Activation: -20.5 eu
- Enthalpy of Activation: 10.8 kcal/mole
Figure 28. Eyring plot for the signal averaging of the benzylic resonance of compound 4 in THF.
Figure 29. Experimental $^{13}$C NMR line shapes of the benzylic resonance of compound 4 at different concentrations and temperatures.
Figure 30. Calculated line shapes to match the experimental spectra of the benzylic resonance of compound 4 at different concentrations and temperatures shown in figure 29. Rate constants are listed in Table 8.
Table 8. Signal averaging for the $^{13}$C NMR benzylic resonance of compound 4 at different concentrations.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$1/T$ s$^{-1}$</th>
<th>$k_1$ s$^{-1}$</th>
<th>$k_2$ s$^{-1}$</th>
<th>$k_3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.00333</td>
<td>26</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>305</td>
<td>0.00328</td>
<td>28</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>310</td>
<td>0.00323</td>
<td>37</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>315</td>
<td>0.00317</td>
<td>43</td>
<td>25</td>
<td>16</td>
</tr>
<tr>
<td>Line Width</td>
<td>3.5 Hz.</td>
<td>3.5 Hz.</td>
<td>3.5 Hz.</td>
<td></td>
</tr>
<tr>
<td>Chemical Shift</td>
<td>2586 Hz.</td>
<td>2586 Hz.</td>
<td>2586 Hz.</td>
<td></td>
</tr>
<tr>
<td>Coupling Constant</td>
<td>3.4 Hz.</td>
<td>3.4 Hz.</td>
<td>3.4 Hz.</td>
<td></td>
</tr>
</tbody>
</table>

Within experimental error, the rate constants for the signal averaging showed a second order concentration dependence. Therefore the exchange is bimolecular.

As was stated in the introduction, delocalized anions have not shown carbon lithium coupling$^{3,6}$. Once it had been established that the benzyl lithium bond in this system was at least partially covalent, it was desired to determine the cause of this unexpected result. The first effect that we wanted to eliminate was the silicon atom. An all carbon analog to compound 3 was prepared (figure 31). The $^{13}$C NMR (figure 32) chemical shifts of compound 5 at 210 K are similar to those of compound 3.

![Figure 31. Synthesis of compound 5.](image-url)
Figure 32. $^{13}$C NMR of compound 5 in THF-d$_8$ at 210 K.
Figure 33. The benzylic $^{13}$C resonance of naturally abundant compound 5 (0.088 M) in THF-$d_8$ under different conditions: top) 295 K; middle) 210 K; bottom) 210 K with $^6$Li decoupled.
At room temperature the benzyl resonance of compound 5 was a sharp singlet with a line width of 5.0 Hz. At 210 K the line broadened to 23.0 Hz., but never became a triplet. When the $^6$Li was decoupled, the line sharpened to 5.0 Hz. This is almost definitive proof that the benzyl lithium bond is at least partially covalent; but more proof, i.e. a measurable coupling constant, was desired. If the broadening of the resonance is caused by the same exchange as with compounds 3 and 4, then conditions in which the carbon lithium exchange rate is lower permit observation of the $^{13}$C-$^6$Li coupling constant. This can be accomplished by either lowering the temperature or reducing the concentration. Compound 5 was not soluble at temperatures below 210 K at the concentrations studied. Using currently available equipment, it is only possible to acquire spectra for approximately 5 hours at 210 K; for this period of time, a concentration of at least 0.05 M is necessary to provide acceptable spectra. It was therefore not possible to change the experimental conditions enough to sufficiently reduce the intermolecular carbon lithium exchange rate using compound 5.

If one remembers that $^{13}$C makes up only approximately 1% of naturally occurring carbon, then a way to further dilute the sample while maintaining the $^{13}$C concentration becomes obvious. In a naturally occurring 0.05 M sample of compound 5, the concentration of $^{13}$C is 0.0005 M. If the benzyl carbon consists entirely of $^{13}$C, then the sample can be diluted to 0.0005 M while maintaining the same $^{13}$C NMR signal to noise ratio as for the 0.05 M naturally abundant sample. The net effect of making this change is shown in equations 26 and 27, for the 0.05 M naturally abundant sample and the 0.0005 M $\alpha-^{13}$C enriched sample respectively.

\[
C, Li \text{ exchange rate} = k_2(^{13}C^6Li)(^{12}C^6Li) = k_2(0.0005)(0.05) = 2.5 \times 10^{-9}k_2 \tag{26}
\]

\[
C, Li \text{ exchange rate (enriched sample)} = k_2(^{13}C^6Li)^2 = k_2(0.0005)^2 = 2.5 \times 10^{-7}k_2 \tag{27}
\]

Clearly the second exchange rate is one hundredth the size of the first. If a measurable $\alpha-^{13}$C-$^6$Li coupling constant exists, then the chance of observing it would be vastly improved.
While it would be possible to synthesize compound 5 enriched with $^{13}\text{C}$ at the benzyl carbon, it would be easier to use a commercially available compound that is enriched at the correct position; it is possible to buy toluene that has been enriched selectively on the methyl group. Benzyl lithium TMEDA complex was prepared from both toluene with $^{13}\text{C}$ in natural abundance and (α-$^{13}\text{C}$)toluene. Their syntheses are shown in figure 33. The $^{13}\text{C}$ NMR spectra are shown in figures 34 and 35.

Figure 34. Synthesis of benzyl lithium TMEDA complex.
Figure 35. $^{13}$C NMR of benzyl(6Li)lithium TMEDA complex in THF-d$_8$ at 260 K.
Figure 36. $^{13}$C NMR of (α-13C)benzyl(6Li)lithium TMEDA complex in THF-d$_8$ (0.0005 M) at 303 K.
The benzylic carbon resonance for $^{13}$C naturally abundant benzyllithium TMEDA complex remains a sharp singlet from 260 K to 180 K. This is exactly what Seebach$^{10}$ had seen previously. The benzyl carbon resonance of ($\alpha$-$^{13}$C)benzyl($^6$Li)lithium TMEDA complex in THF-d$_6$ (0.0005 M) became a triplet at 180 K (figure 35) with a coupling constant of 3.8 Hz. Before the lithium spectra could be acquired, this particular sample tube was accidentally broken. A new sample was prepared in Et$_2$O-d$_{10}$. The lithium resonance (figure 36) was a doublet at 160 K with a coupling constant of 4.0 Hz. While the carbon resonance showed broadening (figure 37) that became sharper (figure 38) upon being decoupled from lithium, it never displayed the expected triplet. These series of spectra show that coupling, and therefore at least detectable covalent bonding, exists between the benzylic carbon and lithium in some benzylic lithium compounds. This is despite the fact that the aromatic $^{13}$C resonance chemical shifts reflect considerable delocalization of the charge into the aromatic ring (table 9). Using the equation developed by O'Brien, Hart, and Russell$^{9}$ (see equation 2), the $\delta(^{13}$C)$_{\text{average}}$ for the conjugated system should be equal to 110.9 ppm; this number must be corrected for alkyl substituents. Muller and Pritchard$^{11}$ derived that:

\begin{equation}
\rho_{\text{C-H}} = 0.20 \, J(\text{C,H}) \tag{28}
\end{equation}

Where $\rho_{\text{C-H}}$ is the percent "s" character of a carbon hydrogen bond and $J$ is the coupling constant. For ($\alpha$-$^{13}$C)benzyl($^6$Li)lithium TMEDA complex the coupling constant between the carbon and lithium was 132.7 Hz. Using equation 28 this translates to 26.5% "s" character or a sp$^{2.8}$ hybridized carbon.
Table 9. Average chemical shift of the π systems of the benzylic lithium compounds studied.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta(^{13}C)_{\text{average}}$</th>
<th>$\delta(^{12}C)_{\text{average, corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>115.5</td>
<td>114.8</td>
</tr>
<tr>
<td>2</td>
<td>115.3</td>
<td>114.6</td>
</tr>
<tr>
<td>3</td>
<td>114.1</td>
<td>113.8</td>
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<tr>
<td>4</td>
<td>115.1</td>
<td>112.9</td>
</tr>
<tr>
<td>5</td>
<td>112.7</td>
<td>110.8</td>
</tr>
<tr>
<td>benzyllithium+TMEDA</td>
<td>113.2</td>
<td>113.2</td>
</tr>
</tbody>
</table>

The crystal structure of the polymeric benzyllithium DABCO complex$^{30}$ (figure 39) indicate that the lithium is almost equidistant from the benzyl, ipso, and ortho carbons. This is in contrast to what was observed for the NOE experiment of compound 3 (figure 18) which indicated that the benzyl hydrogen was significantly closer to the lithium than the ortho hydrogen. The short (1.39 Å) benzyl carbon bond in the crystal structure is typical for a conjugated bond. The lithium benzyl bond length (2.21 Å) is short enough for there to be a covalent component to the bond. Except for the lithium ortho carbon bond distance, the crystal structure and NMR studies are in agreement.
Figure 37. Benzyl carbon resonance of (α-^{13}C)benzyl(^{6}Li)lithium TMEDA complex in THF-d₈ (0.0005 M) at 180 K.
Figure 38. Lithium resonance of (α-13C)benzyl(6Li)lithium TMEDA complex in Et₂O-d₁₀ (0.0005 M) at 160 K.
Figure 39. Benzyl carbon resonance of (α-^{13}C)benzyl(^{6}Li)lithium TMEDA complex in Et_{2}O-d_{10} (0.0005 M) at 160 K.
Figure 40. $^6$Li Decoupled benzylic carbon resonance of (α-$^{13}$C)benzyl($^6$Li)lithium TMEDA complex in Et$_2$O-d$_{10}$ (0.0005 M) at 160 K.
Figure 41. Crystal structure\textsuperscript{31} of the unit cell of polymeric benzyllithium DABCO complex.
Conclusion

The benzylic lithium compounds studied showed evidence of both covalent and ionic bonding. The upfield shifts of the aromatic $^{13}$C resonances indicate that the negative charge is delocalized over the entire aromatic ring. The activation parameters for rotation around the benzyl ipso bond are consistent with a partial double bond between these two carbons. From this data one would assume that the benzyl carbon is $sp^2$ hybridized, but the $^{13}$C, $^1$H coupling constant show it to be closer to $sp^3$ than $sp^2$. The NOE experiment of compound 3 showed that the lithium is closer to the ligand than the carbanion part of the molecule. The motion of the ligand of compound 4, and presumably the lithium, show that the benzyl carbon bond is ionic enough to allow limited movement of lithium around the carbon. These data are consistent with a tight ion pair. But the $^{13}$C, $^6$Li coupling indicates that there is least some covalent nature to the benzyl lithium bond.

The $^{13}$C, $^6$Li coupling constants of approximately 3 Hz. for the monomeric compounds studied in this thesis do not fit either with Schleyer's prediction$^3$ prediction of 17 Hz. for all monomeric organolithium compounds or Seebach's$^{10}$ observation that $^{13}$C, $^6$Li coupling does not exist for delocalized carbanions. Recent calculations by Bauer$^{15}$ show that the carbon-lithium covalent bond order changes with the hybridization of the carbon. The $^{13}$C, $^6$Li coupling constants observed in this thesis provide experimental data that there is a continuum from totally to partially covalent for carbon lithium bonding.
Experimental

General procedures.

The solvents and common reagents used were purchased from the Ohio State University stores. The deuterated solvents and $^{13}$C enriched toluene were bought from Cambridge Isotopes. The enriched $^6$Li was purchased from Oak Ridge National Laboratory. Chloro-(chloromethyl)dimethylsilane was purchased from Petrarch Systems. All other chemicals were purchased from Aldrich. Dr. Jose Cabral prepared the bis-(2-methoxyethyl)methylamine.

FT-NMR spectra were obtained on either a Bruker AC-200 or a Bruker AM-250 at the Ohio State University chemistry department, or a Bruker MSL-300 at the Ohio State University Campus Chemical Instrument Center. The NMR spectra were referenced to the solvent. Accurate mass spectra were obtained at the Ohio State University Campus Chemical Instrument Center by use of a VG-250S or Kratos MS-30 mass spectrometer.

Toluene used in organometallic reactions was distilled from calcium hydride. Tetramethylethlenediamine was distilled from potassium hydroxide; the main fraction was then freshly distilled from calcium hydride. Diethyl ether, tetrahydrofuran, and alkanes used in organometallic reactions were freshly distilled from sodium with benzophenone under commercial grade argon; the reactions were then carried out either under a blanket of high purity argon or in a dry box.

Preparation and handling of organolithium compounds.

Organolithium compounds are extremely sensitive to moisture and oxygen. The glassware used in the preparation or reaction of organolithium reagents was baked in an oven overnight; the glassware was assembled while it was still warm. The glassware was then flamed dried under vacuum and flushed at least three times with purified argon with the use of a
Firestone valve. Syringes were dried overnight in an oven and assembled while still warm. The needles were then placed in a flask filled with argon until the syringe was cool. Organolithium compounds were handled either in Schlenk flasks or in a dry box.

**Titration of organolithium compounds.**

Organolithium reagents were titrated for both total base content and alkoxide content. The total amount of base was determined by adding a 1 mL sample of organolithium solution to a solution of menthol in THF. The base was then titrated with a 0.1 M solution of benzoic acid in toluene with methylene blue as an indicator. The amount of alkoxide was then determined by first quenching the organolithium sample with allyl bromide and then carrying out a similar titration. The concentration of carbon bound base is the difference between these titrations.

**Preparation of NMR samples.**

NMR sample tubes were connected to a 14/20 joint with a short section of hard glass with an outside diameter of 5 mm. The tubes were dried in an oven overnight. An adapter was then attached to the tube and it was evacuated to approximately 5 microns and flamed dried. The tube and sample were then placed in the dry box. The sample was placed in the tube either as a solid or in solution. The tube was then placed on the high vacuum line, residual solvent was removed slowly, then the tube was evacuated to below 5 microns. Deuterated solvent, previously dried with sodium and benzophenone, was then vacuum transferred into the NMR tube. The resulting solution was degassed by using two freeze, pump, thaw cycles. The sample was frozen with liquid nitrogen, the headspace was evacuated, and the hard glass was heated with a hot pinpoint flame in order to seal off the NMR tube.

**Synthesis of n-butyl(6Li)lithium.**

Enriched (96%) (6Li)lithium (1.51 g, 251 mmol) was cut into pea sized pieces in the dry box and placed in 250 mL Ehrlemeyer flask equipped with a rubber septum. The flask was removed from the dry box and placed under a blanket of argon. Pentane (60 mL) and n-butylbromide (6.4 mL, 60 mmol) were introduced via a syringe. The mixture was placed in an ultrasound apparatus for 4 h. A small sample was removed and quenched with water; the
organic layer was then monitored for butylbromide by gas chromatography. The resulting purple precipitate was allowed to settle overnight. The pentane layer was removed with a syringe and split into two centrifuge tubes equipped with rubber septa. The last remnants of precipitate were removed by centrifuging for 30 min. The pentane layer was removed with a syringe and transferred under a blanket of argon into a flame dried 100 mL Schlenk flask equipped with a glass stopcock. The precipitate was washed with additional pentane (10 mL). The solution was titrated as explained in the previous section. The sample was 0.832 M in total base and 0.004 M in alkoxide. The overall yield of 0.828 M carbon bound base was 96%.

Synthesis of α-trimethylsilyltoluene.

A 500 mL 3 neck round bottom flask was equipped with a condenser, a glass stopcock and an argon inlet. After flame drying under argon, the flask was charged with a solution of TMEDA (10.2 mL, 67.6 mmol) in toluene (200 mL, 1.88 mol); a 2.5 M solution of n-butyllithium in hexane (27.0 mL, 67.5 mmol) was then added. The solution was heated to 90 °C for 1 h. After the resulting red solution was cooled to room temperature, freshly distilled chlorotrimethylsilane (9.6 mL, 75.6 mmol) was added and left to stir overnight. Excess toluene was removed by distillation through a 30 cm Vigreux column. The remaining solution was then placed in a smaller pot, and the product was fractionally distilled at normal temperature to yield a clear liquid (9.98 g, 62%): bp 175-180 °C (lit.\textsuperscript{28} bp 93°C [35 mm Hg]);\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz.) \delta 7.31-7.03 (structured m, 5 H), 2.13 (s, 1 H), 0.68 (s, 9 H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 50.3 MHz.) \delta 141, 128.4, 128.2, 124, 27, -1.8.
Figure 42. $^1$H NMR of α-trimethylsilyltoluene in CDCl$_3$ at 297 K.
Figure 43. $^{13}$C NMR of $\alpha$-trimethylsilyltoluene in CDCl$_3$ at 297 K.
Synthesis of (α-trimethylsilylbenzyl)lithium TMEDA complex.

A 20 mL Schlenk flask equipped with Firestone valve and a glass stopcock was charged via a syringe with a solution of α-trimethylsilyltoluene (0.50 mL, 2.7 mmol) and TMEDA (0.38 mL, 2.5 mmol) in diethyl ether (5.0 mL). After cooling to -70 °C, a 2.5 M solution of n-butyllithium (1.0 mL, 2.5 mmol) was added by syringe. The solution was stirred at -70 °C for 1 h and at room temperature overnight. The ether was removed via house vacuum and then replaced with pentane. At this time a solid precipitate formed. The solvent was removed with a syringe. The precipitate was washed with 2 portions (5 mL) of pentane. The last traces of solvent were removed by pumping under vacuum (1.5 mm Hg). The solid was transferred to the dry box. An NMR sample, 80 mg in 3.8 mL deuterated diethyl ether (0.073 M), was prepared as outlined above: $^1$H NMR (Et$_2$O-d$_{10}$, 303 K, 300 MHz.) δ 6.59 (t, J = 7.1 Hz., 2 H), 6.34 (d, J = 7.5 Hz. 2 H), 5.81 (t, J = 7.1 Hz. 1 H), 2.34 (s, 4 H), 2.13 (s, 12 H), -0.03 (s, 9 H); $^{13}$C NMR (Et$_2$O-d$_{10}$, 300 K, 75.5 MHz.) 157.2, 130.1, 119.2, 109.7, 57.6, 45.6, 41.5, 2.5.

Synthesis of (α-trimethylsilylbenzyl)lithium bis-(2-methoxyethyl)methylamine complex.

A 20 mL Schlenk flask equipped with Firestone valve and a glass stopcock was charged via a syringe with a solution of α-trimethylsilyltoluene (0.92 mL, 5.0 mmol) and bis-(2-methoxyethyl)methylamine (0.74 g, 5.0 mmol) in diethyl ether (5.0 mL). A 2.5 M solution of n-butyllithium (2.0 mL, 5.0 mmol) was added by syringe. The solution was stirred at room temperature overnight. The ether was removed via house vacuum and then replaced with pentane. At this time a solid precipitate formed. The solvent was removed with a syringe. The precipitate was washed with 2 portions (5 mL) of pentane. The last traces of solvent were removed by pumping under vacuum (1.5 mm Hg). The solid was transferred to the dry box. An NMR sample, 34 mg in 1.0 mL deuterated diethyl ether (0.20 M), was prepared as outlined above: $^1$H NMR (THF-d$_{6}$, 303 K, 300 MHz.) δ 6.46 (t, J = 7.1 Hz., 2 H), 6.31 (d, J = 7.4 Hz.), 5.69 (td, J = 5.8 Hz., 1.0 Hz., 1 H), 3.48 (t, J = 5.4 Hz.), 3.24 (s, 6 H), 2.53 (t, J = 5.4 Hz.), 2.22 (s, 3 H), 1.40 (s, 1 H), -0.04 (s, 9 H); $^{13}$C NMR (THF-d$_{6}$, 303 K, 75.5 MHz.) δ 150.0, 128.7, 128.1, 120.7, 108.0, 71.9, 58.9, 57.7, 43.6, 40.5, -0.5.
Figure 44. $^1$H NMR of (α-trimethylsilylbenzyl)lithium TMEDA complex in Et$_2$O-d$_{10}$ at 303 K.
Figure 45. $^1$H NMR of (α-trimethylsilylbenzyl)lithium bis-(2-methoxyethyl)methylamine complex in THF-$d_8$ at 303 K.
Synthesis of α-(chloromethyl(dimethyl)silyl)toluene.

A 500 mL 3-neck flask equipped with a condenser, an addition funnel, argon inlet, and a magnetic stir bar was charged with commercial magnesium shavings (2.44 g, 100 mmol) which were then covered with Et₂O (100 mL). Benzyl chloride (8.8 mL, 76 mmol) in Et₂O (100 mL) was added through the addition funnel at such a rate as to maintain a steady reflux (ca. 30 min). The mixture was then heated to reflux for an additional 2 h and then cooled to room temperature. Chloro(chloromethyl)dimethylsilane (10.0 mL, 76 mmol) in Et₂O (20 mL) was added through the addition funnel over 30 min and then heated to reflux overnight. After cooling to room temperature, the reaction was carefully quenched with 2 N aqueous HCl (200 mL). After separation of layers, the aqueous phase was extracted with Et₂O (100 mL). The combined organic phases were washed with H₂O (100 mL), sat. aqueous NaHCO₃ (100 mL), and brine (100 mL). The ethereal layer was dried by passing through Drierite and then concentrated in vacuo. The remaining liquid was vacuum distilled through a Vigreux column. The first fraction yielded α-trimethylsilyltoluene as a clear liquid (1.26 g, 44%): bp. 37-40 °C (0.8 mm Hg). The second fraction yielded α-(chloromethyl(dimethyl)silyl)toluene as a clear liquid (7.35 g, 48%): bp 57-60 °C (0.8 mm Hg) [lit.²⁹ bp 89-90 °C (4 mm Hg)]; \(^1\)H NMR (CDCl₃, 200 MHz.) \(\delta 7.29-7.26 \text{ (m, 2 H)}\), \(7.24-7.14 \text{ (m, 3 H)}\), \(2.75 \text{ (s, 2 H)}\), \(2.24 \text{ (s, 2 H)}\), \(0.11 \text{ (s, 6 H)}\); \(^{13}\)C NMR (CDCl₃, 50.0 MHz.) \(\delta 138.9, 128.4, 128.1, 124.4, 29.5, 23.5, -4.9\); mass spectrum, exact mass calculated for C₁₀H₁₅ClSi m/e 198.0633, observed 198.0643. Note: the α-trimethylsilyltoluene resulted from the α-(chloromethyl(dimethyl)silyl)toluene reacting with the excess magnesium; it would be advisable to either use only a stoichiometric amount of magnesium or remove the initial Grignard reagent from the excess magnesium.
Figure 46. $^1$H NMR of $\alpha$-(chloromethylidemethylsilyl)toluene in CDCl$_3$ at 297 K.
Figure 47. $^{13}$C NMR of $\alpha$-(chloromethyldimethylsilyl)toluene in CDCl$_3$ at 297 K.
Synthesis of \([\alpha-[[\text{bis}(2\text{-methoxyethyl})\text{amino}]\text{methyl}]\text{dimethyl}silyl]\text{toluene}].

A solution of \(\alpha-\text{(chloromethyl} \text{dimethyl}silyl)\text{toluene} \ (7.35 \text{ g, 36.8 mmol})\) in \(\text{bis-(2-methoxy} \text{ethyl)amine} \ (17 \text{ mL, 116 mmol})\) was heated in a 100 mL 1 neck flask, equipped with a condenser and an argon inlet, to 120 °C overnight. The resulting hydrochloride salts of the amines were quenched with 2 N aqueous KOH (40 mL). The free amines were then extracted with CHCI₃ (3 x 50 mL). The combined organic layers were dried by passing through Drierite and concentrated \text{in vacuo}. The remaining liquid was vacuum distilled through a Vigreux column. The first fraction yielded recovered \(\text{bis-(2-methoxyethyl)amine} \) as a clear liquid (2.75 g, 20 mmol): bp. 25-27 °C (0.45 mm Hg). The second fraction yielded \([\alpha-[[\text{bis}(2\text{-methoxyethyl})\text{amino}]\text{methyl}]\text{dimethyl}silyl]\text{-toluene} \) as a clear liquid (8.63 g, 80%): bp. 114-116 °C (0.45 mm Hg); \(^1\text{H NMR (CDCl}_3, 200 MHz.) \delta 7.26-7.00 \text{ (m, 5 H)}, 3.44 \text{ (t, } J = 6.2 \text{ Hz., 4 H)}, 3.33 \text{ (s, 6 H)}, 2.65 \text{ (t, } J = 6.2 \text{ Hz., 4 H)}, 2.14, 2.09 \text{ (overlapping s’s, 4 H)}, 0.01 \text{ (s, 6 H)}; \(^{13}\text{C NMR (CDCl}_3, 50.0 MHz.) \delta 139.8, 128.0, 127.9, 123.7, 70.9, 58.5, 57.1, 45.4, 24.9, -3.3\); mass spectrum, exact mass calculated for \(\text{C}_{16}\text{H}_{29}\text{NO}_2\text{Si} m/e 295.1969, \) observed 295.1970.
Figure 48. $^1$H NMR of [α-[[bis(2-methoxyethyl)amino]methyl]dimethylsilyl]toluene in CDCl$_3$ at 297 K.
Figure 49. $^{13}$C NMR of $\gamma$-[bis(2-methoxyethyl)amino]methyl[dimethylsilyl]toluene in CDCl$_3$ at 297 K.
Synthesis of $\alpha-[[\text{bis}(2\text{-methoxyethyl})\text{amino}]\text{methyl}]\text{dimethyl}silyl][\text{benzyl}]-^6\text{Li}\text{lithium}$.

A 40 mL Schlenk flask equipped with Firestone valve and a glass stopcock was charged via a syringe with a solution of $\alpha-[[\text{bis}(2\text{-methoxyethyl})\text{amino}]\text{methyl}]\text{dimethyl}silyl][\text{toluene}]$ (0.88 g, 2.96 mmol) in diethyl ether (10.0 mL). A 2.8 M solution of $n$-butyl$^6\text{Li}\text{lithium}$ (1.0 mL, 2.8 mmol) was slowly added by syringe; the reaction is slightly exothermic at room temperature. Even though a precipitate formed almost immediately, the reaction was stirred for an additional 15 min. The precipitate was allowed to settle, and then the ether was removed by a syringe. The precipitate was washed with two more 10 mL portions of ether. The last traces of solvent were removed in vacuo, and the solid was transferred to the dry box. An NMR sample of 90 mg in 4.0 mL of THF-d$_8$ was prepared as noted previously (0.075 M): $^1\text{H NMR (THF-d}_8$, 293 K, 300 MHz.) $\delta$ 6.48 (structured m, 2 H), 6.31 (structured m, 2 H), 5.69 (structured m, 1 H), 3.46 (t, $J = 5.4$ Hz., 4 H), 3.10 (s, 6 H), 2.62 (t, $J = 5.4$ Hz., 4 H), 2.06, (s, 2 H), 1.50 (s, 1 H), -0.07 (s, 6 H); $^{13}\text{C NMR (THF-d}_8$, 230 K, 75.5 MHz.) $\delta$ 158.6, 128.5, 128.3, 121.8, 117.5, 107.1, 69.6, 58.7, 56.5, 46.8, 36.7, -0.5.
Figure 50. $^1$H NMR of $[\alpha-\{[[\text{bis}(2\text{-methoxyethyl})\text{amino}][\text{methyl}][\text{dimethylsilyl}][\text{benzyl}]]^6\text{Li}\}^\text{Li}]$ in THF-$d_8$ at 293 K.
Synthesis of para-tert-butyl-α-(chloromethyldimethylsilyl)toluene.

A 250 mL 3 neck flask equipped with a condenser, an addition funnel, argon inlet, and a magnetic stirbar was charged with commercial magnesium shavings (1.32 g, 54.3 mmol) which were then covered with Et₂O (40 mL). A solution of α-bromo-para-tert-butyltoluene (10.0 mL, 54.4 mmol) in Et₂O (40 mL) was added through the addition funnel at such a rate as to maintain a steady reflux (ca. 60 min). The mixture was heated to reflux for 1 h and then cooled to room temperature. The ethereal layer was added via a cannula to a solution of chloro(chloromethyl)-dimethylsilane (8.0 mL, 61 mmol) in Et₂O (40 mL). The reaction was allowed to stir overnight. The resulting salt was removed by filtration. The ether was concentrated in vacuo to give a white semi-solid. Recrystallization from ether gave a white solid (3.36 g, 42%): mp 148-151 °C.

¹H NMR (CDCl₃, 200 MHz.) δ 7.35 (d, J = 8.4 Hz., 2 H), 7.22 (d, J = 8.4 Hz., 2 H), 2.91 (s, 2 H), 1.34 (s, 9 H); the ¹H NMR spectrum is consistent with the Wurtz coupled product. The mother liquor from the recrystallization were concentrated in vacuo; the remaining liquid was vacuum distilled to give para-tert-butyl-α-(chloromethyldimethylsilyl)toluene (4.75 g, 34%): bp 92-95 °C (0.75 mm Hg); ¹H NMR (CDCl₃, 250 MHz.) δ 7.32 (d, J = 8.4 Hz., 2 H), 7.03 (d, J = 8.4 Hz., 2 H), 2.81 (s, 2 H), 2.26 (s, 2 H), 1.38 (s, 9 H), 0.18 (s, 6 H); ¹³C NMR (CDCl₃, 62.9 MHz.) δ 147.1, 135.6, 127.8, 125.6, 34.2, 31.5, 29.6, 22.9, -4.8; mass spectrum calculated for C₁₄H₂₃ClSi m/e 254.1259, observed 254.1260.
Figure 51. $^1$H NMR of para-tert-butyl-$\alpha$-(chloromethyltrimethylsilyl)toluene in CDCl$_3$ at 303 K.
Figure 52. $^{13}$C NMR of para-tert-butyl-α-(chloromethylmethylsilyl)toluene in CDCl$_3$ at 303 K.

A solution of para-tert-butyl-α-(chloromethyl)dimethylsilyl]toluene (4.57 g, 17.8 mmol) in bis-(2-methoxyethyl)amine (6.6 mL, 45 mmol) was heated in a 100 mL 1 neck flask, equipped with a condenser and an argon inlet, to 100 °C overnight. The resulting hydrochloric salt of the amines was quenched with 2 N aqueous KOH (20 mL). The free amines were then extracted with CHCl₃ (3 x 25 mL). The combined organic layers were dried by passing through Drierite and concentrated *in vacuo*. The remaining liquid was vacuum distilled through a Vigreux column. The first fraction yielded recovered bis-(2-methoxyethyl)amine as a clear liquid (1.31 g, 10 mmol): bp. 29-31 °C (1.0 mm Hg). The second fraction yielded para-tert-butyl-[α-[[bis(2-methoxyethyl)amino]methyl]dimethylsilyl]toluene as a clear liquid (4.55 g, 73%): bp. 146-149 °C (1.0 mm Hg); ¹H NMR (CDCl₃, 250 MHz.) δ 7.24 (d, J = 8.3 Hz., 2 H), 6.97 (d, J = 8.3 Hz., 2 H), 3.45 (t, 6.2 Hz., 4 H), 3.34 (s, 6 H), 2.67 (t, 6.2 Hz., 4 H), 2.11 (s, 4 H), 1.32 (s, 9 H), 0.06 (s, 6 H); ¹³C NMR (CDCl₃, 62.9 MHz.) δ 146.6, 136.7, 127.9, 124.9, 71.1, 58.7, 57.3, 45.7, 34.1, 31.4, 24.4, -3.0; mass spectrum calculated for C₂₀H₃₇NO₂Si m/e 351.2595, observed 351.2603.
Figure 53. $^1$H NMR of para-tert-butyl-[o-[[bis(2-methoxyethyl)amino]methyl]-dimethylsilyl]toluene in CDCl$_3$ at 303 K.
Figure 5. $^{13}$C NMR of para-tert-butyl-[α-[[bis(2-methoxyethyl)amino]methyl]dimethylsilyl]toluene in CDCl$_3$ at 303 K.
Synthesis of \([\text{para-}^\text{tert-butyl}]-[\alpha-[\text{bis}(2\text{-methoxyethyl})\text{amino}]\text{methyl}]-\text{dimethyl}silyl]\text{benzyl}]-^6\text{Li}\text{lithium.}

A 20 mL Schlenk flask equipped with Firestone valve and a glass stopcock was charged via a syringe under argon with a solution of \([\text{para-}^\text{tert-butyl}]-[\alpha-[\text{bis}(2\text{-methoxyethyl})\text{amino}]\text{methyl}]-\text{dimethyl}silyl]toluene (1.09 g, 3.08 mmol) in diethyl ether (5.0 mL). A 0.89 M solution of \(n\text{-butyl}^6\text{Li}\text{lithium} (3.5 mL, 3.1 mmol) was slowly added by syringe; the reaction is slightly exothermic at room temperature. Even though a precipitate formed almost immediately, the reaction was stirred for an additional 15 min. The precipitate was allowed to settle, and then the ether was removed by syringe. The precipitate was washed with two more 5 mL portions of ether. The last traces of solvent were removed in vacuo, and the solid was transferred to the dry box. An NMR sample of 86 mg in 2.8 mL of THF-d8 (0.086 M) was prepared as described previously: \(^1\text{H NMR (THF-d8, } 315 \text{ K, } 300 \text{ MHz.}) \delta 6.59 (\text{d, } J = 8.4 \text{ Hz., } 2 \text{ H}), 6.29 (\text{d, } J = 8.4 \text{ Hz., } 2 \text{ H}), 3.44 (\text{t, } J = 5.4 \text{ Hz., } 4 \text{ H}), 3.07 (\text{s, } 6 \text{ H}), 2.62 (\text{t, } J = 5.4 \text{ Hz., } 4 \text{ H}), 2.06 (\text{s, } 2 \text{ H}), 1.43 (\text{s, } 1 \text{ H}), 1.13 (\text{s, } 9 \text{ H}), -0.03 (\text{s, } 6 \text{ H}); \(^{13}\text{C NMR (THF-d8, } 180 \text{ K, } 75.5 \text{ MHz.}) \delta 156.0, 128.6, 125.0, 124.8, 121.1, 116.1, 69.2, 59.0, 57.5, 57.2, 55.3, 46.9, 34.2, 33.8, 32.3, 1.1, -2.1.\)
Figure 55. $^1$H NMR of [para-tert-butyl-[α-][bis(2-methoxyethyl)amino][methyl]-dimethylsilyl]benzyl(\textsuperscript{6}Li)lithium in THF-d\textsubscript{8} at 315 K.

A solution of 1-chloro-3-phenylpropane (7.03 g, 45.5 mmol) in bis-(2-methoxy-ethyl)amine (20 mL, 137 mmol) was heated in a 100 mL 1 neck flask, equipped with a condenser and an argon inlet, to 125 °C overnight. The resulting hydrochloride salts of the amines were quenched with 2 N aqueous KOH (45 mL). The free amines were then extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried by passing through Drierite and concentrated in vacuo. The remaining liquid was vacuum distilled through a Vigreux column.

The first fraction yielded recovered bis-(2-methoxyethyl)amine as a clear liquid (4.64 g, 34.8 mmol): bp. 25-27 °C (0.7 mm Hg). The second fraction yielded [3-[bis(2-methoxyethyl)amino]propyl]benzene (9.83 g, 86%): bp 115-117 °C (0.7 mm Hg); 1H NMR (CDCl3, 200 MHz.) δ 7.31-7.12 (m, 5 H), 3.43 (t, J = 6.1 Hz., 4 H), 3.32 (s, 6 H), 2.70 (t, J = 6.1 Hz., 4 H), 2.64-2.53 (m, 4 H), 1.86-1.71 (m, 2 H); 13C NMR (CDCl3, 50.0 MHz.) δ 142.2, 128.2, 128.1, 125.5, 71.1, 58.6, 54.6, 53.8, 22.4, 28.6; mass spectrum calculated for C15H25N02 m/e 251.1887, observed 251.1886.
Figure 56. $^1$H NMR of [3-bis(2-methoxyethyl)amino]propyl]benzene in CDCl$_3$ at 297 K.
Figure 57. $^{13}$C NMR of [3-bis(2-methoxyethyl)amino]propyl]benzene in CDCl$_3$ at 297 K.

A 20 mL Schlenk flask equipped with Firestone valve and a glass stopcock was charged via a syringe with a solution of [3-[bis(2-methoxyethyl)amino]propyl]benzene (1.24 g, 4.93 mmol) in diethyl ether (10 mL). A 0.98 M solution of n-butyl-[6Li]lithium (5.0 mL, 4.9 mmol) was slowly added by syringe; the reaction is slightly exothermic at room temperature. Even though a precipitate formed almost immediately, the reaction was stirred for an additional 15 min. The precipitate was allowed to settle, and then the ether was removed using a syringe. The precipitate was washed with two more 10 mL portions of ether. The last traces of solvent were removed in vacuo, and the solid was transferred to the dry box. An NMR sample of 86 mg in 3.8 mL of THF-d₈ (0.088 M) was prepared as described previously: ¹H NMR (THF-d₈, 294 K, 300 MHz.) δ 6.24 (broad s [due to slow rotation around the ipso-benzyl bond], 2 H), 5.79 (broad s [due to slow rotation around the ipso-benzyl bond], 2 H), 5.17 (structured m, 1 H), 3.41 (t, J = 5.3 Hz., 4 H), 3.18 (s, 6 H), 2.59 (t, J = 5.3 Hz., 4 H), 2.58-2.44 (m, 2 H), 2.09-2.07 (m, 2 H), 1.70 (s, 1 H); ¹³C NMR (THF-d₈, 210 K, 75.5 MHz.) δ 155.6, 129.3, 127.6, 117.0, 108.0, 100.9, 69.5, 67.4, 58.6, 54.8, 53.3, 29.8.
Figure 58. $^1$H NMR of [[3-[bis(2-methoxyethyl)amino]propyl]benzyl]-($^6$Li)lithium in THF-d$8$ at 294 K.
Synthesis of benzyl(\textit{^6}Li)lithium TMEDA complex.

A 20 mL Schlenk flask equipped with Firestone valve and a glass stopcock was charged via a syringe with a solution of toluene (0.98 mL, 9.2 mL) in TMEDA (1.4 mL, 9.3 mmol). A 0.77 M solution of n-butyl(\textit{^6}Li)lithium (12.0 mL, 9.2 mmol) was added and then stirred for two days. The resulting precipitate was allowed to settle, and the solvent was removed with a syringe. The precipitate was washed with two 10 mL portions of pentane. The solvent was then removed \textit{in vacuo}. The solid was then brought into the dry box. An NMR sample of 34 mg in 0.8 mL of THF-d\textsubscript{8} (0.20 M) was prepared as described previously: \textit{\textsuperscript{1}H NMR} (THF-d\textsubscript{8}, 260 K, 300 MHz.) \(\delta\) 6.27 (td, \(J = 6.9\) Hz., 1.5 Hz., 2 H), 6.05 (dd, \(J = 8.2\) Hz., 1.1 Hz., 2 H), 5.35 (td, \(J = 6.9\) Hz., 1.5 Hz., 1 H) 2.29 (s, 4 H), 2.15 (s, 12 H), 1.55 (s, 2 H); \textit{\textsuperscript{13}C NMR} (THF-d\textsubscript{8}, 260 K, 75.5 MHz.) \(\delta\) 161.1, 128.3, 116.6, 104.3, 58.6, 46.4, 37.1.

Synthesis of (\textit{\alpha}-\textsuperscript{13}C)benzyl(\textit{^6}Li)lithium TMEDA complex.

A 20 mL Schlenk flask a glass stopcock was placed in a dry box and then charged via a syringe with a solution of (\textit{\alpha}-\textsuperscript{13}C)toluene (0.50 mL, 4.9 mmol) in TMEDA (0.80 mL, 5.3 mmol). A 0.83 M solution of n-butyl(\textit{^6}Li)lithium in pentane (6.0 mL, 5.0 mmol) was then added and stirred for 2 days. The resulting precipitate was allowed to settle and then the solvent was removed via a syringe. The precipitate was washed with two 10 mL portions of pentane. The excess solvent was removed \textit{in vacuo}. An NMR sample of 3 mg in 3.2 Et\textsubscript{2}O-d\textsubscript{10} (0.005 M) was prepared as explained previously: \textit{\textsuperscript{1}H NMR} (THF-d\textsubscript{8}, 303 K, 300 MHz.) \(\delta\) 6.27 (td, \(J = 6.9\) Hz., 1.5 Hz., 2 H), 6.05 (ddd, \(J = 8.2\) Hz., 3.0, 1.1 Hz., 2 H), 5.38 (td, \(J = 6.9\) Hz., 1.5 Hz., 1 H) 2.29 (s, 4 H), 2.15 (s, 12 H), 1.55 (d, \(J = 132.7\) Hz., 2 H); \textit{\textsuperscript{13}C NMR} (THF-d\textsubscript{8}, 303 K, 75.5 MHz.) \(\delta\) 161.1(d, \(J = 140.2\) Hz.), 128.3(s), 116.6 (d, \(J = 5.4\) Hz), 104.8(s), 58.7(s), 46.2(s), 36.6(s).
Figure 59. $^1$H NMR of benzyl(6Li)lithium TMEDA complex in THF-d$_4$ at 260 K.
Figure 60. $^1$H NMR of ($\alpha$-$^{13}$C)benzyl($^6$Li)lithium TMEDA complex in THF-$d_8$ (0.0005 M) at 303 K.
ADDENDUM

The question of whether the d orbitals of second row elements such as sulfur can interact with carbon π systems has been extensively studied$^{32}$. Fraenkel et. al.$^{33}$ have presented evidence that the d orbitals of sulfur in 4,4-dioxy-4-thia-1-acetyl-1,4-dihydropyridine do interact with the carbon π system. This was accomplished by measuring the barrier to rotation around the carbon-nitrogen bond of a 4,4-dioxy-4-thia-1-acetyl-1,4-dihydropyridine and comparing it with the barrier to rotation of related heterocycles (table 10).

The concept was based on the fact that in the transition state for amide rotation the non-bonding electrons on nitrogen are only minimally in conjugation with the carbonyl group; hence they become part of a six electron system. If the system overlaps with the d orbitals of sulfur on the sulfone, there is the possibility of cycloconjugation. This stabilization of the transition state for amide rotation and a normal structure for the ground state of the amide would result in a lower barrier than is observed for normal N,N-dialkylcarboxamides. Qualitatively this is the case as the published experimental data show.

The barrier to rotation around the carbon-nitrogen bond of 1-acetyl-4,4-dimethyl-1,4-dihydropyridine has an enthalpy of activation of 17.2 kcal/mole. This is a typical value for tertiary amides. The barrier to rotation for 4-acetyl-2,3,5,6-tetrahydro-1,4-thiazine-1,1-dioxide has a similar enthalpy of activation of 17.3 kcal/mole. If one double bond is added to the ring, then the enthalpy of activation drops by 0.8 kcal/mole. For 4,4-dioxy-4-thia-1-acetyl-1,4-dihydropyridine the enthalpy of activation is 11.7 kcal/mole. This value is extremely close to the enthalpy of activation of 12.0 kcal/mole for rotation around the carbon-nitrogen bond of N-acetylpyrole$^{34}$. These data show that the lone pair on the nitrogen of
Table 1035. Barrier to rotation around the carbon-nitrogen bond of some nitrogen containing heterocycles.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^\circ$ (kcal/mole)</th>
<th>$\Delta S^\circ$ (eu)</th>
<th>IR (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure" /></td>
<td>17.2</td>
<td>1</td>
<td>1700</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure" /></td>
<td>17.3</td>
<td>1</td>
<td>1637</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure" /></td>
<td>16.5</td>
<td>6</td>
<td>1688</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical Structure" /></td>
<td>11.7</td>
<td>1</td>
<td>1735</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical Structure" /></td>
<td>12.0</td>
<td>-0.6</td>
<td>1735</td>
</tr>
<tr>
<td><img src="image6" alt="Chemical Structure" /></td>
<td>13.4</td>
<td>-6.3</td>
<td>1746</td>
</tr>
</tbody>
</table>
4,4-dioxy-4-thia-1-acetyl-1,4-dihydropyridine is involved in cycloconjugation. The only way that this is possible is if the d orbitals on sulfur interact with the carbon \( \pi \) system.

The barrier to amide rotation in 4,4-dioxy-4-thia-1-acetyl-1,4-dihydropyridine calculated\(^{33}\) using the Gaussian 80 series of programs at the STO 3G* level of approximation including the 3d orbitals of sulfur was found to be 11.3 kcal/mole. The calculation was originally simplified by modeling a hydrogen for the methyl group. It was desired to confirm this value by measuring the barrier of amide rotation in 4,4-dioxy-4-thia-1-formyl-1,4-dihydropyridine itself by NMR line shape analysis. Its synthesis is shown in figure 61.

![Figure 61. Synthesis of in 4,4-dioxy-4-thia-1-formyl-1,4-dihydropyridine.](image)

\( \text{O} \quad \text{O} \quad \text{NH} \quad + \quad (\text{H}_3\text{C})_3\text{CCOCH} \quad \xrightarrow{\text{CH}_3\text{CN}} \quad \text{O} \quad \text{O} \quad \text{N} \quad \text{H} \quad \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ 6 \quad \text{43\%} \)

Figure 62. Rotation around the carbon nitrogen double bond of 4,4-dioxy-4-thia-1-formyl-1,4-dihydropyridine.
At 254 K each proton has a unique resonance with the shifts and coupling constants indicated in table 11. As the temperature is raised, protons 4 and 2 signal average with 5 and 3 respectively. The highest temperature that can be reached using acetonitrile as solvent is 354 K. At this temperature the peaks are almost completely averaged. The program DNMR3 run on a mainframe IBM 3801 was used to calculate the $^1$H NMR line shapes as a function of the rate of amide rotation. This program has the advantage of being able to generate the matrix for up to a five spin system. The chemical shifts, line widths, coupling constants, mode of exchange, and rate constants are input to the program via job control language. The program then generates the appropriate matrix and calculates the NMR spectrum. The line shapes for the downfield and upfield protons are shown in figures 63 and 64 respectively. The data (table 11) were then plotted using the Eyring equation (figure 65). The value of 13.4 kcal/mole for the enthalpy of activation is in agreement with the value calculated by Gaussian 80. Qualitatively the results for amide rotation in 4,4-dioxy-4-thia-1-formyl-1,4-dihydropyridine support the proposal for cycloconjugation interactions in 4-dioxy-4-thia-1,4-dihydropyridines that have been calculated by theory and seen by previous experiments.$^{33}$
Figure 63. Downfield $^1$H NMR lineshapes for compound 6 in CD$_3$CN: left) experimental spectra at different temperatures; right line shapes calculated with rate constants to match spectra.
Figure 63. Continued from previous page
Figure 64. Upfield $^1$H NMR lineshapes for compound 6 in CD$_3$CN: left) experimental spectra at different temperatures; right line shapes calculated with rate constants to match spectra.
Figure 64. Continued from previous page.
Table 11. Signal averaging of the $^1$H shifts for compound 6.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>1/T</th>
<th>k ( \text{s}^{-1} )</th>
<th>ln(k/T)</th>
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<tbody>
<tr>
<td>254</td>
<td>0.00394</td>
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</tr>
<tr>
<td>275</td>
<td>0.00364</td>
<td>12</td>
<td>-3.13</td>
</tr>
<tr>
<td>296</td>
<td>0.00338</td>
<td>93</td>
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</tr>
<tr>
<td>310</td>
<td>0.00323</td>
<td>205</td>
<td>-0.41</td>
</tr>
<tr>
<td>321</td>
<td>0.00312</td>
<td>380</td>
<td>0.17</td>
</tr>
<tr>
<td>332</td>
<td>0.00301</td>
<td>850</td>
<td>0.94</td>
</tr>
<tr>
<td>343</td>
<td>0.00292</td>
<td>1900</td>
<td>1.71</td>
</tr>
<tr>
<td>354</td>
<td>0.00282</td>
<td>5000</td>
<td>2.65</td>
</tr>
</tbody>
</table>

Line Widths 0.5 Hz.

Chemical Shifts

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<tbody>
<tr>
<td>H (1)</td>
<td>2122.3 Hz.</td>
</tr>
<tr>
<td>H (2)</td>
<td>1929.1 Hz.</td>
</tr>
<tr>
<td>H (3)</td>
<td>1846.4 Hz.</td>
</tr>
<tr>
<td>H (4)</td>
<td>1596.5 Hz.</td>
</tr>
<tr>
<td>H (5)</td>
<td>1578.8 Hz.</td>
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</table>

Coupling Constants

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<tr>
<td>J (1,3)</td>
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<tr>
<td>J (1,4)</td>
<td>1.1 Hz.</td>
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<tr>
<td>J (1,5)</td>
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</tr>
<tr>
<td>J (2,3)</td>
<td>2.5 Hz.</td>
</tr>
<tr>
<td>J (2,4)</td>
<td>9.6 Hz.</td>
</tr>
<tr>
<td>J (2,5)</td>
<td>0.0 Hz.</td>
</tr>
<tr>
<td>J (3,4)</td>
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<td>J (3,5)</td>
<td>9.4 Hz.</td>
</tr>
<tr>
<td>J (4,5)</td>
<td>4.2 Hz.</td>
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Concentration 0.37 M

Regression Output

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<tbody>
<tr>
<td>Constant</td>
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<tr>
<td>Std Err of Y Est</td>
<td>0.74</td>
</tr>
<tr>
<td>R Squared</td>
<td>0.96</td>
</tr>
<tr>
<td>No. of Observations</td>
<td>11.00</td>
</tr>
<tr>
<td>Degrees of Freedom</td>
<td>9.00</td>
</tr>
</tbody>
</table>

Slope -6757.28
Std Err of Slope 450.13

Activation Parameters

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<tr>
<td>Entropy of Activation</td>
<td>-6.3 eu</td>
</tr>
<tr>
<td>Enthalpy of Activation</td>
<td>13.4 kcal/mole</td>
</tr>
</tbody>
</table>
Figure 65. Eyring plot for the signal averaging of the $^1$H resonances of compound 6.

Synthesis of 4,4-dioxy-4-thia-1-formyl-1,4-dihydropyridine.

A solution of 4H-1,4-thiazine-1,1-dioxide (1.00 g, 7.62 mmol) and pivoyl formyl anhydride (2.5 mL) in acetonitrile (25 mL) was stirred for 24 h under argon. The solution was concentrated in vacuo to give a tan solid (1.10 g). The solid was passed through a Davisiil column (30 g, 22 x 2 cm; eluent: 50/50 ethyl acetate/petroleum ether) to give the product as a white solid (0.519 g, 43%): mp 250-253 °C (after decarboxylating at 175 °C); $^1$H NMR (CDCl$_3$, 250 MHz.) $\delta$ 8.48 (d, $J = 1.1$ Hz, 1 H), 7.72 (dd, $J = 9.6$ Hz, 2.5 Hz, 1 H), 7.39 (dd, $J = 9.4$ Hz, 2.5 Hz, 1 H), 6.39 (ddd, $J = 9.6$ Hz, 4.2 Hz, 1.1 Hz, 1 H), 6.32 (dd, $J = 9.4$ Hz, 4.2 Hz, 1 H); IR (KBr pellet) 3069, 1746, 1732, 1644, 1219, 1170, 1125, 1102, 810, 725, 704 cm$^{-1}$; mass spectrum, exact mass calculated for C$_9$H$_5$NO$_3$S $m/e$ 158.9991, observed 159.0006.
Figure 66. $^1$H NMR of compound 6.
Figure 67. IR of compound 6.
LIST OF REFERENCES


5. Structures were taken from reference 4.


26. Taken from reference 25 (b).

31. Taken from reference 30.


35. The values for the first and fourth entries are from reference 33 (a). The values for the second and third entries are from reference 33 (b). The value for the fifth entry are from reference 34. The value for the last entry is this work.