Lithium 2,2,6,6-Tetramethylpiperidide (LiTMP) and Lithium 2,2,4,6,6-Pentamethylpiperidide (LiPMP): Influence of TMEDA and Related Chelating Ligands on the Solution Structures. Characterization of Higher Cyclic Oligomers, Cyclic Dimers, Open Dimers, and Monomers.

Julius F. Remenar, Brett L. Lucht, Dmitriy Kruglyak, and David B. Collum*
Department of Chemistry, Baker Laboratory
Cornell University
Ithaca, New York 14853-1301

Figure I. NMR spectra of samples containing 0.10 M LiPMP and TMEDA (A).

Figure II. NMR spectra of samples containing 0.10 M LiPMP and TEEDA (B).

Figure III. NMR spectra of samples containing 0.10 M LiPMP and Et(Me)NCH₂CH₂N(Me)Et (C).

Figure IV. NMR spectra of samples containing 0.10 M LiPMP and Et₂NCH₂CH₂NMe₂ (D).

Figure V. NMR spectra of samples containing 0.10 M LiPMP and Me₂NCH₂CH₂N(Me)Et (E).

Figure VI. NMR spectra of samples containing 0.10 M LiPMP and either dipyrrrolidinoethane (F) or dipiperidinoethane (G).

Figure VII. NMR spectra of samples containing 0.10 M LiPMP and Me₂NCH₂CH₂N(CH₂)₄ (H).

Figure VIII. NMR spectra of samples containing 0.10 M LiPMP and MeOCH₂CH₂NMe₂ (I).

Figure IX. NMR spectra of samples containing 0.10 M LiPMP and either MeOCH₂CH₂N(CH₂)₃ (K) or MeOCH₂CH₂N(CH₂)₅ (M).

Figure X. NMR spectra of samples containing 0.10 M LiPMP and MeOCH₂CH₂N(CH₂)₄ (L).

Figure XI. NMR spectra of samples containing 0.10 M LiPMP and EtOCH₂CH₂N(CH₂)₄ (M).

Figure XII. NMR spectra of samples containing 0.10 M LiPMP and TMPDA (O).

Figure XIII. NMR spectra of samples containing 0.10 M LiPMP and TMCDCA (P).

Figure XIV. NMR spectra of samples containing 0.10 M LiPMP and TMCDCA (P) at various temperatures.

Figure XV. NMR spectra of samples containing 0.10 M LiPMP and trans-2-(dimethylamino)-methoxycyclohexane (Q).

Figure XVI. NMR spectra of samples containing 0.10 M LiPMP and either sparteine (R).

Figure XVII. NMR spectra of samples containing 0.10 M LiPMP with THF and either TMEDA
(A), TMCD (P), or dipyrrolidinoethane (F).

Figure XVIII. NMR spectra of samples containing 0.10 M LiPMP with THF and either Et(Me)CH₂CH₂NMe₂ (E), Me₂NCH₂CH₂N(CH₂)₄ (H), or Et₂CH₂CH₂NMe₂ (D).

Figure XIX. NMR spectra of samples containing 0.10 M LiPMP with THF and either trans-2-(dimethylamino)methoxy cyclohexane (Q), MeOCH₂CH₂N(CH₂)₄ (L), MeOCH₂CH₂N(CH₂)₅ (M), or EtOCH₂CH₂N(CH₂)₄ (N).

![Structures 14 and 15](image-url)

Chart 2

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NMe₂</td>
<td>NMe₂</td>
<td>I</td>
<td>NMe₂</td>
</tr>
<tr>
<td>B</td>
<td>NEt₂</td>
<td>NEt₂</td>
<td>J</td>
<td>NMe₂</td>
</tr>
<tr>
<td>C</td>
<td>N(Me)Et</td>
<td>N(Me)Et</td>
<td>K</td>
<td>N</td>
</tr>
<tr>
<td>D</td>
<td>NMe₂</td>
<td>NEt₂</td>
<td>L</td>
<td>N</td>
</tr>
<tr>
<td>E</td>
<td>NMe₂</td>
<td>N(Me)Et</td>
<td>M</td>
<td>N</td>
</tr>
<tr>
<td>F</td>
<td>N</td>
<td>N</td>
<td>NMe₂</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>N</td>
<td>N</td>
<td>OMe</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>NMe₂</td>
<td>N</td>
<td>OEt</td>
<td></td>
</tr>
</tbody>
</table>
Figure I. NMR spectra of samples containing 0.10 M LiPMP varying amounts of TMEDA in 2:1 toluene:pentane. (A) $^6$Li-$^{15}$N HMQC spectrum of [${^6}$Li,$^{15}$N] LiPMP with 0.75 equiv of TMEDA at -105 °C. The top and left hand traces are the $^{15}$N ($^1$H) and $^6$Li NMR spectra; (B) $^6$Li-$^{15}$N HMQC spectrum of [${^6}$Li,$^{15}$N] LiPMP with 0.75 equiv of TMEDA at -95 °C. The top and left hand traces are the $^{15}$N ($^1$H) and $^6$Li NMR spectra; (C) $^6$Li spectrum of [${^6}$Li] LiPMP with 0.50 equiv of TMEDA at -105 °C; (D) $^6$Li spectrum of [${^6}$Li] LiPMP with 2.0 equiv of TMEDA at -105 °C; (E) $^6$Li spectrum of [${^6}$Li] LiPMP with 5.0 equiv of TMEDA at -105 °C.
Figure II. NMR spectra of samples containing 0.10 M $[{}^6\text{Li},{}^{15}\text{N}]\text{LiPMP}$ and Et$_2$NCH$_2$CH$_2$NEt$_2$ in 2:1 toluene:pentane at -90 °C. (A) $^6\text{Li}$ NMR spectrum with 5 equiv Et$_2$NCH$_2$CH$_2$NEt$_2$; (B) $^6\text{Li}$ NMR spectrum with 10 equiv Et$_2$NCH$_2$CH$_2$NEt$_2$; (C) $^6\text{Li}$ NMR spectrum with 20 equiv Et$_2$NCH$_2$CH$_2$NEt$_2$; (D) $^{15}\text{N}$ NMR spectrum with 20 equiv Et$_2$NCH$_2$CH$_2$NEt$_2$. 
Figure III. NMR spectra of samples containing 0.10 M LiPMP and EtMeNCH$_2$CH$_2$NETMe in 2:1 toluene:pentane at -100 °C. Samples (A)-(E) contain [6Li,15N]LiPMP and 0.75 equiv of EtMeNCH$_2$CH$_2$NETMe: (A) 6Li NMR spectrum; (B) 6Li NMR spectrum with 15N single-frequency decoupled at 81.9 ppm; (C) 6Li NMR spectrum with 15N single-frequency decoupled at 92.5 ppm; (D) 6Li NMR spectrum with 15N single-frequency decoupled at 103.5 ppm; (E) 15N NMR spectrum with 6Li broad-band decoupled. Samples (F)-(H) contain [6Li]LiPMP and: (F) 0.5 equiv of EtMeNCH$_2$CH$_2$NETMe; (G) 1.0 equiv of EtMeNCH$_2$CH$_2$NETMe; (F) 2.0 equiv of EtMeNCH$_2$CH$_2$NETMe.
Figure IV. NMR spectra of samples containing 0.10 M LiPMP and Et$_2$NCH$_2$CH$_2$NMe$_2$ in 2:1 toluene:pentane at -100 °C. Samples (A)-(E) contain [6Li,15N]LiPMP and 0.75 equiv of Et$_2$NCH$_2$CH$_2$NMe$_2$: (A) 6Li NMR spectrum; (B) 6Li NMR spectrum with 15N single-frequency decoupled at 81.9 ppm; (C) 6Li NMR spectrum with 15N single-frequency decoupled at 95.4 ppm; (D) 6Li NMR spectrum with 15N single-frequency decoupled at 104.0 ppm; (E) 15N NMR spectrum with 6Li broad-band decoupled. Samples (F)-(H) contain [6Li]LiPMP and: (F) 0.5 equiv of Et$_2$NCH$_2$CH$_2$NMe$_2$; (G) 1.0 equiv of Et$_2$NCH$_2$CH$_2$NMe$_2$; (F) 2.0 equiv of Et$_2$NCH$_2$CH$_2$NMe$_2$. 
Figure V. NMR spectra of samples containing 0.10 M LiPMP and EtMeNCH₂CH₂NMe₂ in 2:1 toluene:pentane at -100 °C. Samples (A)-(E) contain [⁶Li,¹⁵N]LiPMP and 0.75 equiv of EtMeNCH₂CH₂NMe₂: (A) ⁶Li NMR spectrum; (B) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 81.9 ppm; (C) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 95.4 ppm; (D) ⁶Li NMR spectrum with ¹⁵N single-frequency decoupled at 104.0 ppm; (E) ¹⁵N NMR spectrum with ⁶Li broad-band decoupled. Samples (F)-(H) contain [⁶Li]LiPMP and: (F) 0.5 equiv of EtMeNCH₂CH₂NMe₂; (G) 1.0 equiv of EtMeNCH₂CH₂NMe₂; (F) 2.0 equiv of EtMeNCH₂CH₂NMe₂.
Figure VI. NMR spectra of samples containing 0.10 M $^{6}$Li,$^{15}$N LiPMP in 2:1 toluene:pentane at -100 °C. (A) $^{6}$Li NMR spectrum with 2 equiv of dipyrrolidinoethane; (B) $^{6}$Li NMR spectrum with 2 equiv of dipiperidinoethane; (C) $^{15}$N NMR spectrum with 2 equiv of dipyrrolidinoethane; (D) $^{15}$N NMR spectrum with 2 equiv of dipiperidinoethane.
Figure VII. NMR spectra of samples containing 0.10 M [\textsuperscript{6}Li,\textsuperscript{15}N] LiPMP and 0.75 equiv of Me\textsubscript{2}N\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}N(CH\textsubscript{2})\textsubscript{4} in 2:1 toluene:pentane at -100 °C. (A) \textsuperscript{6}Li NMR spectrum; (B) \textsuperscript{15}N NMR spectrum with \textsuperscript{6}Li broad-band decoupled; (C) \textsuperscript{6}Li NMR spectrum with \textsuperscript{15}N single-frequency decoupled at 81.7 ppm; (D) \textsuperscript{6}Li NMR spectrum with \textsuperscript{15}N single-frequency decoupled at 96.2 ppm; (E) \textsuperscript{6}Li NMR spectrum with \textsuperscript{15}N single-frequency decoupled at 102.2 ppm.
Figure VIII. NMR spectra of samples containing 0.10 M LiPMP in 2:1 toluene:pentane at -100 °C. (A) $^6$Li NMR spectrum of $[^6$Li,$^{15}$N]$^7$LiPMP and 0.5 equiv of MeOCH$_2$CH$_2$NMe$_2$; (B) $^6$Li decoupled $^{15}$N NMR spectrum of $[^6$Li,$^{15}$N]$^7$LiPMP and 0.5 equiv of MeOCH$_2$CH$_2$NMe$_2$; (C) $^6$Li NMR spectrum of $[^6$Li]$^7$LiPMP and 0.5 equiv of MeOCH$_2$CH$_2$NMe$_2$; (D) $^6$Li NMR spectrum of $[^6$Li]$^7$LiPMP and 1.0 equiv of MeOCH$_2$CH$_2$NMe$_2$; (E) $^6$Li NMR spectrum of $[^6$Li]$^7$LiPMP and 2.0 equiv of MeOCH$_2$CH$_2$NMe$_2$. 
Figure IX. NMR spectra of samples containing 0.10 M $[^6\text{Li},^{15}\text{N}]$LiPMP in 2:1 toluene:pentane at -100 °C. (A) $^6\text{Li}$ NMR spectrum containing 0.5 equiv of 2-azetidino-methoxyethane; (B) $^6\text{Li}$ NMR spectrum containing 0.75 equiv of 2-piperidino-methoxyethane; (C) $^{15}\text{N}$ NMR spectrum containing 0.5 equiv of 2-azetidino-methoxyethane; (D) $^{15}\text{N}$ NMR spectrum containing 0.75 equiv of 2-piperidino-methoxyethane.
Figure X. NMR spectra of samples containing 0.10 M \([{}^6\text{Li},{}^{15}\text{N}]\text{LiPMP}\) and 0.75 equiv of 2-pyrroolidino-methoxyethane in 2:1 toluene:pentane at -100 °C. (A) \(^6\text{Li}\) NMR spectrum; (B) \(^6\text{Li}\) decoupled \(^{15}\text{N}\) NMR spectrum; (C) \(^6\text{Li}\) NMR spectrum with \(^{15}\text{N}\) single frequency decoupling at 80.3 ppm; (D) \(^6\text{Li}\) NMR spectrum with \(^{15}\text{N}\) single frequency decoupling at 96.7 ppm; (E) \(^6\text{Li}\) NMR spectrum with \(^{15}\text{N}\) single frequency decoupling at 101.8 ppm.
Figure XI. NMR spectra of samples containing 0.10 M [\(^{6}\text{Li},{^{15}\text{N}}}\)LiPMP and 0.75 equiv of 2-pyrroldino-ethoxyethane in 2:1 toluene:pentane at -100 °C. (A) \(^{6}\text{Li}\) NMR spectrum; (B) \(^{6}\text{Li}\) decoupled \(^{15}\text{N}\) NMR spectrum; (C) \(^{6}\text{Li}\) NMR spectrum with \(^{15}\text{N}\) single frequency decoupling at 80.3 ppm; (D) \(^{6}\text{Li}\) NMR spectrum with \(^{15}\text{N}\) single frequency decoupling at 92.7 ppm; (E) \(^{6}\text{Li}\) NMR spectrum with \(^{15}\text{N}\) single frequency decoupling at 102.7 ppm.
Figure XII. NMR spectra of samples containing 0.10 M $[^6\text{Li},^{15}\text{N}]\text{LiPMP}$ and varying amounts of TMPDA in 2:1 toluene:pentane at -100 °C. (A) $^6\text{Li}$ NMR spectrum with 5 equiv of TMPDA; (B) $^6\text{Li}$ NMR spectrum with 10 equiv of TMPDA; (A) $^6\text{Li}$ NMR spectrum with 20 equiv of TMPDA; (A) $^{15}\text{N}$ NMR spectrum with 20 equiv of TMPDA.
Figure XIII. NMR spectra of a sample containing 0.10 M $[^6]_{[6Li}^{15N]}LiPMP$ and 0.75 equiv of TMCDA in 2:1 toluene:pentane at -100 °C. (A) $^{6}Li$ NMR spectrum; (B) $^{15}N$ NMR spectrum; (C) $^{6}Li$ broad-band decoupled $^{15}N$ NMR spectrum; (D) $^{6}Li$ NMR spectrum with $^{15}N$ single-frequency decoupling at 82.8 ppm; (E) $^{6}Li$ NMR spectrum with $^{15}N$ single-frequency decoupling at 96.6 ppm; (F) $^{6}Li$ NMR spectrum with $^{15}N$ single-frequency decoupling at 102.9 ppm.
Figure XIV. $^6$Li NMR spectra of a sample containing 0.10 M $[^6$Li,$^{15}$N]$\text{LiPMP}$ and 0.75 equiv of TMCDA in 2:1 toluene:pentane at -100 °C. The spectra were acquired at: (A) -100 °C; (B) -90 °C; (C) -80 °C; (D) -70 °C.
Figure XV. NMR spectra of a sample containing 0.10 M [6Li,15N]LiPMP and 0.75 equiv of trans-2-(N,N-dimethylamino)methoxycyclohexane in 2:1 toluene:pentane at -100 °C. (A) 6Li NMR spectrum; (B) 6Li broad-band decoupled 15N NMR spectrum; (C) 6Li NMR spectrum with 15N single frequency decoupling at 81.6 ppm; (D) 6Li NMR spectrum with 15N single-frequency decoupling at 97.8 ppm; (E) 6Li NMR spectrum with 15N single-frequency decoupling at 102.8 ppm.
Figure XVI. NMR spectra of a sample containing 0.10 M [\textsuperscript{6}\text{Li},\textsuperscript{15}\text{N}]LiPMP and 5 equiv of sparteine in 2:1 toluene:pentane at -100 °C. (A) \textsuperscript{6}\text{Li} NMR spectrum; (B) \textsuperscript{15}\text{N} NMR spectrum; (C) \textsuperscript{6}\text{Li} NMR spectrum with \textsuperscript{15}\text{N} single-frequency decoupling at 94.4 ppm; (D) \textsuperscript{6}\text{Li} NMR spectrum with \textsuperscript{15}\text{N} single-frequency decoupling at 94.9 ppm.
Figure XVII. $^6$Li NMR spectra of samples containing 0.1 M $[^6$Li]$\text{LDA}$ in 2:1 toluene:pentane at -100 °C. The samples also contain: (A) 2 equiv of THF and 2 equiv of TMEDA; (B) 5 equiv of THF and 5 equiv of TMEDA; (C) 2 equiv of THF and 5 equiv of TMEDA; (D) 5 equiv of THF and 2 equiv of TMEDA; (E) 2 equiv of TMCDA and 5 equiv of THF; (F) 2 equiv of TMCDA and 20 equiv of THF; (G) 2 equiv of dipyrrolidinoethane and 2 equiv of THF.
Figure XVIII. $^6\text{Li}$ NMR spectra of samples containing 0.1 M $[^6\text{Li}]$LDA in 2:1 toluene:pentane at -100 °C. The samples also contain: (A) 2 equiv of THF and 2.1 equiv EtMeNCH$_2$CH$_2$NMMe$_2$; (B) 2 equiv of THF and 5.3 equiv EtMeNCH$_2$CH$_2$NMMe$_2$; (C) 5 equiv of THF and 2 equiv of Me$_2$NCH$_2$CH$_2$N(CH$_2$)$_4$; (D) 10 equiv of THF and 2 equiv of Me$_2$NCH$_2$CH$_2$N(CH$_2$)$_4$; (E) 2 equiv of THF and 2 equiv of Me$_2$NCH$_2$CH$_2$NEt$_2$. 
Figure XIX. $^6$Li NMR spectra of samples containing 0.1 M $[^6$Li$]$LDA in 2:1 toluene:pentane at -100 °C. The samples also contain: (A) 2 equiv of THF and 2 equiv of trans-2-(dimethylamino)-methoxycyclohexane; (B) 2 equiv of THF and 5 equiv of trans-2-(dimethylamino)-methoxycyclohexane; (C) 2 equiv of THF and 3.4 equiv of MeOCH$_2$CH$_2$N(CH$_2$)$_4$; (D) 2 equiv of THF and 9 equiv of MeOCH$_2$CH$_2$N(CH$_2$)$_4$; (E) 2 equiv of THF and 10 equiv of MeOCH$_2$CH$_2$N(CH$_2$)$_5$; (F) 2 equiv of THF and 2 equiv of EtOCH$_2$CH$_2$N(CH$_2$)$_4$; (G) 2 equiv of THF and 5 equiv of EtOCH$_2$CH$_2$N(CH$_2$)$_4$; (H) 2 equiv of THF and 10 equiv of EtOCH$_2$CH$_2$N(CH$_2$)$_4$. 