NMR Spectroscopic Studies of Lithium Diethylamide: Insights into Ring Laddering

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Abstract: [6]Li and ^{15}N NMR spectroscopic studies of lithium diethylamide (Et$_2$NLi) solvated by oxetane, THF, and Et$_2$O are described. Four-, five-, and six-rung ladders, as well as cyclic dimers and trimers, are identified. In addition, dynamic processes within the trimers and ladders are detected. The symmetries of the aggregates facilitated the determination of relatively complex solution structures and equilibria.

Introduction

Over the last two decades a consortium of European chemists have carried out detailed investigations of *N*-lithiated species including lithium imides (R$_2$C=NLi, **1**) and lithium amides

1   **2**   **3**

4   **5**
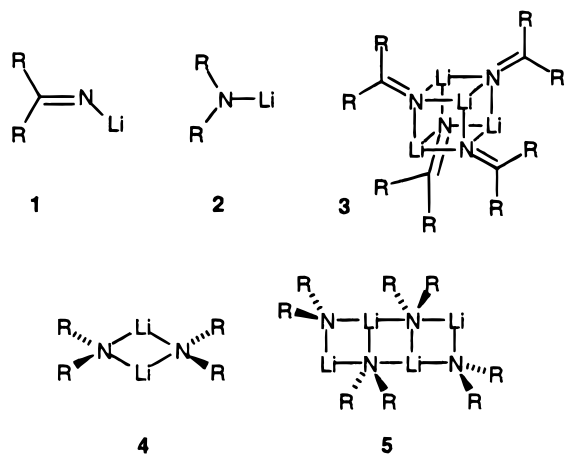
(R$_2$NLi, **2**) using a range of crystallographic, spectroscopic, and computational methods.[1] From their distinctly inorganic perspective and in large part due to their crystallographic investigations of the lithium imides, they have developed the general principles underlying "ring stacking" and "ring laddering". Lithium imides often crystallize from hydrocarbons as prismatic oligomers such as **3** — a vertical stack of two or more (LiN)$_n$ rings. If R is small or planar, this stacking can often be extensive. Although spectroscopic investigations of lithium imides are considerably less exhaustive, there is evidence that the prismatic structures persist in solution.[1]

Lithium dialkylamides (**2**) also show a strong tendency to form oligomers, but are more sterically congested than the corresponding lithium imides (**1**). The basic structural building blocks are again (LiN)$_n$ rings, but in contrast to the lithium imides, the R groups on the lithium amide nitrogen are orthogonal to the (LiN)$_n$ planes. As a consequence, lithium dialkylamides generally crystallize and exist in solution as cyclic oligomers (primarily cyclic dimers, **4**).[1,2] Lithium dialkylamide ladders (**5**) and cyclic ladders (prisms) have been documented rarely and only in the least hindered cases.[3−5]

Our group's distinctly organic perspective has led us to focus upon lithium dialkylamides that are commonly employed in organic synthesis and emphasize the relationship between solution structures and reactivities. While we have observed R$_2$NLi/LiX mixed trimers and tetramers displaying spectral data consistent with laddering,[6] we have not detected ladders of homonuclear lithium dialkylamides to date.

We describe herein [6]Li and ^{15}N NMR spectroscopic studies of lithium diethylamide (Et$_2$NLi) solvated by Et$_2$O, THF, and the strongly coordinating[7] oxetane. Et$_2$NLi was chosen due to its role in organic synthesis[8] and to provide a benchmark for the more sterically hindered analogues such as lithium diisopropylamide (LDA), lithium hexamethyldisilazide (LiHMDS), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP).[2] We will

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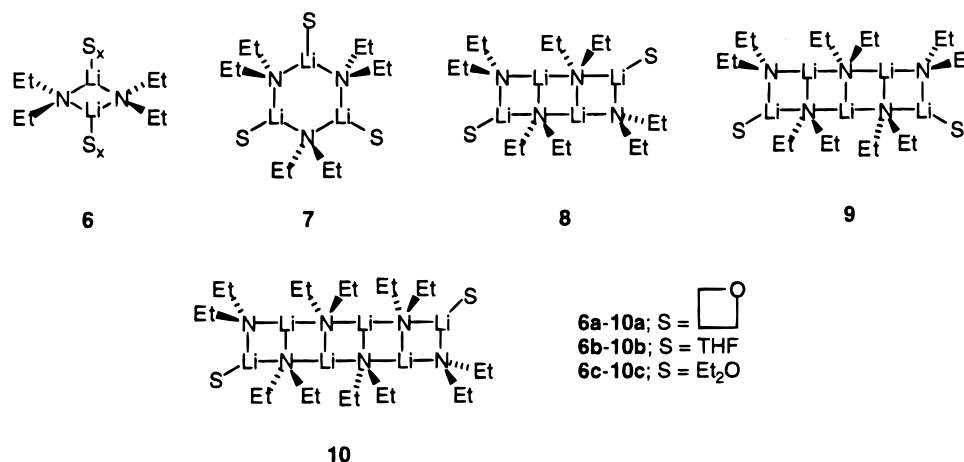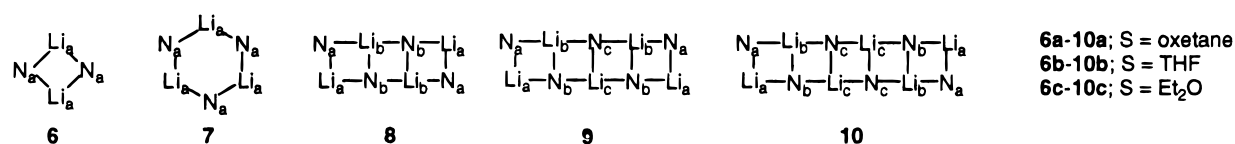
(2) Collum, D. B. *Acc. Chem. Res.* **1993**, *26*, 227. Also see ref 6.

(3) Open and cyclic ladders (prisms) of lithium dialkyl-amides (R$_2$NLi)$_n$: Barr, D.; Clegg, W.; Hodgson, S. M.; Lamming, G. R.; Mulvey, R. E.; Scott, A. J.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1241. Boche, G.; Langlotz, I.; Marsch, M.; Harms, K.; Nudelman, N. E. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1205. Gardiner, M. G.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 4047. Gardiner, M. G.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 4162. Gardiner, M. G.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4206. Also see ref 16.

(4) A polymer of lithium diisopropylamide has been observed. Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1991**, *113*, 8187.

(5) Open and cyclic ladders (prisms) of lithium monoalkylamides (RNHLi)$_n$: Kowach, G. R.; Warren, C. J.; Haushalter, R. C.; DiSalvo, F. J. *Inorg. Chem.* **1998**, *37*, 156. Clegg, W.; Liddle, S. T.; Mulvey, R. E.; Robertson, A. *Chem. Commun.* **1999**, 511. Kennedy, A. R.; Mulvey, R. E.; Robertson, A. *Chem. Commun.* **1998**, 89. Clegg, W.; Horsburgh, L.; Mackenzie, F. M.; Mulvey, R. E. *J. Chem. Soc., Chem. Commun.* **1995**, 2011. Barnett, N. D. R.; Clegg, W.; Horsburgh, L.; Lindsay, D. M.; Liu, Q.; Mackenzie, F. M.; Mulvey, R. E.; Williard, P. G. *Chem. Commun.* **1996**, 2321. Aubrecht, K. B.; Lucht, B. L.; Collum, D. B. *Organometallics* **1999**, *18*, 2981.

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(7) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1995**, *117*, 9863.

Chart 1

6a-10a; S = ▢
6b-10b; S = THF
6c-10c; S = Et₂O

Chart 2

6a-10a; S = oxetane
6b-10b; S = THF
6c-10c; S = Et₂O

Table 1. ^{6}Li and ^{15}N NMR Spectral Data[a]

structure	T, °C	^{6}Li, δ (mult, J_{LiN})			^{15}N, δ (mult, J_{LiN})		
		Li$_a$	Li$_b$	Li$_c$	N$_a$	N$_b$	N$_c$
6a	−110	0.75 (t, 4.7)			47.7 (qt, 4.7)		
7a	−105	1.27 (q, 3.5)			44.8 (st, 3.3)		
7a	−125	1.21 (t, 5.2)			44.9 (qt, 5.1)		
8a	−105	1.15 (t, 4.6)	1.81 (m)		46.5 (m)	33.9 (m)	
8a	−125	0.63 (m)	1.85 (m)		45.7 (m)	34.7 (m)	
9a	−105	0.83 (dd, 2.7,5.4)	1.60 (m)	1.95 (m)	44.9 (m)	34.4 (m)	32.7 (m)
10a	−105	0.93 (m)	1.56 (m)	1.86 (m)	44.7 (m)	33.5 (m)	33.9 (m)
6b	−115	1.51 (t, 5.1)			46.5 (qt, 4.9)		
7b	−115	1.78 (q, 3.5)			43.1 (st, 3.4)		
8b	−87	1.99 (t, 4.8)	1.83 (m)		46.5 (m)	33.6 (m)	
6c	−100	2.51 (t, 5.1)			43.8 (qt, 5.3)		

[a] Spectra were recorded on samples containing 0.1−0.15 M total lithium concentration (normality). Coupling constants were measured after resolution enhancement. Multiplicities are denoted as follows: d = doublet, dd = doublet of doublets, t = triplet, q = quartet, qt = quintet, st = septet, m = multiplet. The chemical shifts are reported relative to 0.3 M ^{6}LiCl/MeOH at −90 °C (0.0 ppm) and neat Me₂NEt at −90 °C (25.7 ppm). All J values are reported in hertz.

show that Et₂NLi tends to form a mixture of structures including a number of ladders (Chart 1).

Results

Lithiation of [^{15}N]Et₂NH using recrystallized [^{6}Li]*n*-BuLi[9] affords [^{6}Li,^{15}N]Et₂NLi as a hydrocarbon-insoluble white solid. Recrystallization from hexane/diethyl ether and evacuation affords solvent-free [^{6}Li,^{15}N]Et₂NLi. ^{6}Li and ^{15}N NMR spectra were recorded using methods described previously.[2] A combination of single-frequency decoupling,[10] broad-band decoupling, and ^{6}Li,^{15}N-heteronuclear multiple quantum correlation (HMQC) spectroscopy[11] provided the ^{6}Li−^{15}N resonance correlations critical to the structural assignments. In some cases, analyses

at several temperatures to exploit the highly temperature-dependent chemical shifts were necessary to deconvolute the complex spectra. The spectral data are summarized in Table 1, and the spectra are given in the Supporting Information. The discussion of individual resonances refers to the partial structures **6**−**10** depicted in Chart 2.

Oxetane. Although oxetane affords the most complex equilibria involving five distinct species, it also offers optimal solubility and the clearest structural assignments. Spectra recorded on [^{6}Li,^{15}N]Et₂NLi (0.1 M) in neat oxetane (15.4 M) show exclusively cyclic dimer **6a** containing an indeterminate number of coordinated oxetane ligands. As the oxetane concentration is decreased using pentane/toluene mixtures as cosolvent, cyclic trimer **7a** appears, becomes the major species at <9.0 equiv of oxetane per lithium, and remains dominant even at <1.0 equiv of oxetane per lithium (Figure 1). Dimer **6a** appears as a ^{6}Li triplet and ^{15}N quintet characteristic of all cyclic oligomers. ^{6}Li-detected ^{15}N zero-quantum NMR spectroscopy[12] confirmed **6a** to be a dimer rather than a higher cyclic

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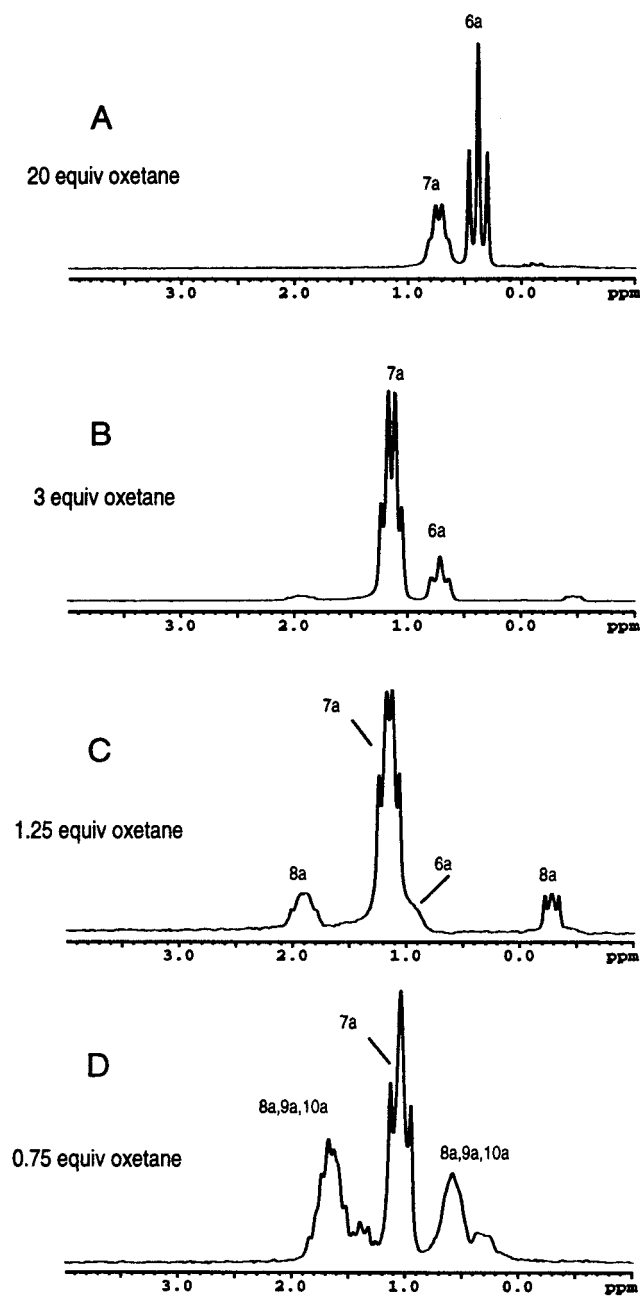
Figure 1. ^{6}Li NMR spectra of 0.1 M [^{6}Li,^{15}N]Et$_2$NLi in 3:2 pentane–toluene at −115 °C with (A) 20 equiv of oxetane, (B) 3 equiv of oxetane, (C) 1.25 equiv of oxetane, and (D) 0.75 equiv of oxetane.

oligomer. At intermediate temperatures (−105 °C) trimer **7a** exhibits a ^{6}Li quartet and an ^{15}N septet initially attributed to a cubic tetramer (**11**). However, at reduced probe temperature (−125 °C), the ^{6}Li quartet simplifies to a ^{6}Li triplet (Figure 2A,B) while the ^{15}N septet simplifies to an ^{15}N quintet.[13] This spectroscopic behavior is consistent with a rapid *intra-aggregate* exchange[14] in which all ^{6}Li and ^{15}N nuclei exchange slowly on the NMR time scale only at the lowest temperatures. The preference for **7a** at low oxetane concentrations indicates a lower per-lithium solvation number compared to dimer **6a**.

A number of additional resonances begin to appear at <3.0 equiv of oxetane per lithium (Figure 1). ^{15}N broad-band

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(13) At >6.0 equiv of oxetane (per lithium), the ^{6}Li quartet and ^{15}N septets become broad mounds while two minor ^{15}N resonances appear. We suspect that different solvation states of the static lithium trimer or a static three-rung ladder are forming.
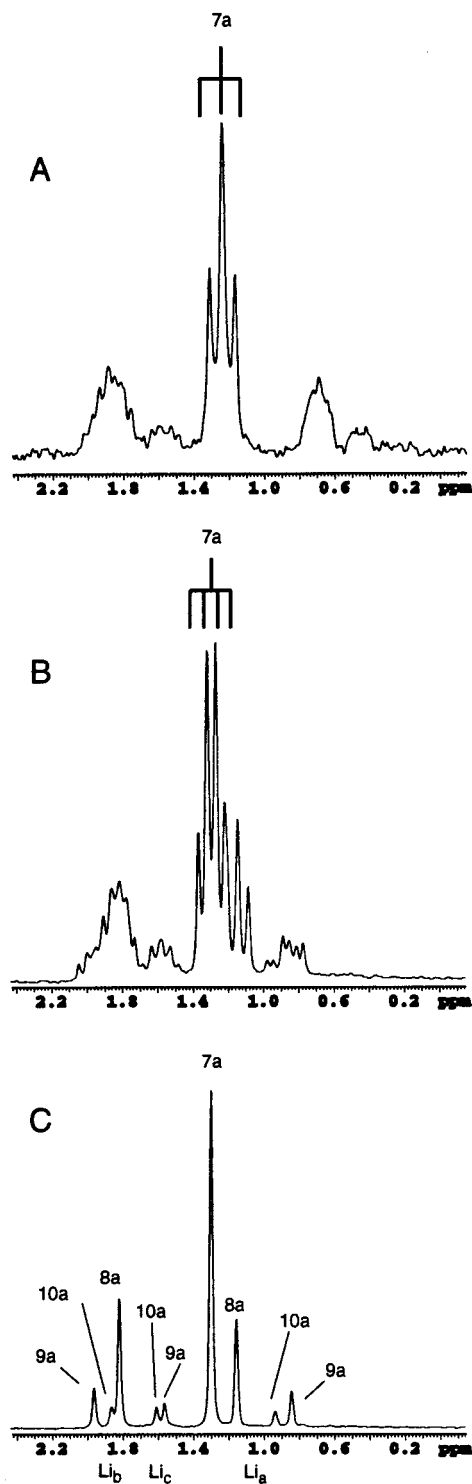

Figure 2. ^{6}Li NMR spectra of 0.15 M [^{6}Li,^{15}N]Et$_2$NLi in 3:2 pentane–toluene with 0.75 equiv of oxetane: (A) ^{6}Li NMR spectrum at −125 °C; (B) ^{6}Li NMR spectrum at −105 °C; and (C) ^{6}Li{^{15}N} NMR spectrum at −105 °C.

irradiation of [^{6}Li,^{15}N]Et$_2$NLi (0.15 M) containing 0.75 equiv of oxetane affords a ^{6}Li NMR spectrum containing eight resonances in addition to those attributed to **7a** (Figure 2).
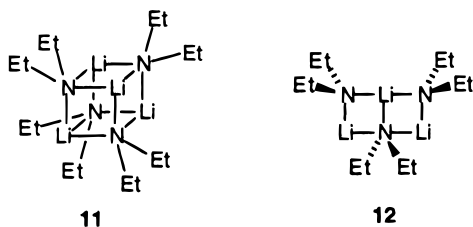
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Despite the problems presented by the complex mixtures and complex structures, the symmetries of ladders **8a**−**10a** allowed for compelling assignments.

Oligomer **8a** exhibits two ^{6}Li resonances (1:1) and two ^{15}N resonances (1:1) showing coupling consistent with the ladder topology. Single-frequency irradiation of the resonance corresponding to N_a (−125 °C) causes the anticipated collapse of Li_a to a doublet and Li_b to a triplet (Chart 2). Similarly, irradiation of N_b causes the collapse of Li_a and Li_b to doublets. A ^{6}Li,^{15}N-HMQC spectrum[11] recorded at −125 °C on [^{6}Li,^{15}N]Et$_2$NLi (0.1 M, 0.88 equiv oxetane) confirmed the assignment as ladder **8a**. Once again, however, an unanticipated dynamic process proved confusing at the outset. Single-frequency irradiation of either N_a or N_b of **8a** at a higher temperature (−105 °C) causes *both* Li_a and Li_b to collapse to singlets. In addition, the complex multiplets corresponding to Li_a and Li_b observed at lower temperature (−125 °C) become notably sharper and simplify at −105 °C (especially the multiplet corresponding to Li_a). We attribute this behavior to an intra-aggregate exchange within ladder **8a** that is slow enough at −105 °C to afford discrete ^{6}Li and ^{15}N resonances, yet sufficiently fast to allow essentially a spin-saturation transfer. Both one- and two-dimensional ^{6}Li−^{6}Li exchange (EXSY)[15] spectra recorded at −105 °C confirmed the Li_a−Li_b exchange within the 4-rung ladder **8a**.

The remaining six ^{6}Li resonances observable in the samples containing 0.75 equiv of oxetane are assigned to five- and six-rung ladders **9a** and **10a** by exploiting their highly characteristic symmetries. The five-rung ladder **9a** displays three resonances in 2:2:1 ratios, while the six-rung ladder **10a** displays three resonances in 1:1:1 (2:2:2) ratios. Ladders **9a** and **10a** (as well as **8a**) display ^{15}N resonances clustered in two distinct regions of the ^{15}N spectrum characteristic of the external (N_a) or internal (N_b and N_c) sites. Although totally selective decouplings were not possible, regional decoupling afforded connectivities fully consistent with the assignments. A ^{6}Li,^{15}N-HMQC spectrum[11] provided further support (Figure 3). In contrast to the 4-rung ladder, no unusual exchange processes were detected in **9a** or **10a**.

THF. Spectra recorded on [^{6}Li,^{15}N]Et$_2$NLi (0.1 M) in neat THF reveal a ^{6}Li triplet and an ^{15}N quintet. A ^{6}Li-detected ^{15}N zero-quantum NMR spectrum[12] confirms this species as the cyclic dimer **6b**. Dimer **6b** persists at all THF concentrations; however, at low THF concentrations (2−10 equiv) a minor ^{6}Li quartet and an ^{15}N septet are readily observable. Although cooling the probe to −130 °C fails to simplify the ^{6}Li quartet to a triplet expected for trimer **7b**, drawing analogy to the oxetane-solvated trimer **7a** strongly implicates **7b** rather than tetramer **11**.

Figure 3. ^{6}Li,^{15}N-heteronuclear multiple quantum correlation (HMQC) spectrum of 0.1 M [^{6}Li,^{15}N]Et$_2$NLi in 3:2 pentane−toluene with 0.75 equiv of oxetane at −105 °C.

Spectra recorded on samples containing 1.0 equiv of THF display an ensemble of overlapping ^{6}Li multiplets shown by broad-band ^{15}N irradiation to be comprised of four discrete ^{6}Li resonances. The chemical shifts are highly temperature dependent, making assignments possible by varying the probe temperature. A ^{6}Li,^{15}N-HMQC experiment[11] at −87 °C offers the clearest structural assignment, showing the two major peaks (1:1) to derive from four-rung ladder **8b** and the two minor peaks deriving from dimer **6b** and trimer **7b**. Ladder **8b** is present in higher proportions at higher temperatures. Higher-order ladders **9b** and **10b** are not observed within the solubility limits of Et$_2$NLi.

Diethyl Ether. [^{6}Li,^{15}N]Et$_2$NLi dissolves only with ≥5 equiv of Et$_2$O, affording a single species displaying a ^{6}Li triplet and an ^{15}N quintet characteristic of a cyclic oligomer. A ^{6}Li-detected ^{15}N zero-quantum NMR experiment[12] confirms that this species is the cyclic dimer **6c**.

Discussion

Ring laddering of *N*-lithiated species is well documented by crystallographic methods, with additional support provided by computational and NMR spectroscopic studies.[1] The investigations of [^{6}Li,^{15}N]Et$_2$NLi described herein provide an unusually clear view of lithium dialkylamide ladders in solution (Chart 1). The most striking examples come from Et$_2$NLi/oxetane mixtures in which low oxetane concentrations afford 4-, 5-, and 6-rung ladders **8a**−**10a** and cyclic trimer **7a**. The analogous 3-rung ladder **12** is conspicuously absent. These higher oligomers give way to exclusively cyclic dimer **6a** at high oxetane concentrations. When THF is used in place of the strongly coordinating oxetane, a slight drop in solubility is accompanied by measurably different solution behaviors. Dimer **6b** is the sole observable form at the highest concentrations of THF. The four-rung ladder **8b**, cyclic trimer **7b**, and cyclic dimer **6b** are present at the lowest THF concentrations. Last, the poor solubility of Et$_2$NLi in Et$_2$O coincides with the formation of only cyclic dimer **6c**.

We have taken the liberty of depicting solvation numbers on oligomers **6**−**10** (Chart 1) in the absence of definitive assignments. What we can say is that the shifting oligomer distribu-

11

12

(15) (a) One-dimensional exchange spectroscopy: Hoffman, R. A.; Forsén, S. *J. Chem. Phys.* **1966**, *45*, 2049. Dahlquist, F. W.; Longmuir, K. J.; Du Vernet, R. B. *J. Magn. Reson.* **1975**, *17*, 406. Morris, G. A.; Freeman, R. A. *J. Magn. Reson.* **1978**, *29*, 433. (b) Two-dimensional EXSY: Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546. Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033.
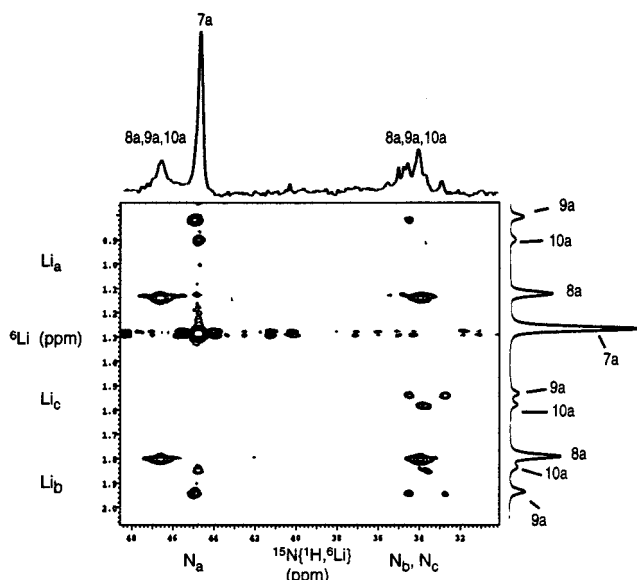
tions, with changes in solvent concentrations, reveal that the per-lithium solvation numbers follow the orders (1) **6a** > **7a** > **8a** > **9a** > **10a** and (2) **6b** > **7b** > **8b**. Crystallographic and computational studies are fully consistent with the ladders being capped by solvents only on the ends.[16] The preference for cyclic trimer **7a** over 3-rung ladder **12** possibly implicates an advantage of forfeiting a transannular linkage in **12** for an additional oxetane−Li interaction in **7a**. Although substantial evidence suggests that the cyclic trimers are not strongly solvated for hindered lithium dialkylamides,[17] a trisolvated trimer for such a sterically unhindered amide seems reasonable. Moreover, the persistence of trimer **7a** even at relatively high oxetane concentrations is in accord with the assignment. If **7a** is indeed a trisolvate, then cyclic dimer **6a** would, by inference, be assigned as either a tri- or tetrasolvated dimer. Although this is not consistent with spectroscopic investigations of more steri-cally congested lithium dialkylamides,[7] once again it seems quite reasonable for such an unhindered lithium amide. Even so, it is less clear whether similar conclusions can be drawn for the THF- and Et$_2$O-solvated cyclic dimers and trimers.

Several interesting and initially confusing dynamic processes surfaced during the structural studies. For example, cyclic trimer **7a** undergoes an intra-aggregate exchange. The consequent coupling of all three ^{6}Li nuclei with all three ^{15}N nuclei afford a ^{6}Li quartet and ^{15}N septet in the fast exchange limit. This could be incorrectly attributed to a prismatic structure such as cubic tetramer **11** if the slow exchange limit showing a cyclic oligomer connectivity had not been attained. The mechanism of this intra-aggregate exchange is not at all obvious. Four-rung ladder **8a** also displays an intra-aggregate exchange of the external and internal lithium sites (Li$_a$ and Li$_b$). Although the exchange is sufficiently slow to afford two distinct resonances, it was detected by single-frequency decoupling experiments and confirmed by one- and two-dimensional ^{6}Li−^{6}Li EXSY spec-troscopy.

In summary, the structures elucidated in this study provide compelling evidence that lithium dialkylamides can form ladders in solution and contribute to the "laddering principle" developed by Snaith and co-workers.[1] The synthetic importance of lad-dering in organolithium solution chemistry is not immediately clear at this time. However, we are only now beginning to understand how lithium amide structure influences reactivity. Our investigations of lithium amide reactivities often reveal the importance of structural features only after the fact. The study also highlights how ^{6}Li and ^{15}N NMR spectroscopies comple-ment the crystallographic methods and underscores the impor-tance of aggregate symmetries in determining solution structures.

Experimental Section

Reagents and Solvents. All solvents and ligands were distilled from blue or purple solutions containing sodium benzophenone ketyl. The hydrocarbon stills contained 1% tetraglyme to dissolve the ketyl. ^{6}Li metal (95.5% enriched) was obtained from Oak Ridge National Laboratory. The [^{6}Li]*n*-butyllithium used to prepare the [^{6}Li,^{15}N]-Et$_2$NLi was prepared and purified as described previously.[9] The synthesis of [^{15}N]Et$_2$NH and general protocols are described in the Supporting Information.

NMR Spectroscopic Analyses. Samples for spectroscopic analyses were prepared as described in detail elsewhere.[6] Standard ^{6}Li and ^{15}N NMR spectra were recorded on a Varian XL-400 spectrometer operating at 58.8 and 40.5 MHz (respectively) or on a Varian Unity 500 spectrometer operating at 73.6 and 58.8 MHz, respectively. The ^{6}Li and ^{15}N resonances are referenced to 0.3 M [^{6}Li]LiCl/MeOH at −90 °C (0.0 ppm) and neat Me$_2$NEt at −90 °C (25.7 ppm), respectively. The ^{6}Li,^{15}N-HMQC spectra[11] were recorded on the Varian Unity 500 spectrometer equipped with a custom-built 3-channel probe designed to accommodate ^{6}Li and ^{15}N pulses with concurrent proton decoupling. The ^{6}Li-detected ^{15}N zero-quantum NMR spectra[12] were recorded using the same spectrometer configuration as for the ^{6}Li,^{15}N-HMQC experi-ments with a pulse sequence described previously.[11] The ^{6}Li-^{6}Li exchange (EXSY) experiments were also recorded on the Varian Unity 500 spectrometer and the custom-built 3-channel probe using known protocols.[15]

Supporting Information Available: ^{6}Li and ^{15}N NMR spectra and syntheses of labeled compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA992169M

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