Polymorphism in Lithium Amides: A Structural and Theoretical Study. Synthesis, Mechanism, and NMR Studies of the Lithiation of *N,N′*-Di-*tert*-butylethylenediamine

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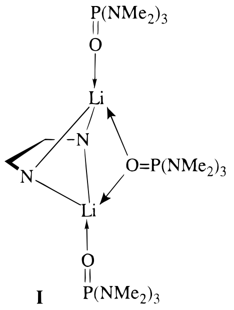
The lithiation of *N,N′*-di-*tert*-butylethylenediamine by MeLi in benzene has been shown by ^{1}H NMR spectroscopy to proceed *via* the partially lithiated species [*cis*-{Li[*μ*-N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$], **2**, and [{Li[N(*t*-Bu)$CH_2$$CH_2$N(H)*t*-Bu]}$_2$Li{N(*t*-Bu)$CH_2CH_2$N*t*-Bu}Li], **3**, prior to the formation of the dilithiated species {Li[N(*t*-Bu)CH_2CH_2N*t*-Bu]Li}, **4**. The solid state structures of **2**, **3**, and a dimeric form of **4** (**4a**) have been determined. A sparingly soluble form of **4** (**4b**) has also been isolated which has a proposed polymeric ladder structure. These structures are discussed with respect to the alternatives available for the aggregation of the dilithiated species; stacking to form dimeric Li_4N_4 cages and laddering to form Li_nN_n ladders. *Ab initio* molecular orbital calculations give insight into the energetics of these aggregates and the possible structures adopted by solvated and unsolvated dilithium ethylenediamide complexes. Crystals of **2** are monoclinic, of space group *C*2/*c* (No. 15), $a = 19.222(7)$, $b = 8.734(2)$, $c = 17.149(5)$ Å, $\beta = 119.40(1)°$, $Z = 4$. Crystals of **3** are monoclinic, of space group $P2_1/c$ (No. 14), $a = 9.836(8)$, $b = 17.821(3)$, $c = 21.78(2)$ Å, $\beta = 101.57(4)°$, $Z = 4$. Crystals of **4a** are monoclinic, of space group $P2_1/c$ (No. 14), $a = 15.990(7)$, $b = 10.0162(9)$, $c = 16.42(1)$ Å, $\beta = 104.49(2)°$, $Z = 4$. Crystals of **6** are monoclinic, of space group $P2_1/c$ (No. 14), $a = 10.124(8)$, $b = 17.861(3)$, $c = 22.21(2)$ Å, $\beta = 102.05(4)°$, $Z = 4$.

Introduction

The interest in the structural chemistry of group 1 metal complexes has escalated in recent years in response to the need to understand the nature of these synthetically important compounds in organic synthesis and metathesis reactions in transition metal organometallic chemistry, for example. Specifically, in amidolithium chemistry this has resulted in an understanding of the aggregation of "simple amide" complexes, but much has yet to be systematized for the association of polylithiated and functionalized lithium amide compounds.[1,2] The formation of polymeric/cyclic oligomeric aggregates featuring Li_nN_n ladder cores has been found to be the preferential aggregation mode for simple lithium amide species by extensive *ab initio* molecular orbital calculations on unsolvated and solvated model compounds. Despite this, there is a lack of direct experimental evidence to support this, in fact the only polymeric lithium amide yet to be structurally characterized in the solid state, {Li(*μ*-N*i*-Pr$_2$)}$_n$ (= LDA), exhibits a coiled linear Li_nN_n framework.[3] The solid state structures of [{LiN(CH_2)$_4$}$_4$(*N,N,N′,N′*-tetramethylethylenediamine)$_2$][4] and [{LiN(CH_2)$_4$}$_6$(N,N,N′,N″,N″-pentamethyldiethylenetriamine)$_2$][5] which exhibit four-rung ladder Li_4N_4 cores have given credence to the suggestion that the structure of unsolvated lithium pyrrolidide is an indefinite length ladder. Similarly, the partially lithiated piperidide−piperidine complex [{Li[N(CH_2)$_5$][HN(CH_2)$_5$]}$_4$][6] exhibits the same Li_4N_4 structural framework and this is suggestive of a polymeric ladder for the structure of the completely lithiated complex. This complex is one of the few examples of characterized lithiation intermediates in the literature.[7,8]

We have focused attention on *N*-substituted lithiated ethylenediamines in this and previous papers.[9,10] Structural investigations thus far have yielded intriguing results which demonstrate the number of options available for the aggregation of these species. Monomeric and dimeric complexes ([(hexamethylphosphoramide)$_3$Li$_2${N(Ph)CH_2}$_2$],[11] **I**, and [{Li[N(SiMe$_3$)$CH_2$$CH_2$NSiMe$_3$]Li·OEt$_2$}$_2$],[10] **II**) have been isolated for oxygen donor solvated species while unsolvated dimers and trimers have been observed for unsolvated cases ([{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N*t*-Bu]Li}$_2$],[9] **III**, [{Li$_2$[N(2,6-*i*-Pr$_2$$C_6H_3$)$CH_2$]$_2$}$_2$],[12] **IV**, and [{Li[N(SiMe$_3$)CH_2CH_2NSiMe$_3$]Li}$_3$],[10] **V**).



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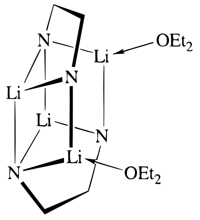

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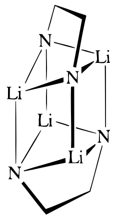

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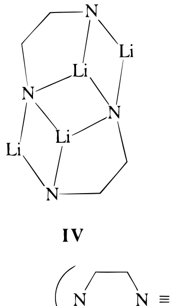

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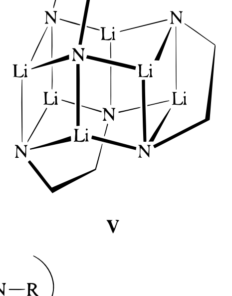

V

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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Herein we report the synthesis of the lithium amides produced by the lithiation of *N*,*N*′-di-*tert*-butylethylenediamine, **1**, by alkyllithium species. The compounds [*cis*-{Li[*μ*-N(*t*-Bu)-CH$_2$CH$_2$N(H)*t*-Bu]}$_2$], **2**, and [{Li[N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$-Li{N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu}Li], **3**, are formed prior to the completely dilithiated species {Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}, **4**, which can be isolated in two forms exhibiting either a dimeric Li_4N_4 cage, **4a**, or possibly a polymeric Li_nN_n ladder, **4b**. NMR studies have shown that these species are the only compounds present in solution during the lithiation of **1** by methyllithium in benzene. The structures of **2** and **3** provide mechanistic information of the early stages of ladder formation and direct evidence for the assembly of polymeric structures in amidolithium chemistry including identification of the end groups present in ladder formation. *Ab initio* molecular orbital calculations have been used to investigate the energetics of aggregation of these complexes. The calculations show that of the species featuring the "dilithium bridged" Li_2N_2 ring of the monomer (*viz*, the Li_4N_4 cage of **4a** and the Li_nN_n ladder of **4b**), polymeric ladders are energetically favored over stacked dimers. This is despite the seemingly ideal geometry of the monomeric unit having a butterfly-shaped Li_2N_2 ring necessary for the stacking of amidolithium compounds without any steric congestion.

Experimental Section

Syntheses. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried then freeze/thaw degassed prior to use. *N*,*N*′-Di-*tert*-butylethylenediamine, **1**, was prepared according to a literature procedure.[13] [{Li[N(SiMe$_3$)CH$_2$CH$_2$NSiMe$_3$]Li·OEt$_2$}$_2$], **5**, was prepared by our literature procedure.[10] *n*-BuLi was obtained from Metallgesellschaft (AG), Germany, as a 1.60 M solution in hexanes and was standardized prior to use. All other reagents were obtained from Aldrich. ^{1}H NMR spectra were recorded on Bruker WM-250 and Varian Gemini-200 and Unity-400 spectrometers in deuterated benzene and toluene and referenced to the residual ^{1}H resonances of the solvent (*δ* 7.15 and 6.98, respectively). ^{7}Li NMR spectra were recorded on a Varian Unity-400 spectrometer operating 155.5 MHz, respectively, in deuterated benzene and referenced to external LiNO$_3$ (1 M in D$_2$O, *δ* 0.00). ^{13}C NMR spectra were recorded in deuterated benzene on Bruker WM-250 and Varian Gemini-200 spectrometers operating at 162.8 and 50 MHz, respectively, using broad band proton decoupling and were referenced to the ^{13}C resonances of the deuterated solvents (*δ* 128.0). Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, and the Chemical and MicroAnalytical Services Pty. Ltd., Melbourne. Melting points were determined in sealed glass capillaries under argon and are uncorrected. IR spectra were recorded as Nujol mulls on NaCl plates using a Perkin-Elmer 1725X Fourier-transformed infrared spectrometer.

Synthesis of [*cis*-{Li[*μ*-N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$], 2. To a stirred solution of *N*,*N*′-di-*tert*-butylethylenediamine, **1** (4.90 g, 28.43 mmol), in hexane (10 mL) was added *n*-BuLi (18.5 mL, 1.54 M, 28.43 mmol) dropwise over 10 min at 0 °C. The pale yellow solution was warmed to room temperature and stirred for 1 h. The solution was concentrated *in vacuo* and cooled to −30 °C, whereupon colorless crystals of **2** deposited overnight. Subsequent cropping of the crystals yielded further product (4.61 g, 91% yield). Mp 117−120 °C, >145 °C (dec); ^{1}H NMR (250 MHz, C$_6$D$_6$) *δ* 0.39 (2 H, b, NH), 0.93, 1.44 (2 × 18 H, bs, Me), 2.70 (4 H, bs, N−CH$_2$), 3.06 (2 H, bs, N−CH$_2$), 3.43 (2 H, bs, N−CH$_2$); ^{13}C NMR (62.8 MHz, C$_6$D$_6$) *δ* 28.9, 31.6 (Me), 45.2 (N−CH$_2$), 50.4 (N−*C*Me$_3$), 51.2 (N−CH$_2$), 53.8 (N−*C*Me$_3$); ^{7}Li NMR (155.5 MHz, C$_6$D$_6$) *δ* 2.32; found C 67.30, H 13.12, N 15.87, calcd C 67.38, H 13.01, N 15.72.

Synthesis of [{Li[N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$Li{N(*t*-Bu)CH$_2$-CH$_2$N*t*-Bu}Li], 3. Method a. To a stirred solution of *N*,*N*′-di-*tert*-butylethylenediamine, **1** (1.23 g, 7.11 mmol), in hexane (10 mL) was added *n*-BuLi (6.95 mL, 1.54 M, 10.66 mmol) dropwise over 10 min at 0 °C. The pale yellow solution was warmed to room temperature and stirred for 4 h. The solution was concentrated *in vacuo* and cooled to −30 °C, whereupon colorless needles of **3** deposited overnight. Subsequent cropping of the crystals yielded further product with difficulty (1.02 g, 79% yield). Mp 139 °C (dec); ^{1}H NMR (200 MHz, C$_6$D$_6$) *δ* 0.93 (**2**), 0.99 (18 H, s, Me), 1.14 (**4**), 1.38 (18 H, s, Me), 1.41 (18 H, s, Me), 1.44 (**2**), 2.6−3.5 (bm, N−CH$_2$), 3.09 (**4**); ^{13}C NMR (50 MHz, C$_6$D$_6$) *δ* 28.8, 28.9, 30.4, 31.5, 32.0, 32.5 (Me); ^{7}Li NMR (155.5 MHz, C$_6$D$_6$) *δ* 1.39, 1.43, 2.06, 2.31; IR (nujol) υ (cm^{-1}) 3274 (w, N−H); found C 65.67, H 13.57, N 14.98, calcd C 66.64, H 12.68, N 15.54.

Method b. To a stirred solution of [*cis*-{Li[*μ*-N(*t*-Bu)CH$_2$CH$_2$N-(H)*t*-Bu]}$_2$], **2** (1.00 g, 2.81 mmol), in hexane (10 mL) was added *n*-BuLi (0.61 mL, 1.54 M, 0.94 mmol) dropwise over 10 min at 0 °C. The pale yellow solution was warmed to room temperature and stirred for 4 h. The solution was concentrated *in vacuo* and cooled to −30 °C, whereupon colorless needles of **3** deposited overnight. Subsequent cropping of the crystals yielded further product with difficulty (0.75 g, 74% yield). (This product was spectroscopically identical to the above synthesis).

Synthesis of {Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}, 4. To a stirred solution of *N*,*N*′-di-*tert*-butylethylenediamine, **1** (1.00 g, 5.80 mmol), in hexane (10 mL) was added *n*-BuLi (7.5 mL, 1.54 M, 11.60 mmol) dropwise over 10 min at 0 °C. The pale yellow solution was warmed to room temperature and allowed to stand for 6 days. The volume of the solution was halved and slowly cooled to −30 °C, whereupon a microcrystalline sample of **4** (form B) deposited overnight. The product was collected, washed with hexane (2 × 10 mL), and then dried *in vacuo* (0.90 g, 84% yield). Alternatively, after 1 day, rapid cooling of the reaction mixture to −196 °C followed by thawing of the solution to −30 °C yielded crystals of **4** (form A) after 30 min in low yield. Mp 145 °C (dec); ^{1}H NMR (200 MHz, C$_6$D$_6$) *δ* 1.14 (18 H, s, Me), 3.09 (4 H, s, N−CH$_2$); ^{13}C NMR (50 MHz, C$_6$D$_6$) *δ* 30.4 (Me), 50.7 (N−CH$_2$), 53.2 (N−*C*Me$_3$); ^{7}Li NMR (155.5 MHz, C$_6$D$_6$) *δ* 1.52; found C 64.98, H 12.37, N 15.31, calcd C 65.21, H 12.04, N 15.21.

Synthesis of [{Li[N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$Li{N(SiMe$_3$)CH$_2$-CH$_2$NSiMe$_3$}Li], 6. A hexane solution (10 mL) of [*cis*-{Li[*μ*-N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$], **2** (0.61 g, 1.71 mmol), and [{Li[N(SiMe$_3$)CH$_2$-CH$_2$NSiMe$_3$]Li·Et$_2$}$_2$], **5** (0.50 g, 0.86 mmol), was stirred at room temperature for 30 min. The colorless solution was concentrated *in vacuo* and cooled to −30 °C, whereupon colorless needles of **6** deposited overnight. Subsequent cropping of the crystals yielded further product with difficulty (0.55 g, 56% yield). Mp 152−155 °C (dec); ^{1}H NMR (200 MHz, C$_6$D$_6$) *δ* 0.34 (18 H, s, SiMe$_3$), 0.87 (18 H, s, Me), 1.34 (18 H, s, Me), 2.5−3.7 (bs, N−CH$_2$); ^{13}C NMR (50 MHz, C$_6$D$_6$) *δ* 2.7 (b, SiMe$_3$), 29.1, 32.2 (Me); ^{7}Li NMR (155.5 MHz, C$_6$D$_6$) *δ* 1.6−2.3 (b), 2.98; IR (nujol) υ (cm^{-1}) 3267 (w, N−H); found C 58.58, H 12.04, N 14.73, calcd C 58.71, H 11.97, N 14.67.

Structure Determinations. Crystals of **2**, **3**, and **6** suitable for X-ray structure determination were grown from hexane solutions at −30 °C and were mounted in sealed capillaries under an argon atmosphere. Crystals of **4a** suitable for X-ray structure determination were grown from slow thawing of a rapidly frozen hexane solution to −30 °C and were mounted in sealed capillaries under an argon atmosphere. Unique diffractometer data sets were measured using an Enraf-Nonius CAD4 diffractometer at ambient temperature. Reflections with $I > 2.5\sigma(I)$ were considered observed and used in the full matrix least squares refinements, minimizing $\Sigma w\Delta^2$ after solution of the structures by direct methods. Conventional residuals on F at convergence are quoted. No

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Table 1. Crystallographic Data for [*cis*-{Li[μ-N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$] (**2**), [{Li[N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$Li{N(*t*-Bu)CH_2CH_2N*t*-Bu}Li] (**3**), [{Li[N(*t*-Bu)CH_2CH_2N*t*-Bu]Li}$_2$] (**4a**), and [{Li[N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$Li{N($SiMe_3$)CH_2CH_2N$SiMe_3$}Li] (**6**)

2: $C_{20}H_{46}N_4Li_2$	fw 356.49
$a = 19.222(7)$ Å	space group $C2/c$ (No. 15)
$b = 8.734(2)$ Å	$T = 24$ °C
$c = 17.149(5)$ Å	$\lambda = 0.710\ 69$ Å
$\beta = 119.40(1)°$	$\rho_{calcd} = 0.944$ g cm^{-3}
$V = 2508(1)$ Å^3	$\mu = 0.50$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.062$
	$R_w(F_o)^b = 0.059$
3: $C_{30}H_{68}N_6Li_4$	fw 540.67
$a = 9.836(8)$ Å	space group $P2_1/c$ (No. 14)
$b = 17.821(3)$ Å	$T = 24$ °C
$c = 21.78(3)$ Å	$\lambda = 0.71069$ Å
$\beta = 101.57(4)°$	$\rho_{calcd} = 0.960$ g cm^{-3}
$V = 3660.5(5)$ Å^3	$\mu = 0.60$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.058$
	$R_w(F_o)^b = 0.054$
4a: $C_{20}H_{44}N_4Li_4$	fw 368.36
$a = 15.990(7)$ Å	space group $P2_1/c$ (No. 14)
$b = 10.0162(9)$ Å	$T = 24$ °C
$c = 16.42(1)$ Å	$\lambda = 0.71069$ Å
$\beta = 104.49(2)°$	$\rho_{calcd} = 0.958$ g cm^{-3}
$V = 2546(2)$ Å^3	$\mu = 0.51$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.157$
	$R_w(F_o)^b = 0.159$
6: $C_{28}H_{68}N_6Li_4Si_2$	fw 572.82
$a = 10.124(8)$ Å	space group $P2_1/c$ (No. 14)
$b = 17.861(3)$ Å	$T = 24$ °C
$c = 22.21(2)$ Å	$\lambda = 0.71069$ Å
$\beta = 102.05(4)°$	$\rho_{calcd} = 0.969$ g cm^{-3}
$V = 3928(4)$ Å^3	$\mu = 1.12$ cm^{-1}
$Z = 4$	$R(F_o)^a = 0.053$
	$R_w(F_o)^b = 0.053$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Non-hydrogen and Refined Amine Hydrogen Atom Coordinates and Isotropic Thermal Parameters for [*cis*-{Li[μ-N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$] (**2**)

atom	*x*	*y*	*z*	*U*, Å^2
Li	0.4575(3)	0.1957(7)	0.2796(4)	0.051(3)^a
N(1)	0.3691(2)	0.3486(4)	0.2550(2)	0.049(1)^a
N(4)	0.4251(2)	0.1834(3)	0.1486(2)	0.046(1)^a
C(1)	0.3697(2)	0.4542(5)	0.3241(3)	0.060(2)^a
C(2)	0.3723(3)	0.4193(5)	0.1789(3)	0.057(2)^a
C(3)	0.3633(2)	0.2985(5)	0.1109(3)	0.057(2)^a
C(4)	0.4059(2)	0.0510(5)	0.0884(2)	0.054(2)^a
C(11)	0.4493(4)	0.5377(7)	0.3678(4)	0.087(3)^a
C(12)	0.2998(5)	0.5646(9)	0.2849(5)	0.116(4)^a
C(13)	0.3642(4)	0.3540(7)	0.3932(4)	0.077(3)^a
C(41)	0.3400(4)	-0.0508(7)	0.0882(4)	0.088(3)^a
C(42)	0.4821(3)	-0.0437(6)	0.1228(4)	0.076(3)^a
C(43)	0.3797(3)	0.0963(7)	-0.0088(3)	0.074(3)^a
H(1)	0.328(2)	0.301(4)	0.235(2)	0.05(1)

[a] Isotropic equivalent thermal parameters.

Table 3. Non-hydrogen Atom Coordinates and Isotropic Thermal Parameters for [{Li[N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$Li{N(*t*-Bu)CH_2CH_2-N*t*-Bu}Li] (**3**)

atom	*x*	*y*	*z*	*U*, Å^2
Li(1)	0.8631(9)	0.4062(5)	0.7359(4)	0.055(4)^a
Li(2)	0.8747(9)	0.3669(5)	0.6349(4)	0.059(4)^a
Li(3)	0.750(1)	0.2455(5)	0.6128(5)	0.062(4)^a
Li(4)	0.619(1)	0.2510(6)	0.5107(4)	0.063(4)^a
N(1)	0.8305(4)	0.5159(3)	0.7587(2)	0.057(2)^a
N(4)	1.0066(4)	0.4357(2)	0.6885(2)	0.050(2)^a
N(5)	0.7536(4)	0.3141(2)	0.6915(2)	0.049(2)^a
N(8)	0.7155(4)	0.3429(2)	0.5602(2)	0.050(2)^a
N(14)	0.6893(5)	0.1591(2)	0.5571(2)	0.059(2)^a
N(17)	0.4247(5)	0.2015(3)	0.4796(2)	0.068(2)^a
C(1)	0.7076(6)	0.5496(3)	0.7791(3)	0.067(3)^a
C(2)	0.8666(6)	0.5466(3)	0.7012(3)	0.064(3)^a
C(3)	1.0048(6)	0.5167(3)	0.6919(3)	0.063(3)^a
C(4)	1.1486(6)	0.4071(3)	0.6913(3)	0.056(2)^a
C(5)	0.7478(6)	0.2646(3)	0.7458(3)	0.059(2)^a
C(6)	0.6166(6)	0.3325(3)	0.6549(3)	0.057(2)^a
C(7)	0.6261(5)	0.3786(3)	0.5981(3)	0.059(2)^a
C(8)	0.7383(6)	0.3908(3)	0.5073(3)	0.063(3)^a
C(14)	0.8113(7)	0.1136(4)	0.5528(3)	0.076(3)^a
C(15)	0.5661(8)	0.1138(4)	0.5530(3)	0.090(3)^a
C(16)	0.4343(7)	0.1588(4)	0.5370(3)	0.087(3)^a
C(17)	0.2876(7)	0.2345(4)	0.4504(3)	0.075(3)^a
C(11)	0.7006(8)	0.5137(4)	0.8421(3)	0.105(4)^a
C(12)	0.7231(7)	0.6352(4)	0.7889(3)	0.086(3)^a
C(13)	0.5787(6)	0.5332(4)	0.7300(4)	0.107(4)^a
C(41)	1.2269(6)	0.4469(4)	0.6462(3)	0.078(3)^a
C(42)	1.1365(6)	0.3251(3)	0.6716(3)	0.081(3)^a
C(43)	1.2368(6)	0.4122(4)	0.7580(3)	0.091(3)^a
C(51)	0.8931(9)	0.2542(6)	0.7822(4)	0.172(5)^a
C(52)	0.660(1)	0.2959(5)	0.7896(4)	0.181(6)^a
C(53)	0.6940(9)	0.1871(4)	0.7269(3)	0.121(4)^a
C(81)	0.8021(8)	0.4682(4)	0.5278(3)	0.114(4)^a
C(82)	0.8412(9)	0.3505(5)	0.4759(4)	0.134(5)^a
C(83)	0.6074(7)	0.4065(5)	0.4586(3)	0.110(4)^a
C(141)	0.8082(9)	0.0854(5)	0.4858(4)	0.140(5)^a
C(142)	0.9395(7)	0.1637(4)	0.5716(3)	0.093(3)^a
C(143)	0.8316(8)	0.0453(4)	0.5976(4)	0.116(4)^a
C(171)	0.2544(8)	0.2959(5)	0.4928(5)	0.140(5)^a
C(172)	0.1721(7)	0.1752(5)	0.4389(3)	0.107(4)^a
C(173)	0.3046(8)	0.2663(5)	0.3877(4)	0.124(4)^a

[a] Isotropic equivalent thermal parameters.

extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.[14] Computation used the XTAL 3.0[15] program system implemented on a Sun SPARCstation 2 computer. Molecular core geometries, atom coordinates, and crystal data are given in Tables 1−9, and molecular projections showing numbering schemes are given in Figures 2, 4, and 5. Averaged structural parameters will be used in the structural comparisons where appropriate and are distinguished by the absence of the least squares deviation term from the determined quantity. Anisotropic thermal parameters were refined for all non-hydrogen atoms in **2**, **3**, and **6**. All non-hydrogen atoms in **4a** were refined isotropically due to the limited number of observed reflections. All hydrogen atoms were located and refined in *x*,*y*,*z* and U_{iso} for **2**. Methyl and methylene hydrogen atoms for **3**, **4a**, and **6** were calculated and constrained at estimated values (C−H 1.0 Å). Temperature factors for methyl hydrogen atoms for **3**, **4a**, and **6** were estimated at 1.5U_{ii}(average) of the attached carbon atom and 1.25U_{ii}(average) for methylene hydrogen atoms. Amine hydrogen atoms were located and, for **3**, positionally constrained with fixed temperature factors estimated at 1.25U_{ii}(average) of the attached nitrogen atom and refined in *x*,*y*,*z* and U_{iso} for **2**.

Theoretical Calculations

Ab initio molecular orbital calculations (HF) were carried out on model complexes using Gaussian 92/DFT.[16] The structures were found initially either with the minimal basis set STO-3G and then minimized with the 3-21G* basis set or adapted from the crystal structure data of compounds **2**, **3**, **4a**, **5**,[10] and [{Li[N($SiMe_3$)CH_2CH_2N$SiMe_3$]Li}$_3$][10] and minimized directly with the 3-21G* basis set. Structures were then minimized with the

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(14) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(15) XTAL User's Manual - Version 3.0, Hall, S. R., Stewart, J. M., Eds.; The Universities of Western Australia and Maryland, 1990.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/DFT*, Revision G.4; Gaussian, Inc.: Pittsburgh, 1993.

Table 4. Non-hydrogen Atom Coordinates and Isotropic Thermal Parameters for [{Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}$_2$] (**4a**)

atom	*x*	*y*	*z*	*U*, Å^2
Li(1)	0.214(3)	0.630(5)	0.223(3)	0.06(1)
Li(2)	0.319(2)	0.627(4)	0.121(2)	0.025(9)
Li(3)	0.280(3)	0.443(4)	0.178(3)	0.05(1)
Li(4)	0.172(2)	0.592(4)	0.079(3)	0.04(1)
N(1)	0.346(1)	0.599(2)	0.243(1)	0.05(1)
N(4)	0.228(1)	0.770(2)	0.136(1)	0.04(1)
N(5)	0.261(1)	0.473(2)	0.058(1)	0.05(1)
N(8)	0.154(1)	0.468(2)	0.169(1)	0.04(1)
C(1)	0.412(2)	0.530(3)	0.311(2)	0.06(2)
C(11)	0.394(2)	0.380(3)	0.288(2)	0.08(2)
C(12)	0.402(2)	0.549(3)	0.396(2)	0.08(2)
C(13)	0.504(2)	0.562(3)	0.306(2)	0.12(3)
C(2)	0.349(2)	0.741(3)	0.256(2)	0.09(2)
C(3)	0.296(2)	0.824(2)	0.196(2)	0.10(2)
C(4)	0.169(2)	0.875(2)	0.084(2)	0.04(2)
C(41)	0.102(2)	0.795(2)	0.019(2)	0.10(2)
C(42)	0.220(2)	0.952(3)	0.035(2)	0.09(2)
C(43)	0.126(2)	0.953(3)	0.136(2)	0.08(2)
C(5)	0.308(1)	0.461(2)	−0.006(2)	0.04(2)
C(51)	0.380(2)	0.572(2)	0.008(2)	0.08(2)
C(52)	0.365(2)	0.332(3)	0.004(2)	0.09(2)
C(53)	0.258(2)	0.470(3)	−0.096(2)	0.09(2)
C(6)	0.197(2)	0.370(3)	0.050(2)	0.08(2)
C(7)	0.138(2)	0.377(3)	0.101(2)	0.09(3)
C(8)	0.092(2)	0.455(3)	0.220(2)	0.05(2)
C(81)	0.106(2)	0.566(3)	0.283(2)	0.06(2)
C(82)	0.104(2)	0.323(3)	0.268(2)	0.11(3)
C(83)	-0.001(2)	0.465(3)	0.172(2)	0.08(2)

Table 5. Non-hydrogen and Refined Amine Hydrogen Atom Coordinates and Isotropic Thermal Parameters for [{Li[N(*t*-Bu)-CH$_2$CH$_2$N(H)*t*-Bu]}$_2$Li{N(SiMe$_3$)CH$_2$CH$_2$NSiMe$_3$}Li] (**6**)

atom	*x*	*y*	*z*	*U*, Å^2
Li(1)	0.1471(9)	0.9052(5)	0.2638(4)	0.052(3)[aa]
Li(2)	0.1496(9)	0.8729(5)	0.3659(4)	0.053(3)[a]
Li(3)	0.2598(9)	0.7454(5)	0.3842(4)	0.058(3)[a]
Li(4)	0.387(1)	0.7463(5)	0.4871(4)	0.061(4)[a]
N(1)	0.1764(5)	1.0140(2)	0.2388(2)	0.054(2)[a]
N(4)	0.0146(4)	0.9354(2)	0.3120(2)	0.048(2)[a]
N(5)	0.2691(4)	0.8200(2)	0.3104(2)	0.044(1)[a]
N(8)	0.3011(4)	0.8423(2)	0.4413(2)	0.044(1)[a]
N(14)	0.3094(4)	0.6576(2)	0.4386(2)	0.056(2)[a]
N(17)	0.5726(5)	0.6947(3)	0.5134(3)	0.070(2)[a]
C(1)	0.2948(6)	1.0445(3)	0.2173(3)	0.063(2)[a]
C(2)	0.1471(6)	1.0456(3)	0.2957(3)	0.063(2)[a]
C(3)	0.0142(6)	1.0168(3)	0.3068(3)	0.062(2)[a]
C(4)	-0.1208(5)	0.9058(3)	0.3077(3)	0.056(2)[a]
Si(5)	0.2690(2)	0.76480(9)	0.24747(7)	0.0568(6)[a]
C(6)	0.4039(5)	0.8346(3)	0.3493(2)	0.049(2)[a]
C(7)	0.3922(5)	0.8790(3)	0.4064(2)	0.049(2)[a]
Si(8)	0.2648(2)	0.89565(9)	0.49992(7)	0.0536(6)[a]
C(14)	0.1865(7)	0.6173(3)	0.4441(3)	0.071(3)[a]
C(15)	0.4252(7)	0.6084(3)	0.4441(3)	0.085(3)[a]
C(16)	0.5563(6)	0.6483(4)	0.4583(3)	0.081(3)[a]
C(17)	0.7068(6)	0.7267(4)	0.5390(3)	0.076(3)[a]
C(11)	0.2931(8)	1.0078(4)	0.1550(3)	0.103(4)[a]
C(12)	0.2879(8)	1.1299(4)	0.2088(3)	0.101(3)[a]
C(13)	0.4231(6)	1.0227(4)	0.2629(3)	0.104(3)[a]
C(41)	-0.2006(6)	0.9439(4)	0.3512(3)	0.087(3)[a]
C(42)	-0.1073(6)	0.8234(4)	0.3255(3)	0.084(3)[a]
C(43)	-0.2073(6)	0.9104(4)	0.2416(3)	0.091(3)[a]
C(51)	0.1084(7)	0.7826(5)	0.1896(3)	0.133(4)[a]
C(52)	0.4125(8)	0.7832(4)	0.2077(3)	0.098(3)[a]
C(53)	0.2768(8)	0.6620(4)	0.2650(3)	0.104(4)[a]
C(81)	0.1914(8)	0.9895(4)	0.4736(3)	0.104(3)[a]
C(82)	0.1369(9)	0.8466(5)	0.5345(3)	0.129(4)[a]
C(83)	0.4129(7)	0.9170(5)	0.5628(3)	0.113(4)[a]
C(141)	0.1870(9)	0.5942(5)	0.5108(4)	0.133(4)[a]
C(142)	0.0680(6)	0.6703(4)	0.4229(3)	0.084(3)[a]
C(143)	0.1581(8)	0.5469(4)	0.4024(4)	0.111(4)[a]
C(171)	0.7347(9)	0.7858(5)	0.4951(5)	0.171(6)[a]
C(172)	0.8192(7)	0.6693(4)	0.5498(3)	0.103(3)[a]
C(173)	0.6985(9)	0.7620(6)	0.6005(4)	0.158(5)[a]
H(1)	0.094(5)	1.023(3)	0.208(2)	0.07(2)
H(17)	0.552(7)	0.659(4)	0.543(3)	0.14(3)

[a] Isotropic equivalent thermal parameters.

larger basis set 6-31G*. The optimized structures (3-21G*) were shown to be true energy minima by frequency analysis. Figure 6 gives schematic representations of the computed structures and the numbering scheme of the computed structures. Table 10 lists the total energies and point group symmetries of the various computed structures. The association energies of the structures are discussed in the text for the 6-31G* basis set calculations (3-21G* association energies in brackets).

Discussion

Synthesis. Lithiation of *N*,*N*′-di-*tert*-butylethylenediamine, **1**, by alkyllithium species gave a number of products varying in their extent of lithiation, as outlined in Scheme 1. Lithiation of **1** with 1 equiv of *n*-BuLi in hexane at 0 °C gives exclusively the monolithiated complex [*cis*-{Li[μ-N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$], **2**. Lithiation of the same substrate with 2 equiv of *n*-BuLi in hexane gives initially the partially dilithiated complex [{Li[N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$Li{N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu}-Li], **3**. Both complexes can be isolated in high yield as very air and moisture sensitive, colorless crystalline solids. Extended reaction periods for the lithiation with 2 equiv of *n*-BuLi in hexane result in the formation of the dilithiated substituted ethylenediamine {Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}, **4**, which can be isolated as a very air and moisture sensitive solid in two forms, dimeric [{Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}$_2$], **4a**, and polymeric {Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}$_n$, **4b**.

The isolation of the monolithiated intermediate **2** by the lithiation of **1** required the reaction temperature to be maintained at 0 °C to avoid obtaining a mixture of **2**, the next higher lithiated product, **3**, and unreacted **1**, from which both compounds **3** and **2** could be fractionally crystallized (**3** having the lower solubility of the two compounds). The intermediate **3** is only slowly further lithiated by *n*-BuLi in hexane or MeLi in Et$_2$O. Reaction periods in excess of 24 h are required for the precipitation of {Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}$_n$, **4b**, from concentrated hexane solutions at −30 °C as a sparingly soluble microcrystalline solid only after complete dilithiation has occurred. Compound **4** can alternatively be isolated as a crystalline solid of high solubility by rapid freezing of hexane solutions followed by slow thawing of the solution to −30 °C. This form of **4** was shown by X-ray crystallography to be the dimer [{Li[N(*t*-Bu)CH$_2$CH$_2$N*t*-Bu]Li}$_2$], **4a**.

The synthesis of **4** by lithiation of **1** in tetrahydrofuran has been reported, and the complex reacted *in situ* for the preparation of main group derivatives.[17] No characterization data have been reported for **4**, and no intermediate lithiation products or mechanistic studies of the lithiation were reported.

The lithiation of **1** by MeLi in benzene has been followed by ^{1}H NMR spectroscopy. Figure 1 shows the ^{1}H NMR spectra of **1** and the crude reaction mixtures after the addition of up to 2 equiv of solid MeLi to a C$_6$D$_6$ solution of **1**. The only intermediates present in solution can be seen to be the partially lithiated complexes **2** and **3** *en route* to the completely dilithiated complex **4**. Upon the addition of *ca.* 0.05 equiv of MeLi the singlet methylene proton resonance of **1** is transformed to a multiplet. Presumably, at the early stages of lithiation by MeLi, N−H exchange processes are slowed giving rise to coupling

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(17) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem.* **1992**, *104*, 1489; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1485.

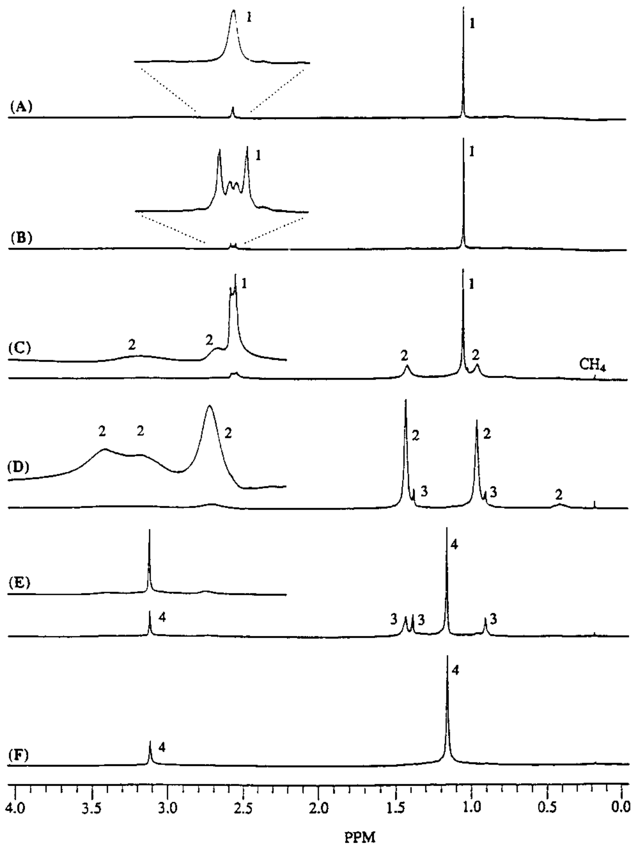
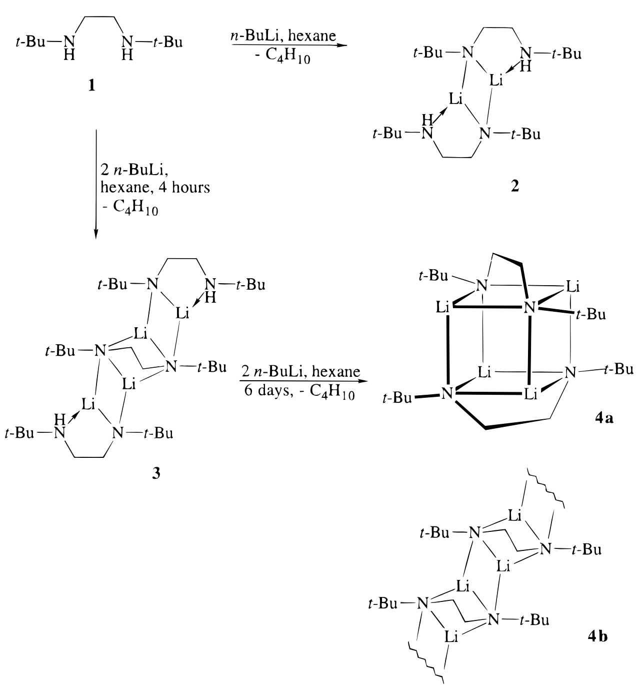


Figure 1. ^{1}H NMR spectra of **1** in C_6D_6, 200 MHz, at 24 °C after the addition of (A) 0 equiv of MeLi, (B) *ca.* 0.05 equiv of MeLi, (C) *ca.* 0.5 equiv of MeLi, (D) *ca.* 1.0 equiv of MeLi, (E) *ca.* 1.7 equiv of MeLi, and (F) 2.0 equiv of MeLi. Resonances in each of the spectra are labeled according to the compound numbering used throughout this paper.

Scheme 1



between the methylene and amine protons. Addition of more MeLi results in the proton resonances for **2** increasing at the expense of unreacted **1**. After the addition of 1 equiv of MeLi, **2** is the only species present in solution. There is no evidence of a fast exchange process between unreacted **1**, **2**, **3**, or **4**; at all stages of the reaction the proton resonances for each of the species are identical to those of the isolated samples. The possible intermediate {HN(*t*-Bu)CH_2CH_2N(H)*t*-Bu}{Li[N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]} is not observed. Molecular models show that **1** coordinated to a molecule of the monolithiated complex, Li{N(*t*-Bu)CH_2CH_2N(H)*t*-Bu}, in chelating fashion results in unreasonable steric interactions between the *tert*-butyl substituents in the molecule. The spectra acquired after the addition of between 1 and 2 equiv of MeLi show the presence of **2**, **3**, and **4** in differing proportions dependent on the extent of lithiation. The ^{1}H NMR spectrum of isolated **3**, *vide infra*, shows that in solution the complex is present as a slowly exchanging mixture of **2**, **3**, and **4** on the NMR time scale. Accordingly, at no stage of the lithiation reaction is **3** the sole product present in solution. The plausible intermediates {Li-[N(*t*-Bu)CH_2CH_2N*t*-Bu]Li}{HN(*t*-Bu)CH_2CH_2N(H)*t*-Bu}$_2$ and {HN(*t*-Bu)CH_2CH_2N(H)*t*-Bu}{Li[N(*t*-Bu)CH_2CH_2N*t*-Bu]Li}{Li[N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]} are not observed in solution, which is again a consequence of the steric crowding of **1** coordinated to a lithiated species in a chelating mode.

The lithium compounds were characterized by ^{1}H, ^{7}Li, and ^{13}C NMR and IR spectroscopy, satisfactory microanalyses, and X-ray crystal structure determinations for **2**, **3**, and **4a**. Microcrystalline samples of **4b** crystallized from hexane solutions were unsuitable for X-ray crystal structure determination. The IR N−H absorption stretches of the remaining secondary amine functionalities of **2** and **3** occur at 3283 and 3274 cm^{-1}, respectively, and are only slightly changed from that of **1**, 3307 cm^{-1}.

The X-ray crystal structure of **2** shows the molecule to be dimeric in the solid state containing a four-membered Li_2N_2 ring core. The monolithiated ethylenediamine acts as a bidentate ligand, chelating a lithium atom and bridging the other lithium atom through the amido nitrogen achieving 3-fold coordination for the lithium atoms, *vide infra*. This crystal structure, along with those of [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN*t*-Bu]}$_2$][9] and [*cis*-{Li[μ-(*R*)-N(CH_2*t*-Bu)CH(Ph)CH_2N(CH_2)$_5$]}$_2$],[18] represents the only examples of internally coordinated *cis* secondary amidolithium dimers. Typically such dimers are centrosymmetric or the *trans* isomer. The primary amidolithium complex [*cis*-{(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)Li[μ-N(H)Si(F)*t*-Bu$_2$]}$_2$][19] has also been shown by crystal structure determination to have C_2 symmetry.

The X-ray crystal structure of **3** reveals the amidolithium complex to contain a four-rung Li_4N_4 ladder core which features intramolecular coordination of the terminal lithium atoms by the secondary amine functionalities, *vide infra*. The ladder structure of **3** is built up from the additional partial lithiation of **2** followed by end-capping of the resulting three-rung ladder by one unit of Li{N(*t*-Bu)CH_2CH_2N(H)*t*-Bu} to satisfy the coordination requirements of the additional lithium atom. The relative stereochemistry of the two ligands in the structure of **2** remains unaltered in the ladder structure of **3**, *viz*, Figure 2, which shows projections of both complexes such that the two ethylenediamide ligands on the right-hand side of **3** are close to superimposable with **2**. Extension of the four-rung ladder of **3** by further lithiation would result in a ladder of infinite length accounting for the precipitation of the completely dilithiated complex from concentrated hexane/benzene solutions as a sparingly soluble powder, **4b**, after extended reaction periods.

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(18) Sato, D.; Kawasaki, H.; Shimada, I.; Arata, Y.; Okamura, K.; Date, T.; Koga, K. *J. Am. Chem. Soc.* **1992**, *114*, 761.

(19) Kottke, T.; Klingebiel, U.; Noltemeyer, M.; Pieper, U.; Walter, S.; Stalke, D. *Chem. Ber.* **1991**, *124*, 1941.

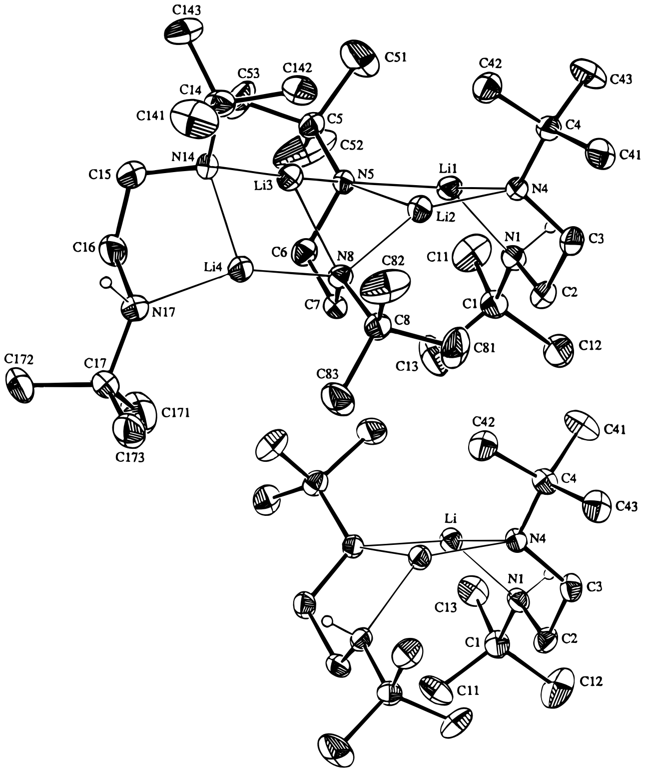

Figure 2. Molecular projections of [*cis*-{Li[μ-N(*t*-Bu)CH$_2$CH$_2$N(H)-*t*-Bu]}$_2$] (below), **2**, and [{Li[N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$Li{N(*t*-Bu)-CH$_2$CH$_2$N*t*-Bu}Li] (above), **3**. For clarity only amine hydrogen atoms are shown as spheres of arbitrary radii.

Compound **4a** can be isolated as a crystalline solid of high solubility by rapid freezing of hexane solutions of **4** followed by slow thawing to −30 °C. The X-ray crystal structure of this solid revealed it to be of dimeric composition. The dimer can be seen to arise from the stacking together of two dilithium bridged *N*,*N*′-dilithioethylenediamide units to form the Li$_4$N$_4$ cage core. The nitrogen atoms are five coordinate, achieving 3-fold coordination for the lithium atoms, *vide infra*. Two forms of **4** are likely to exist in the solid state. Compound **4b** precipitates from solution over time as the most stable polymeric/large oligomeric form, but the compound crystallizes as the less stable dimeric form, **4a**, when crystallized by rapid cooling of solutions of **4**. Presumably the dimeric structure is adopted by **4** in solution and the complex can be isolated in this form only when the crystallization is kinetically controlled.

The formation of the sparingly soluble powder for **4** being the most stable solid state structure contrasts with the dimeric structure of the *rac*-2,3-dimethyl analogue [{Li[*rac*-N(*t*-Bu)-CH(Me)CH(Me)N*t*-Bu]Li}$_2$].[9] The different structures adopted by these two complexes can be explained by the steric buttressing which would result between the 2,3-dimethyl substituents and the *N*-*tert*-butyl substituents of the adjacent ligand of a ladder structure for the 2,3-dimethyl analogue. This would disrupt the ladder, forcing the compound to adopt the stacked dimeric cage as an alternative. This behavior relates to theoretical studies which show the stacking or vertical association of lithium amides to be energetically less favorable relative to laddering or horizontal association in simple amidolithium complexes.[20] It is clear from this study that stacking in lithium amides is unfavorable and is only observed in special circumstances. It is worthy to note that the only other amidolithium complex exhibiting a stacked Li$_4$N$_4$ cage, [{Me$_2$Si{N(Li)*t*-Bu}$_2$}$_2$],[21] also has methyl substituents in similar positions to [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N*t*-Bu]Li}$_2$]. A four-rung ladder structure has been reported for an unsolvated *N*,*N*′-diaryl-substituted *N*,*N*′-dilithioethylenediamine, [{Li$_2$[N(2,6-*i*-Pr$_2$C$_6$H$_3$)-CH$_2$]$_2$}$_2$],[12] albeit having the ethylene linkages bridging differently to the proposed polymeric structure of **4b**. In the solid state dilithiated *N*,*N*′-bis(trimethylsilyl)ethylenediamine exists as a trimer exhibiting a Li$_6$N$_6$ cage core.[10] The formation of insoluble compounds upon lithiation of less hindered secondary amines is well established, and the resulting insoluble compounds are believed to have laddered polymeric structures. The crystal structure of a polymeric lithium amide ladder is yet to be elucidated. Ironically, the only polymeric lithium amide to be structurally characterized exhibits a coiled straight chain polymeric (LiN)$_n$ core.[3]

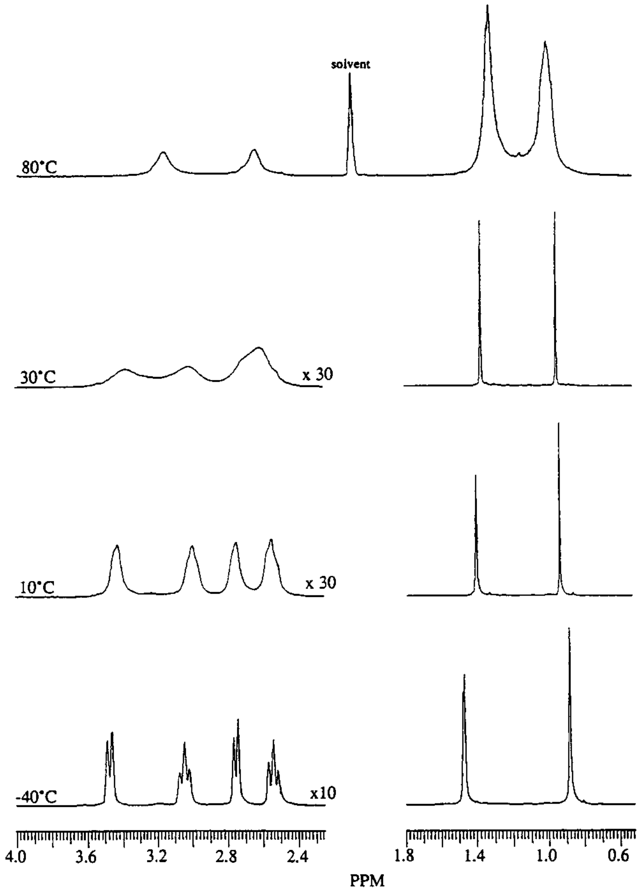

Figure 3. Variable temperature ^{1}H NMR spectra of [*cis*-{Li[μ-N(*t*-Bu)CH$_2$CH$_2$N(H)*t*-Bu]}$_2$], **2**, in C$_6$D$_5$CD$_3$, 400 MHz.

In solution **2** is fluxional, the room temperature ^{1}H NMR spectrum showing clearly that the methylene protons are exchange broadened, Figure 3. Heating the sample to 80 °C gives two broadened resonances for the methylene protons and two resonances for the protons of the *tert*-butyl substituents. At low temperature the proton resonances of the *tert*-butyl substituents sharpen and separate considerably and the two methylene proton resonances each split into two resonances having multiplet structure. The ^{7}Li NMR spectrum over the same temperature range exhibits no marked temperature dependence, indicating that the fluxional process is not the result of an equilibration between different species in solution. The ^{13}C NMR spectrum at room temperature is uninformative, showing broadened resonances for both the methylene carbons and the carbons of the *tert*-butyl substituents of the ligand.

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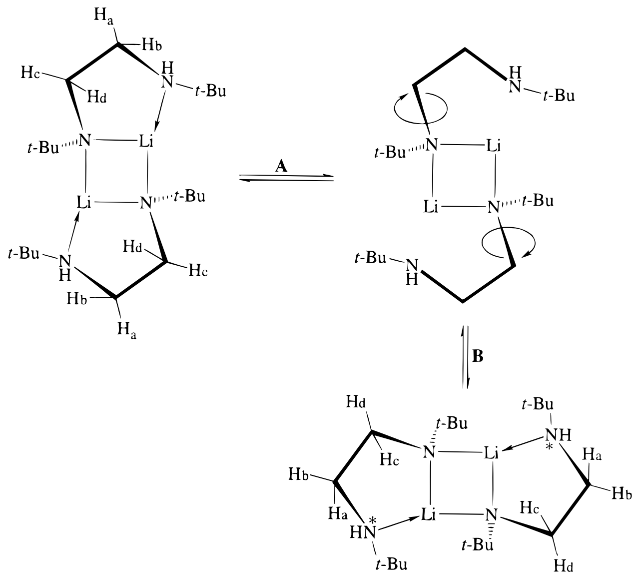
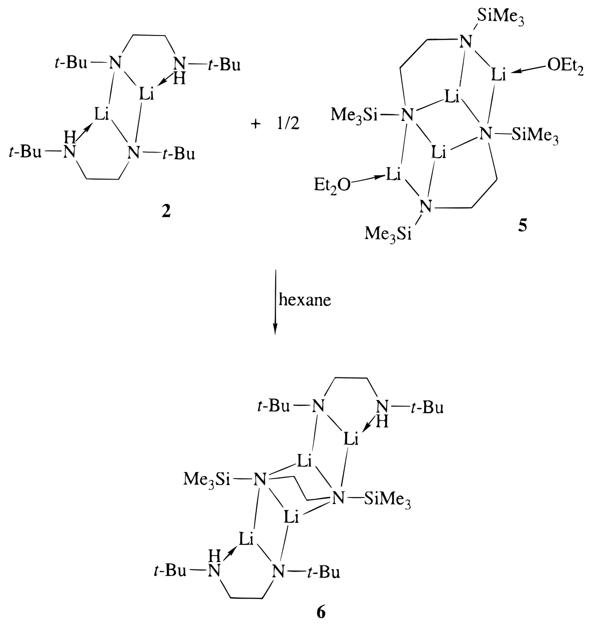
Scheme 2



Scheme 3



The observed fluxional process for **2** is consistent with the reversible complexation/decomplexation of the chelating secondary amine functionality, Scheme 2. At low temperature the ^{1}H NMR spectrum of **2** is consistent with the crystal structure of the complex, exhibiting a structure having two distinguishable *tert*-butyl substituents and four inequivalent methylene protons. The coupling scheme observed for the methylene proton spin system at low temperature is in agreement with the N−C−C−N torsion angle of 59.5(5)° in the crystal structure of **2**. This would result in vicinal couplings comparable to the geminal couplings between only two of the protons, *viz*, two doublets and two pseudotriplets. At higher temperatures each of the two sets of methylene protons can be equilibrated by the decomplexation of the secondary amine from the lithium atom to give the uncomplexed lithium amide dimer, equilibrium **A**, *cf*., two-coordinate lithium centers in the vapor phase and solid state structures of $[\{Li[\mu\text{-}N(SiMe_3)_2]\}_2]$[22] and $[\{Li[\mu\text{-}N(SiMe_3)(2,6\text{-}i\text{-}Pr_2C_6H_3)]\}_2]$,[23] respectively. Inversion of configuration at the secondary amine nitrogen atom and complexation to the other lithium atom of the dimer results in the methylene protons having been exchanged from the position they previously occupied, equilibrium **B**. The observed dynamic behavior does not necessitate invoking equilibrium **B**, but it is a feasible process.

Heteronuclear coupling observed in both the ^{6}Li and ^{15}N NMR spectra of labeled samples of $[cis\text{-}\{Li[\mu\text{-}(R)\text{-}N(CH_2t\text{-}Bu)CH(Ph)CH_2N(CH_2)_5]\}_2]$[18] at −80 °C has shown conclusively that the complex exists as a dimer with the tertiary amine functionality internally coordinating the lithium atoms in toluene solution. In tetrahydrofuran, 1,2-dimethoxyethane, or toluene, with 2 equiv of hexamethylphosphoramide present, the complex exists as a monomer with the chelate ring intact. NMR studies at higher temperatures were not reported for this complex, and no mention was made of the molecule being fluxional in solution.

Fluxional behavior has been recently noted for the chiral bis(amine) functionalized amidolithium dimer $[\{Li[\mu\text{-}N(CH_2CH_2NEt_2)_2]\}_2]$.[24] The preferred process to explain the fluxionality in that case was also the reversible complexation of the lithium atom by the chelating amine functionalities of the ligand, the dimeric Li_2N_2 ring remaining intact.

In benzene solution at room temperature **3** is present as a slowly exchanging mixture of **2**, **3**, and **4**, on the NMR time scale. Near equal concentrations of the three species are observed at room temperature, and there is no concentration or temperature dependence observed for this equilibrium. Complex **3** is, however, fluxional in solution, the methylene proton resonances appearing as broad indistinguishable resonances over the range 2.5−3.7 ppm. Cooling the sample results in coalescence to give several overlapping multiplets for these protons. The dynamic process most likely relates to the process postulated above for **2**. At high temperatures poor resolution prevented interpretation of the spectrum in terms of an exchange process. The room temperature ^{13}C NMR spectrum shows broadened resonances for some of the methylene carbons, and complete assignment of the spectra was not possible. Variable temperature ^{13}C NMR studies were not undertaken as the integrity of the molecule was established by ^{1}H NMR spectroscopy.

The ^{1}H, ^{7}Li, and ^{13}C NMR spectra of the completely dilithiated complex **4** indicate that the complex exists as a single species in solution. The ^{1}H NMR spectrum contains single sharp resonances for the methylene and *tert*-butyl proton substituents which show no marked temperature dependences, ruling out the possibility of **4** existing as a rapidly exchanging mixture of several species in solution. The data at hand would then suggest that **4** forms a single oligomer in benzene solution, perhaps a stacked dimer in light of the solid state structure of **4a**, rather than an exchanging mixture of ladders of varying length.

The mixed ligand complex $[\{Li[N(t\text{-}Bu)CH_2CH_2N(H)t\text{-}Bu]\}_2Li\{N(SiMe_3)CH_2CH_2NSiMe_3\}Li]$, **6**, can be prepared by cocrystallization of a 2:1 stoichiometric mixture of **2** and $[\{Li[N(SiMe_3)CH_2CH_2NSiMe_3]Li{\cdot}OEt_2\}_2]$,[10] **5**, from hexane solution, Scheme 3.

The formation of the mixed ligand complex is in keeping with molecular orbital calculations on solvated $LiNH_2$ aggregates. A four-rung lithium amide ladder capped on the terminal lithium atoms by neutral Lewis base donors is the most stable structure when the number of Lewis base donors is less than or equal to the number of lithium atoms in the structure.[4] However, molecular orbital calculations on model species in

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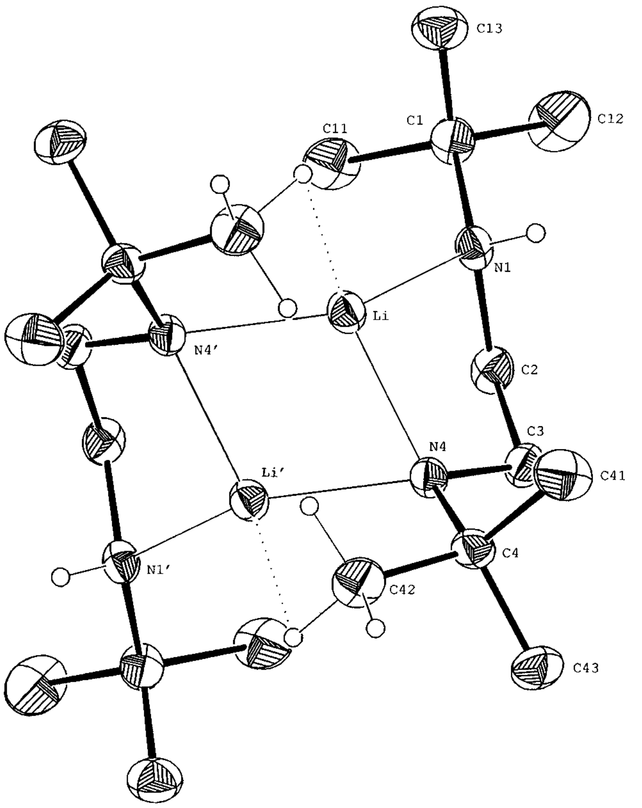

Figure 4. Molecular projection of [*cis*-{Li[*μ*-N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$], **2**, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level. For clarity only amine hydrogen atoms and the methyl hydrogen atoms in close contact with the lithium atoms are shown as spheres of arbitrary radii.

this study, *vide infra*, show that the formation of the single cocrystallized ladder structure is of comparable energy relative to the Li_2N_2 ring and Li_4N_4 ladder in the mixture of the starting materials.

Complex **6** was characterized by X-ray crystal structure determination, ^{1}H, ^{7}Li, and ^{13}C NMR, and IR spectroscopy and gave a satisfactory microanalysis. The complex can be isolated as a very air and moisture sensitive colorless crystalline solid in moderate yield.

The X-ray crystal structure of **6** is both isostructural and isomorphous to that of **3**. The complex exhibits a four-rung Li_4N_4 ladder core capped on the terminal lithium atoms by the chelating secondary amine functionalities of the monolithiated ethylenediamine ligands, *vide infra*.

Complex **6** is present as a single species in solution whose ^{1}H, ^{7}Li, and ^{13}C NMR spectra are consistent with the cocrystallized product. This contrasts with complex **3** which is in equilibrium with the constituent dimeric fragments in benzene solution. Like **3**, complex **6** is fluxional in solution, the methylene protons being clearly exchange broadened. Presumably the process involves a similar complexation/decomplexation exchange process to that proposed for both **2** and **3**. The room temperature ^{13}C NMR spectrum shows broadened resonances for some of the methylene carbons, and complete assignment of the spectra was not possible. Variable temperature ^{13}C NMR studies were not undertaken as the integrity of the molecule was established by ^{1}H NMR spectroscopy.

X-ray Structure Commentary. Complex **2** crystallizes as prismatic crystals in the monoclinic space group *C*2/*c* (No. 15) with four dimers in the unit cell, the asymmetric unit comprising one-half of the dimer, the other half being generated by the 2-fold rotation axis on (1/2, *y*, 1/4), Figures 2 and 4. Complex **3** crystallizes as rod-shaped crystals in the monoclinic space group $P2_1/c$ (No. 14) with four molecules in the unit cell, the asymmetric unit containing one molecule, Figure 2. Complex **4a** crystallizes as prismatic crystals in the monoclinic space group $P2_1/c$ (No. 14) with four dimers in the unit cell, the asymmetric unit comprising one dimer, Figure 5. Diffraction data for **4a** were weak, limiting non-hydrogen atom thermal parameters to isotropic refinement only. The geometry of **4a** is similar to that of [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N*t*-Bu]-Li}$_2$]^9 and will not be discussed in this section. Complex **6** is both isostructural and isomorphous to **3** and also will not be discussed in this section. Selected geometrical parameters for the structures of **2**, **3**, **4a**, and **6** are given in Tables 6−9.

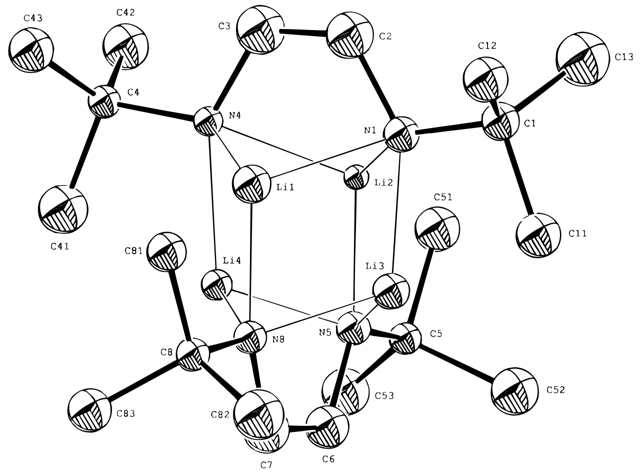

Figure 5. Molecular projection of [{Li[N(*t*-Bu)CH_2CH_2N*t*-Bu]Li}$_2$], **4a**, showing the atom labeling scheme. Thermal ellipsoids are drawn at the 20% probability level.

Table 6. Selected Structural Parameters for [*cis*-{Li[*μ*-N(*t*-Bu)CH_2-CH_2N(H)*t*-Bu]}$_2$] (**2**)^a

Bond Distances (Å)

Li−N1	2.037(7)	N1−C1	1.497(6)	N4−C3	1.444(5)
Li−N4	2.017(7)	N1−C2	1.474(6)	N4−C4	1.472(5)
Li−N4′	1.973(6)	C2−C3	1.518(6)	N1−H1	0.80(3)

Contact Distances (Å)

Li−Li′	2.31(1)	Li−H42b′	2.23(5)
Li−C42′	2.572(8)	Li−H42c′	2.51(4)

Bond Angles (deg)

N1−Li−N4	92.0(2)	N1−C2−C3	110.6(3)
N1−Li−Li′	127.5(4)	N4−C3−C2	112.4(3)
N1−Li−N4′	138.4(3)	Li−N4−C3	101.4(3)
N4−Li−Li′	53.8(2)	Li−N4−C4	131.1(3)
N4−Li−N4′	109.0(4)	C3−N4−C4	111.4(2)
Li−Li′−N4	55.6(2)	C3−N4−Li′	132.8(3)
Li−N1−C1	124.0(3)	C4−N4−Li′	107.3(3)
Li−N1−C2	93.6(3)	Li−N4−Li′	70.6(3)
C1−N1−C2	117.1(3)		

Dihedral Angles (deg)

N4−Li−Li′−N4′	172.4(3)	H2a−C2−C3−H3b	−52(3)
Li−N4−N4′−Li′	169.4(3)	H2b−C2−C3−H3a	175(3)
N1−C2−C3−N4	59.5(5)	H2b−C2−C3−H3b	66(3)
H2a−C2−H3a	58(3)		

^{a} Denotes symmetry operator 1 − *x*, *y*, 0.5 − *z*.

Structure of 2. Complex **2** is best described as an amido nitrogen bridged dimer containing a four-membered Li_2N_2 ring core which features intramolecular coordination of the lithium atoms by the secondary amine functionalities. The complex contains three-coordinate lithium atoms having an agostic type lithium−hydrogen contact. Two of the coordination sites of the lithium atoms are occupied by bridging amido nitrogen atoms, and the other site is occupied by a nitrogen atom of the

Table 7. Selected Structural Parameters for [{Li[N(*t*-Bu)CH_2CH_2N(H)*t*-Bu]}$_2$Li{N(*t*-Bu)CH_2CH_2N*t*-Bu}Li] (**3**)

Bond Distances (Å)

Li1−N1	2.06(1)	Li4−N8	2.08(1)	N14−C15	1.443(9)
Li1−N4	1.98(1)	Li4−N14	1.97(1)	C15−C16	1.51(1)
Li1−N5	2.09(1)	Li4−N17	2.09(1)	C16−N17	1.449(9)
Li2−N4	1.99(1)	N1−C2	1.473(8)	N1−C1	1.495(8)
Li2−N5	2.10(1)	C2−C3	1.511(9)	N4−C4	1.477(7)
Li2−N8	2.064(9)	C3−N4	1.446(7)	N5−C5	1.486(7)
Li3−N5	2.10(1)	N5−C6	1.458(6)	N8−C8	1.486(8)
Li3−N8	2.07(1)	C6−C7	1.505(8)	N14−C14	1.467(9)
Li3−N14	1.98(1)	C7−N8	1.466(8)	N17−C17	1.492(8)

Contact Distances (Å)

Li1−Li2	2.33(1)	Li2−Li3	2.49(1)	Li3−Li4	2.34(1)

Bond Angles (deg)

N1−Li1−N4	92.0(4)	Li2−N5−C5	148.2(4)
N1−Li1−N5	140.1(5)	Li2−N5−C6	98.6(4)
N4−Li1−N5	108.8(5)	Li3−N5−C5	107.9(4)
N4−Li2−N5	108.3(5)	Li3−N5−C6	79.8(4)
N4−Li2−N8	153.4(5)	C5−N5−C6	112.9(4)
N5−Li2−N8	86.5(4)	N5−C6−C7	111.7(5)
N5−Li3−N8	86.5(4)	C6−C7−N8	111.7(4)
N5−Li3−N14	155.4(6)	Li2−N8−Li3	73.9(4)
N8−Li3−N14	108.5(5)	Li2−N8−Li4	140.0(4)
N8−Li4−N14	108.0(4)	Li2−N8−C7	85.0(4)
N8−Li4−N17	142.5(6)	Li2−N8−C8	106.4(4)
N14−Li4−N17	91.2(4)	Li3−N8−Li4	68.5(4)
Li1−N1−C1	128.9(4)	Li3−N8−C7	95.8(4)
Li1−N1−C2	94.2(4)	Li3−N8−C8	151.4(5)
C1−N1−C2	116.8(4)	Li4−N8−C7	111.6(4)
N1−C2−C3	111.1(4)	Li4−N8−C8	100.2(4)
C2−C3−N4	112.3(5)	C7−N8−C8	112.8(4)
Li1−N4−Li2	72.0(4)	Li3−N14−Li4	72.5(4)
Li1−N4−C3	102.8(4)	Li3−N14−C14	108.7(4)
Li1−N4−C4	130.8(4)	Li3−N14−C15	128.2(5)
Li2−N4−C3	129.4(4)	Li4−N14−C14	129.3(5)
Li2−N4−C4	108.2(4)	Li4−N14−C15	103.2(4)
C3−N4−C4	111.3(4)	C14−N14−C15	112.0(5)
Li1−N5−Li2	67.6(4)	N14−C15−C16	112.9(5)
Li1−N5−Li3	139.3(5)	C15−C16−N17	112.5(6)
Li1−N5−C5	101.3(4)	Li4−N17−C16	92.6(4)
Li1−N5−C6	114.2(4)	Li4−N17−C1	131.3(5)
Li2−N5−Li3	72.7(4)	C16−N17−C17	118.1(5)

Dihedral Angles (deg)

N4−Li1−Li2−N5	163.8(5)	Li1−N4−N5−Li2	157.1(7)
N5−Li2−Li3−N8	117.3(5)	Li2−N5−N8−Li3	110.1(6)
N8−Li3−Li4−N14	166.0(6)	Li3−N8−N14−Li4	160.5(8)

Table 8. Selected Structural Parameters for [{Li[N(*t*-Bu)CH_2CH_2N*t*-Bu]Li}$_2$] (**4a**)

Bond Distances (Å)

Li1-N1	2.07(5)	Li3−N8	2.00(5)	N4−C4	1.53(3)
Li1-N4	2.05(5)	Li4−N4	2.11(4)	N5−C5	1.45(4)
Li1-N8	1.98(5)	Li4−N5	1.94(5)	N5−C6	1.42(3)
Li2−N1	1.97(4)	Li4−N8	2.00(5)	C6−C7	1.42(5)
Li2−N4	2.09(4)	N1−C1	1.50(3)	N8−C7	1.41(4)
Li2−N5	1.96(4)	N1−C2	1.44(3)	N8−C8	1.46(4)
Li3−N1	2.03(5)	C2−C3	1.40(4)		
Li3−N5	1.94(5)	N4−C3	1.39(3)		

Contact Distances (Å)

Li1−Li2	2.65(6)	Li1−Li4	2.33(6)	Li2−Li4	2.30(5)
Li1−Li3	2.36(7)	Li2−Li3	2.23(6)	Li3−Li4	2.55(5)

Bond Angles (deg)

N1−Li1−N4	86(2)	Li4−N4−C3	145(2)
N1−Li1−N8	108(2)	Li4−N4−C4	101(2)
N4−Li1−N8	112(2)	Li2−N5−Li3	70(2)
N1−Li2−N4	88(2)	Li2−N5−Li4	72(2)
N1−Li2−N5	112(2)	Li2−N5−C5	100(2)
N4−Li2−N5	110(2)	Li2−N5−C6	149(2)
N1−Li3−N5	110(2)	Li3−N5−Li4	82(2)
N1−Li3−N8	109(2)	Li3−N5−C5	138(2)
N5−Li3−N8	90(2)	Li3−N5−C6	85(2)
N4−Li4−N5	111(2)	Li4−N5−C5	135(2)
N4−Li4−N8	109(2)	Li4−N5−C6	86(2)
N5−Li4−N8	89(2)	Li1−N8−Li3	73(2)
Li1−N1−Li2	82(2)	Li1−N8−Li4	72(2)
Li1−N1−Li3	70(2)	Li1−N8−C7	149(3)
Li1−N1−C1	134(2)	Li1−N8−C8	98(2)
Li1−N1−C2	83(2)	Li3−N8−Li4	79(2)
Li2−N1−Li3	68(2)	Li3−N8−C7	88(2)
Li2−N1−C1	139(2)	Li3−N8−C8	139(2)
Li2−N1−C2	90(2)	Li4−N8−C7	82(2)
Li3−N1−C1	102(2)	Li4−N8−C8	136(2)
Li3−N1−C2	147(2)	C1−N1−C2	111(2)
Li1−N4−Li2	79(2)	N1−C2−C3	120(2)
Li1−N4−Li4	68(2)	N4−C3−C2	120(2)
Li1−N4−C3	89(2)	C3−N4−C4	113(2)
Li1−N4−C4	135(2)	C5−N5−C6	111(2)
Li2−N4−Li4	66(1)	N5−C6−C7	118(3)
Li2−N4−C3	85(2)	N8−C7−C6	119(3)
Li2−N4−C4	139(2)	C7−N8−C8	112(2)

Dihedral Angles (deg)

Li1−N1−N4−Li2	126(2)	Li3−N5−N8−Li4	131(3)

chelating secondary amine functionality of the monolithiated ethylenediamine. The overall molecular symmetry is crystallographically constrained to be C_2.

The Li−N(amido) distances of 2.017(7) and 1.973(6) Å are short for Li−N(dibridging amido) distances, being similar to the Li−N(amido) distances of 2.01(1) and 2.01(2) Å in [*trans*-{Et_2O·Li[*μ*-N(H)B(2,4,6-$Me_3C_6H_2$)$_2$]}$_2$][25] and [{*i*-Pr_2N(H)·Li-[*μ*-N(Ph)C_6H_9]}$_2$],[8] respectively, which also contain three-coordinate lithium atoms with dibridging amido nitrogen atoms. The Li-N distance in [{Et_2O·Li[*μ*-N($SiMe_3$)$_2$]}$_2$],[26,27] 2.055(5) Å, is more typical.

The Li−N(amine) distance of 2.037(7) Å is shorter than the secondary amine Li−N distances in the three-coordinate lithium amides **3**, 2.06−2.09 Å, and [{*i*-Pr_2N(H)·Li[*μ*-N(Ph)C_6H_9]}$_2$],[8] 2.109 Å. The Li−N(amine) distances in the 1:1 piperidine: lithium piperidide complex [{Li[N(CH_2)$_5$][HN(CH_2)$_5$]}$_4$][6] are also much longer, 2.10−2.22 Å, which is in accordance with the coordination number of the terminal lithium atoms being four in that case.

The geometry of the Li_2N_2 ring of **2** is typical for dimeric lithium amides. A close Li···Li distance is observed across the Li_2N_2 ring, 2.31(1) Å, the internal Li−N−Li angle of the Li_2N_2 ring measuring 70.6(3)°. The C_2 symmetry of **2** results in only a slight folding of the Li_2N_2 ring, the Li−N−N−Li dihedral angle measuring 169.4(3)°.

A close Li−H agostic interaction is observed between the lithium atoms and a hydrogen atom of the *tert*-butyl substituents attached to an amido nitrogen (Li′−C41). The distance of 2.23(5) Å to the positionally refined hydrogen atom is *ca.* 0.8 Å less than the sum of the Van der Waals radii of the lithium and hydrogen atoms.

The sum of the N−Li−N angles about each lithium atom in **2** is 339.4° indicating significant nonplanarity of the lithium atom and the three nitrogen centers to which it is principally bound. The ligand bite angle, N(amine)−Li−N(amido), has little flexibility and is quite low at 92.0(2)°. Similarly the N(amido)−Li−N(amido) angle is governed primarily by the geometry of the Li_2N_2 ring, 109.0(4)°, and the remaining N(amine)−Li−N(amido) angle is again constrained to a specific angle, 138.4(3)°, by the requirement of maintaining the carbon substituents on the amido nitrogen atoms close to perpendicular

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Table 9. Selected Structural Parameters For [{Li[N(*t*-Bu)CH_2CH_2-N(H)*t*-Bu]}$_2$Li{N($SiMe_3$)$CH_2CH_2NSiMe_3$}Li] (**6**)

Bond Distances (Å)

Li1−N1	2.06(1)	Li4−N8	2.09(1)	N14−C15	1.449(8)
Li1−N4	1.96(1)	Li4−N14	1.98(1)	C15−C16	1.482(9)
Li1−N5	2.092(9)	Li4−N17	2.07(1)	C16−N17	1.457(9)
Li2−N4	1.964(9)	N1−C2	1.468(8)	N1−C1	1.484(8)
Li2−N5	2.12(1)	C2−C3	1.508(9)	N4−C4	1.453(7)
Li2−N8	2.094(8)	C3−N4	1.459(7)	N5−Si5	1.711(4)
Li3−N5	2.13(1)	N5−C6	1.479(6)	N8−Si8	1.714(4)
Li3−N8	2.135(9)	C6−C7	1.520(7)	N14−C14	1.464(8)
Li3−N14	1.98(1)	C7−N8	1.478(7)	N17−C17	1.474(8)

Contact Distances (Å)

Li1−Li2	2.34(1)	Li2−Li3	2.53(1)	Li3−Li4	2.38(1)

Bond Angles (deg)

N1−Li1−N4	92.4(4)	Li2−N5−Si5	145.9(3)
N1−Li1−N5	135.8(5)	Li2−N5−C6	98.7(4)
N4−Li1−N5	109.2(4)	Li3−N5−Si5	106.0(3)
N4−Li2−N5	107.9(4)	Li3−N5−C6	81.0(3)
N4−Li2−N8	159.3(5)	Si5−N5−C6	115.0(3)
N5−Li2−N8	86.4(4)	N5−C6−C7	110.9(4)
N5−Li3−N8	85.1(4)	C6−C7−N8	111.9(4)
N5−Li3−N14	156.8(6)	Li2−N8−Li3	73.5(3)
N8−Li3−N14	106.6(4)	Li2−N8−Li4	139.9(4)
N8−Li4−N14	108.3(4)	Li2−N8−C7	84.1(4)
N8−Li4−N17	140.0(5)	Li2−N8−Si8	103.0(3)
N14−Li4−N17	91.7(4)	Li3−N8−Li4	68.5(3)
Li1−N1−C1	127.2(4)	Li3−N8−C7	96.5(4)
Li1−N1−C2	93.7(4)	Li3−N8−Si8	148.9(4)
C1−N1−C2	117.2(4)	Li4−N8−C7	112.2(4)
N1−C2−C3	110.9(4)	Li4−N8−Si8	102.7(3)
C2−C3−N4	111.5(5)	C7−N8−Si8	114.1(3)
Li1−N4−Li2	73.1(4)	Li3−N14−Li4	73.7(4)
Li1−N4−C3	102.8(4)	Li3−N14−C14	109.1(4)
Li1−N4−C4	127.4(4)	Li3−N14−C15	129.0(5)
Li2−N4−C3	127.2(4)	Li4−N14−C14	126.4(5)
Li2−N4−C4	111.1(4)	Li4−N14−C15	102.5(4)
C3−N4−C4	111.7(4)	C14−N14−C15	112.4(4)
Li1−N5−Li2	67.3(4)	N14−C15−C16	113.5(5)
Li1−N5−Li3	136.0(4)	C15−C16−N17	113.1(6)
Li1−N5−Si5	96.6(3)	Li4−N17−C16	94.6(4)
Li1−N5−C6	122.6(4)	Li4−N17−C17	130.3(5)
Li2−N5−Li3	73.1(4)	C16−N17−C17	118.6(5)

Dihedral Angles (deg)

N4−Li1−Li2−N5	165.9(5)	Li1−N4−N5−Li2	160.2(6)
N5−Li2−Li3−N8	116.1(4)	Li2−N5−N8−Li3	109.1(6)
N8−Li3−Li4−N14	164.8(5)	Li3−N8−N14−Li4	159.0(7)

to the Li_2N_2 ring. The result is that the nonplanarity of the lithium coordination is not a result of the agostic Li−H interaction present in the vacant coordination site of the lithium atoms but is geometrically imposed. The lithium atom, the two nitrogen atoms and one of the carbon atoms of the chelate ring of **2** form a good plane, C2 deviating some 0.716(6) Å from this plane. This plane makes an angle of 43.4(2)° with the plane defined by the Li_2N_2 ring. The C_2 symmetry of **2** results in the three edge fused rings having a concave conformation. This can be compared with the unsolvated centrosymmetric 8-quinolide dimer [*trans*-{Li[8-μ-N($SiMe_3$)C_9H_6N]}$_2$],[28] which exhibits a stepped structure. Close Li−H contacts were not observed in this structure which differs only slightly from the dimeric diethyl ether adduct [*trans*-{Et_2O•Li[8-μ-N($SiMe_3$)C_9H_6N]}$_2$].[28] In comparison, the environment about the lithium atoms in [*cis*-{Li[μ-N(*t*-Bu)CH(*t*-Bu)CHN*t*-Bu]}$_2$][9] is planar, $\sum(\mathrm{N-Li-N}) = 357.0°$, with only the exocyclic N(imine)−Li−N(amido) angle differing substantially from the lithium coordination in **2**. This is a consequence of the imine functionality not present in **2** altering the torsion angles in the chelate ring. Other bond distances and angles within the molecule are unexceptional and do not require comment.

Structure of 3. Complex **3** contains a four-rung Li_4N_4 ladder core which features intramolecular coordination of the terminal lithium atoms preventing further association. The three-coordination sites of the two central lithium atoms are occupied by three bridging amido nitrogen atoms, while the coordination sphere of the two terminal lithium atoms contains two bridging amido nitrogen atoms and the nitrogen atoms of the chelating secondary amines. The overall molecular symmetry approximates to C_2 but is not crystallographically imposed.

The Li−N(amido) distances in **3** occur in two exclusive ranges. The Li−N distances to the tribridging, five-coordinate amido nitrogens of the central dilithiated ethylenediamine ligand are in the range 2.07(1)−2.10(1) Å, while the Li−N distances to the dibridging, four-coordinate amido nitrogens of the terminal monolithiated ethylenediamine ligands fall within 1.97(1) and 1.99(1) Å. These groupings are close to those observed in the four-rung ladder structures of [{LiN(CH_2)$_4$}$_6$-(*N,N,N′,N″,N″*-pentamethyldiethylenetriamine)$_2$][5] and [{Li[N-($SiMe_3$)$CH_2CH_2NSiMe_3$]Li•OEt_2}$_2$],[10] **5**, whose Li−N(tribridging amido) distances fall in the ranges 2.02−2.13 and 2.03−2.14 Å, respectively, and Li−N(dibridging amido) distances are within 1.95−2.00 and 1.91−1.98 Å, respectively. Comparisons with the crystal structures of the other simple lithium amide ladders [{Li[N(CH_2)$_5$][HN(CH_2)$_5$]}$_4$],[6] [{LiN(CH_2)$_4$}$_4$(*N,N,N′,N′*-tetramethylethylenediamine)$_2$],[4] and [{Li_2[N(2,6-*i*-$Pr_2C_6H_3$)-CH_2]$_2$}$_2$][12] are less valid given the different coordination numbers of the terminal lithium atoms in those cases. The Li−N(dibridging amido) distances in [*cis*-{Li[μ-N(*t*-Bu)CH_2CH_2N-(H)*t*-Bu]}$_2$], **2**, compare with those in **3**. The Li−N distances in the cyclic six-rung ladder structure of [{LiN(CH_2)$_6$}$_6$][29] are in three near-exclusive ranges, 1.99−2.00, 2.06−2.09, and 2.07−2.12 Å, arising from molecular orbital considerations,[1,2,20] all the nitrogen atoms in the structure triply bridge three-coordinate lithium atoms.

The Li−N(amine) distances of 2.06(1) and 2.09(1) Å in **3** compare with the secondary amine Li−N distances in **2** and [{*i*-Pr_2N(H)•Li[μ-N(Ph)C_6H_9]}$_2$],[8] 2.037(7) and 2.109 Å, respectively. The Li−N distances in the 1:1 piperidine:lithium piperidide complex, [{Li[N(CH_2)$_5$][HN(CH_2)$_5$]}$_4$],[6] which contains a similar four-rung Li_4N_4 ladder structure are longer, 2.10−2.22 Å, which is in accordance with the coordination number of the terminal lithium atoms being four-coordinate in that case.

Li···Li contacts across the end Li_2N_2 rings of **3**, 2.33(1) and 2.34(1) Å, are comparable with those in the structure of **2** but shorter than the Li···Li distance in the folded central Li_2N_2 ring of **3**, 2.49(1) Å. The Li···Li contact across the folded Li_2N_2 ring in [(hexamethylphosphoramide)$_3Li_2${N(Ph)CH_2}$_2$][11], at 2.286(6) Å, is shorter presumably as a geometrical consequence of the lithium bridging O centers of the hexamethylphosphoramide molecule. Generally, Li···Li contacts across Li_2N_2 rings vary inversely with the N···N distance, which is in keeping with the Li−Li nonbonding electrostatic description of lithium dibridging organolithium structures.[30]

Close Li−H agostic interactions are again observed between each of the three-coordinate lithium atoms and hydrogen atoms of the *tert*-butyl substituents in **3**. Each lithium atom has one such interaction in the range 2.23−2.41 Å. The coordination environment about each of the lithium atoms in **3** is far from

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(28) Engelhardt, L. M.; Jacobsen, G. E.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 1011.

(29) Barr, D.; Clegg, W.; Hodgson, S. M.; Lamming, G. R.; Mulvey, R. E.; Scott, A. J.; Snaith, R.; Wright, D. S. *Angew. Chem.* **1989**, *101*, 1279; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1241.

(30) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984** *17*, 353 and references therein.

being planar. The sum of the N−Li−N angles about the terminal lithium atoms is 341.7°and 340.9°, similar to that of **2**, 339.4°. The coordination environments of the central lithium atoms are closer to planar, with the sum of their three N−Li−N angles being 348.2°and 350.4°. As argued for the structure of **2**, the nonplanar lithium environments result from geometry constraints of the ligand.

The three edge-fused Li_2N_2 rings in the four-rung ladder of **3** are folded to different extents. The geometry of the terminal Li_2N_2 rings in the structure are subject to the same influences as found in **2**, accordingly the Li−N−N−Li dihedral angles measure 157.1(7)° and 160.5(8)°, being not too dissimilar to those of **2**, 169.4(3)°. The central Li_2N_2 ring is folded along the N−N vector by the ethylene linkage of the dilithiated ethylenediamine bridging the two central nitrogen atoms. The dihedral angle Li−N−N−Li measuring 110.1(6)° is much larger than that for $[(\text{hexamethylphosphoramide})_3Li_2\{N(Ph)CH_2\}_2]$,[11] 90.8°, owing to the lithium bridging hexamethylphosphoramide molecule which increases the folding of the Li_2N_2 ring. Folding of the Li_2N_2 ring in $[\{(\text{tetrahydrofuran})_2Li\}_2\{\mu\text{-}N(p\text{-}MeC_6H_4)\text{-}CPh\}_2]$[31] by the *N,N′*-acetylene linkage also occurs, the Li−N−N−Li dihedral angle measuring 121.7(5)°. Alkyl and silyl bridging groups are also responsible for folding the Li_2N_2 rings in $[\{Li[rac\text{-}N(t\text{-}Bu)CH(Me)CH(Me)Nt\text{-}Bu]Li\}_2]$[9] and $[\{Me_2Si\text{-}[N(Li)t\text{-}Bu]_2\}_2]$,[21] relieving congestion from one side of the Li_2N_2 ring and allowing, otherwise rare, ring stacking to occur.

The effect of the folded central Li_2N_2 ring of **3** can be seen to twist the four-rung ladder. Extension of the ladder by the complete lithiation could be seen to result in a ladder of indefinite length containing alternating planar and folded Li_2N_2 rings giving a helical ladder structure with approximately one quarter turn per dilithium ethylenediamide unit, *viz,* the approximately 90° torsion angle between the ethylene linkages of adjacent ligands in **3**. The computed structure of the linear trimeric ladder of dilithiated ethylenediamine also exhibits this feature of a helical Li_6N_6 core, *vide infra*. In comparison, the Li_4N_4 core of the four-rung ladders in $[\{LiN(CH_2)_4\}_4(N,N,N',N'\text{-tetramethylethylenediamine})_2]$[4] and $[\{LiN(CH_2)_4\}_6(N,N,N',N'',N''\text{-pentamethyldiethylenetriamine})_2]$[5] is essentially planar except for the terminal lithium atoms, suggesting that planar ladders of indefinite length would be found for $\{LiN(CH_2)_4\}_n$. The ladder in the partially lithiated piperidine complex $[\{Li[N(CH_2)_5][HN(CH_2)_5]\}_4]$[6] is slightly concave due to the slight folding of the central Li_2N_2 ring. The ladder of $[\{Li[N(SiMe_3)CH_2CH_2NSiMe_3]Li\cdot OEt_2\}_2]$,[10] **5**, is highly concave owing to the ethylene linkages of the dilithiated ethylenediamines edge-bridging nitrogen atoms along the ladder. The related unsolvated dilithiated ethylenediamine dimer $[\{Li_2[N(2,6\text{-}i\text{-}Pr_2C_6H_3)\text{-}CH_2]_2\}_2]$[12] also has ladder edge-bridging ethylene linkages but has a centrosymmetric stepped structure. Other bond distances and angles within the molecule are unexceptional and do not require comment.

Theoretical Calculations. Molecular orbital calculations have been used to give a quantitative estimate of the relative energetics of the aggregation to various oligomeric/polymeric forms in *N,N′*-dilithium ethylenediamide complexes. Figure 6 shows schematic representations of the computed structures and the numbering scheme of the computed structures. Table 10 lists the total energies and point group symmetries of the various computed structures. Both mono- and dilithium ethylenediamide ($LiN(H)CH_2CH_2NH_2$ and $LiN(H)CH_2CH_2N(H)Li$) have been the subject of a previous theoretical study, but those calculations (6-31G) stopped short of aggregated or solvated species and dealt only with the uncomplexed monomeric molecules.[11] The reported optimized geometries featured a chelating ligand for the monolithiated molecule (C_1 symmetry) and a "Li_2N_2 double bridged" dilithio species featuring a butterfly-shaped Li_2N_2 ring (C_2 symmetry). Our calculations yielded similar structures for these molecules. The study of aggregates was limited to species featuring at most three-coordinate lithium atoms as this has been the limit observed for the coordination environments in the relevant characterized examples, except for the monomeric species $[(\text{hexamethylphosphoramide})_3Li_2\{N(Ph)CH_2\}_2]$[11] which contains the least hindering substituents and a highly prolate Lewis base which

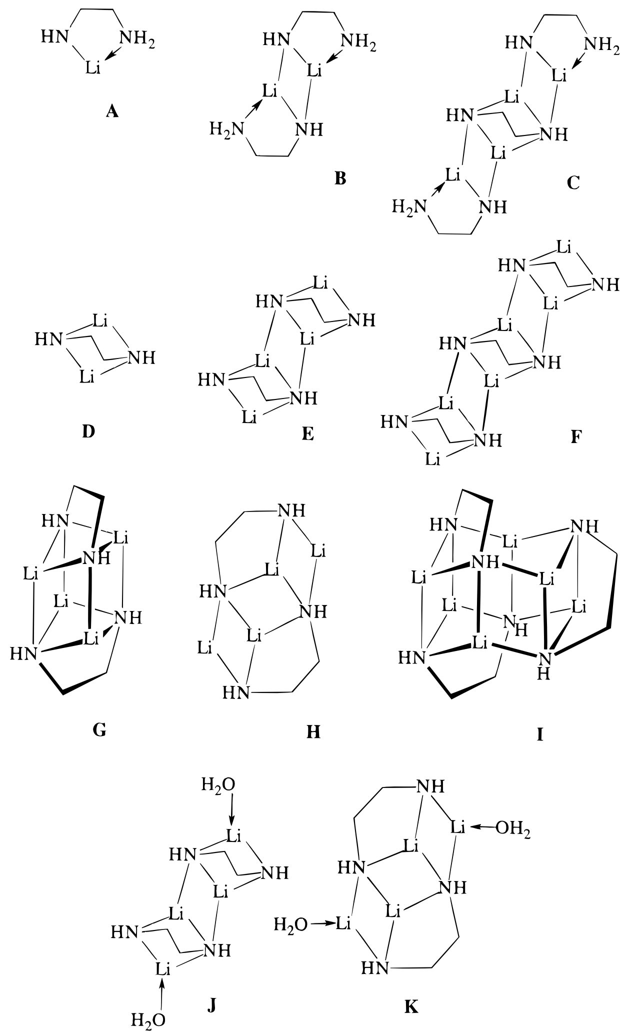

Figure 6. Schematic representations of the computed structures.

Table 10. Computed Total Energies and Point Group Symmetries of the Optimized Structures (See Figure 6 for Structure Numbering Scheme)

molecule	point group	total energy (au)	
		(3-21G*)	(6-31G*)
A	C_1	−195.074 142	−196.151 748
B	C_2	−390.249 192	−392.391 379
C	C_2	−592.269 653	−595.509 094
D	C_2	−201.945 524	−203.053 325
E	C_2	−403.960 443	−406.167 033
F	C_2	−605.979 408	−609.285 062
G	S_4	−403.983 954	−406.190 300
H	C_2	−403.974 986	−406.182 873
I	C_2	−606.022 371	−609.324 558
J	C_2	−555.231 247	−558.243 990
K	C_2	−555.241 198	−558.255 974
H_2O	C_{2v}	−75.5859 60	−76.010 747

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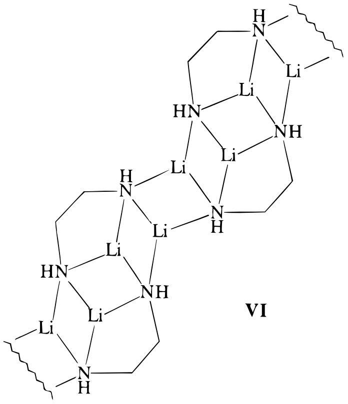
[31] Scholz, J.; Richter, B.; Goddard, R.; Krüger, C. *Chem. Ber.* **1993**, *126*, 57.

occupies a small coordination site of the lithium atom. The search for minima was not exhaustive but primarily aimed at the structures of relevance to the experimental findings.

Many comparisons about the association energies of the various structural types can be obtained through analysis of the data in Table 10. Of primary interest here is the association energies for the dilithiated species associating to the stacked dimeric species, **G**, which was observed for **4a** and the linear polymeric ladder proposed for **4b**. The association energy for dimerization is given by **G**/2 − **D** and has the value −26.25 (−29.15) kcalmol^{-1}.[32] An estimate of the association (per monomeric unit) for the polymerization of the species is given by the energy for insertion of **D** into both **B** and **E** to give the species **C** and **F**, respectively. These energies are given by **C** − **B** − **D** and **F** − **E** − **D** and take the values −40.40 (−47.02) and −40.60 (−46.08) kcal mol^{-1}, respectively. These independent estimates for the association to linear polymeric species show excellent internal agreement and clearly place aggregation to a polymeric ladder as more favorable compared to a stacked dimeric species. This result is consistent with the experimental evidence for **4** preferably crystallizing as a sparingly soluble modification and only crystallizing as a dimer by forcing it to adopt the structure it takes in benzene solution by rapid freezing of solutions of **4**. The *rac*-2,3-dimethyl analogue of **4**, [{Li[*rac*-N(*t*-Bu)CH(Me)CH(Me)N*t*-Bu]Li}$_2$],[9] adopts a dimeric structure in preference to a polymeric ladder presumably due to the steric influence of the 2,3-substituents, *vide supra*.

The centrosymmetric four-rung ethylene edge-bridged ladder structure of [{Li$_2$[N(2,6-*i*-Pr$_2$C$_6$H$_3$)CH$_2$]$_2$}$_2$][12] is some 16.69 (19.75) kcal mol^{-1} in energy above the polymeric ethylene face bridging ladder (**H**/2 − (**F** − **E**)) and remains as an anomaly to the theoretical calculations.[33] This energy difference is close to the energy difference of the polymeric ladder and stacked dimer. In that case the energy difference was surmountable by steric factors and so the influence of the highly hindered aryl group could be responsible here also. 2,6-Disubstituted aryl groups are well-known in the literature for producing novel low coordination number metal complexes by limiting association. Atom connectivities in the case of ethylene edge-bridged ladders restrict the association to dimers of four-rung ladder length with the terminal lithium atoms being two coordinate. The centrosymmetric ethylene edge-bridged dimeric ladders can conceivably further associate into linear polymeric ladders which are stepped due to the contorting influence of the ethylene bridging units, **VI**. The energy of such a polymeric ladder maybe on the order of the ethylene face bridge ladder, but computational restrictions did not permit investigations of oligomers of **H**. The dilithium *N*,*N*′-diphenyl derivative has been prepared as a hexamethylphosphoramide adduct, [(hexamethylphosphoramide)$_3$Li$_2${N(Ph)CH$_2$}$_2$],[11] but is monomeric due to the coordinative saturation of the lithium atoms provided by the donor molecules and so is not of use in resolving the preferred aggregation of less substituted *N*,*N*′-diaryl derivatives.

The *N*,*N*′-bis(trimethylsilyl) derivative, [{Li[N(SiMe$_3$)CH$_2$CH$_2$NSiMe$_3$]Li}$_3$],[10] exhibits a cyclic ladder structure with elements of both the ethylene edge-bridged dimeric ladder and the ethylene face-bridged polymeric ladder proposed of **4b**. The average energy of association (per monomeric unit) of this species is intermediate between the two components at −34.34 (−38.86) kcal mol^{-1} (**I**/3 − **D**). This trimeric structure can be seen as the viable means of achieving coordination saturation of the terminal lithium atoms in C_2 symmetric edge-bridging ladders by insertion of a molecule of **D** across the terminal rungs of the already concave ladder which is energetically very favorable, −55.45 (−63.92) kcal mol^{-1} (**I** − **H** − **D**) (this calculation does however represent the association energy for the formation of an additional four Li−N bonds, whereas the preceding calculations represented the formation of two Li−N bonds). Extension of the ladder for a C_2 symmetric ethylene edge-bridged ladder as in **VI** is seemingly not possible owing to the concavity of the ladder being such that a molecule of **D** is ideal to complete the cyclic arrangement. Clearly the association of these species displays subtle effects, some of which are highlighted by the structures of the complexes discussed above with gross variations in the substituents featuring.



VI

Subtle factors also apparently account for the extent of deaggregation achieved by Lewis base donor molecules in these species. Compound **4** for example, does not form an adduct with diethyl ether while the trimethylsilyl-substituted analogue forms a dimeric adduct, [{Li[N(SiMe$_3$)CH$_2$CH$_2$NSiMe$_3$]Li·OEt$_2$}$_2$],[10] and a monomer is observed for the hexamethylphosphoramide adduct [(hexamethylphosphoramide)$_3$Li$_2${N(Ph)CH$_2$}$_2$].[11]

Of note is the preference for both unsolvated and solvated dimeric ladders to adopt ladder edge-bridging ethylene linkages rather than ladder face-bridging ethylene linkages. Comparisons of the unsolvated ladders, **E** and **H**, and the ladders bearing a single molecule of water on each terminal lithium atom, **J** and **K**, show energy differences of 4.97 (4.56) and 3.76 (3.12) kcal mol^{-1} in favor of the ethylene edge-bridged ladders, respectively (per monomeric unit); ((**H** − **E**)/2 and (**K** − **J**)/2). This is in agreement with the isolation of [{Li[N(SiMe$_3$)CH$_2$CH$_2$NSiMe$_3$]Li·OEt$_2$}$_2$].[10] The preference for ethylene edge-bridging ladder formation appears to be in response to the relief of steric strain in the "Li$_2$N$_2$ double-bridged" butterfly-shaped Li$_2$N$_2$ ring. Both of these edge-bridging ladders have been identified in [{Li[N(SiMe$_3$)CH$_2$CH$_2$NSiMe$_3$]Li·OEt$_2$}$_2$][10] and [{Li$_2$[N(2,6-*i*-Pr$_2$C$_6$H$_3$)CH$_2$]$_2$}$_2$].[11]

A final feature worthy of mention relates to the isolation of **6** from a stoichiometric mixture of **2** and **5** which can be compared with the predicted energy for this transformation, (**C** + H$_2$O) − (0.5**K** + **B**), which is unfavorable by 8.90 kcal mol^{-1} at the 3-21G* level of theory and favorable by 0.30 kcal mol^{-1} at the 6-31G* level of theory. The isolation of **6** would be favored by the chelation stability of the intramolecular Lewis base donor in **6** versus the diethyl ether molecules in **5** but

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[32] The association energies discussed in this section refer to the difference in total energies of the molecules concerned, for example, **G**/2 − **D** refers to the subtraction of the total energy of molecule **D** from half the total energy of molecule **G**. Energies are given at the 6-31G* level of theory (energies at the 3-21G* level of theory are in parentheses).

[33] Only the structure of the ethylene edge-bridged dimeric ladder with C_2 symmetry was calculated; the analogous centrosymmetric ladder should be of comparable energy.

unfavored by the steric strain introduced in forming the "Li_2N_2 double bridged" unit in **6**.

Conclusion

We have been able to identify and structurally characterize two intermediates from the dilithiation of *N*,*N*′-di-*tert*-butylethylenediamine by alkyllithium species in addition to establishing the dimorphic nature of the dilithiated complex in the solid state. The structures adopted by the intermediates have given great insight into the mechanism for the lithiation of secondary amines and provide direct evidence for the assembly of polymeric structures in amidolithium chemistry including the identification of the end groups present in ladder formation. We have also examined the energetics of the aggregation of amidolithium species[1,2] by *ab initio* molecular orbital calculations to investigate the effect that the specific geometrical requirements of the ethylenediamide ligand has on their association.[11] The calculations were in agreement with prior studies on the association of $LiNH_2$ which showed the preferred association to be lateral association to laddered polymeric structures rather than vertical association giving stacked dimers.

Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council, and we thank Colin Kennard and Karl Byriel for collecting the X-ray diffraction data.

Supporting Information Available: Lists of U_{ij} values, hydrogen atom parameters, bond distances and angles, and summaries of the X-ray diffraction data for compounds **2**, **3**, **4a**, and **6** (18 pages). Ordering information is given on any current masthead page.

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