Dis-assembling Lithium Amide Ladder Structures: Structural Elucidation of the Lithium Anilide Solvate [{PhN(H)Li}$_6$·8THF], a Model Intermediate *En route* to Forming Tetra-solvated Ring Dimers

William Clegg,[a] Lynne Horsburgh,[a] Fiona M. Mackenzie[b] and Robert E. Mulvey*[b]

[a] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne, UK NE1 7RU*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK G1 1XL*

Of widespread significance throughout lithium amide chemistry, the key step in dis-assembling ladder structures to give solvated dimeric rings appears to be insertion of solvent molecules into inner rung sites, as implied by the bridging THF ligands in the model intermediate [{PhN(H)Li}$_6$·8THF].

Ladder-shaped conformations are now an established part of lithium amide structural chemistry.[1] They originate from the lateral fusing of small, oligomeric $(NLi)_n$ rings in a self-assembling process governed by electrostatics, but directionally controlled by the stereochemical orientations of the organo R substituents in secondary amides $[(R^1R^2NLi)_n]$. Ladder structures are thought to be widespread, occurring generally where R^1 and R^2 are small or flat. This paper reports a significant advance in the understanding of laddering principles. It discloses a model structure, representative of an intermediate in the process whereby a ladder is dis-assembled into its constituent dimeric rings. Driven by solvation, the disassembly appears to proceed partly *via* the insertion of solvent molecules into inner positions within the ladder framework. This contrasts with previously reported solvated ladders which exhibit solvation only at the sterically accessible ladder ends.[1,2] Formally hexameric, the new (primary) amide [{PhN(H)Li}$_6$·8THF] **1** clearly represents a step on the way to fragmenting into three solvated $(NLi)_2$ dimeric ring molecules.

Lithium anilide [{PhN(H)Li}$_n$] can be prepared by mixing equimolar amounts of aniline and Bu^{n}Li in hexane solution, provided that stringently dry and O_2-free conditions are maintained throughout to guard against decomposition (most notably to aniline black).[3] Subsequent addition of THF (1.5 molar equivalents—close to the 1.33 found in the crystal structure) affords colourless needle crystals of solvate **1**.†

While the core of the structure of **1**‡ may formally resemble a four-runged ladder (Fig. 1), the inner-rung solvation [to Li(3), Li(3a)] coupled with the fact that the outer rungs contain neutral donor atoms [O(4), O(4a)], not anions, signifies that it is not a genuine lithium amide ladder species. Furthermore, such solvated ladders characteristically contain a deficiency of donor molecules (*i.e.* less than one per Li^+ centre),[1] whereas **1** contains an excess (8THF : $6Li^+$). Instead, **1** can be more informatively described as a loose assembly of three linked dimeric $(NLi)_2$ rings [as emphasised in Fig. 1(*b*)], implying that it results from the partial rupturing of a ladder or ladder fragment, of six N–Li rungs in length (unsolvated lithium anilide is predicted to be a ladder from earlier established geometrical considerations[1]). Rupturing occurs when coordinating solvent (THF) molecules are introduced: two bind terminally to outermost Li(1), one binds terminally to innermost Li(3), and most significantly, one bridges Li(2) and Li(3). More than any other factor, it is this bridging role which opens one's eyes to the special, intermediate, transitional nature of structure **1**, as in all previous lithium amide 'frozen' structures (crystal structures) ligated THF ends up terminally attached {indeed, bridging THF is a rarity in all areas of lithium structural chemistry, though it is known, *e.g.* in the mixed lithium tantalum metallocene, $Li_2(THF)_3[(\eta\text{-}C_5Me_5)Ta(S_2)_2]_2(\mu\text{-}O)(THF)^4$}. It is also significant that the bridge bonds in **1** are not symmetrical: O(4a)–Li(2) is decidedly longer [2.217(5) Å] than O(4a)–Li(3a) [2.058(4) Å], supporting our hypothesis (see below) that bis(solvation) of Li(3a) is a prerequisite to THF insertion (bridging) and concomitant opening of the ladder. Not surprisingly, the terminal (THF)O–Li bonds are shorter still (mean length, 1.959 Å). Long interdimer bonds [N(3)–Li(2), N(3a)–Li(2a) 2.145(5) Å] hint at the impending fragmentation into three separate $(NLi)_2$ dimers. However, the 'stretching' of these bonds must be balanced against the distance required for THF to form the bridge. Hence the appearance of an even longer interaction in the central $(NLi)_2$ ring [N(3)–Li(3) 2.199(5) Å] does not conflict with the fragmentation theory, especially as the other central bond [N(3)–Li(3a)] is far shorter [2.022(5) Å] (mean length of the four bonds in the central ring, 2.110 Å), in common with all the bonds in the two outer $(NLi)_2$ rings (mean length, 2.041 Å). Endocyclic bond angles in the central $(NLi)_2$ ring also deviate more [at N, 75.8(2)°; at Li, 104.2(2)°] than those in the outer rings [mean values: at N, 77.0°; at Li, 100.0°]. Note also that as a consequence of the THF insertion, the outer ring planes [Li(1)N(1)Li(2)N(2), Li(1a)N(1a)Li(2a)N(2a)] tilt well out of the central Li(3)N(3)Li(3a)N(3a) plane (by 60.1°).

This valuable new structural information makes it possible to propose a sequence of events (Scheme 1) that would explain the ladder → solvated dimer transformation. In **A**, the unsolvated amide is depicted as a six-runged cyclic ladder. Lithium anilide may be a stepladder of higher aggregation, but it is worthy of note that the secondary amide $[\{H_2\overline{C(CH_2)_5N}Li\}_6]$ is a hexameric cyclical ladder[5] and the primary amide

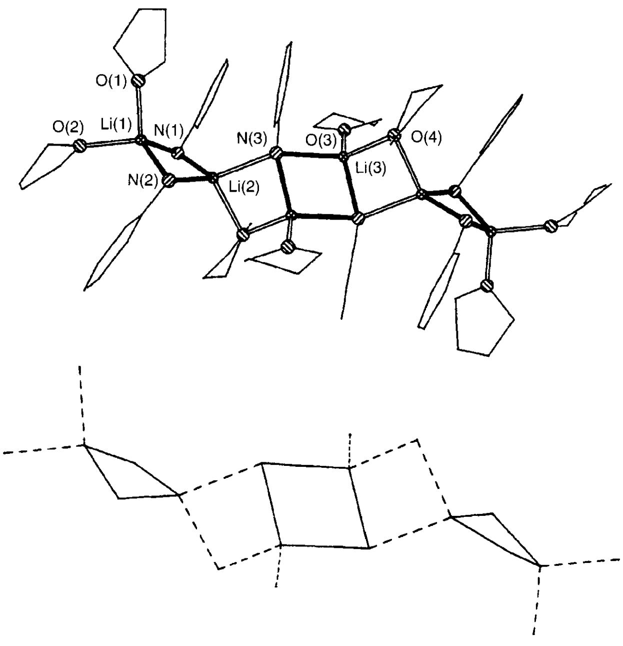
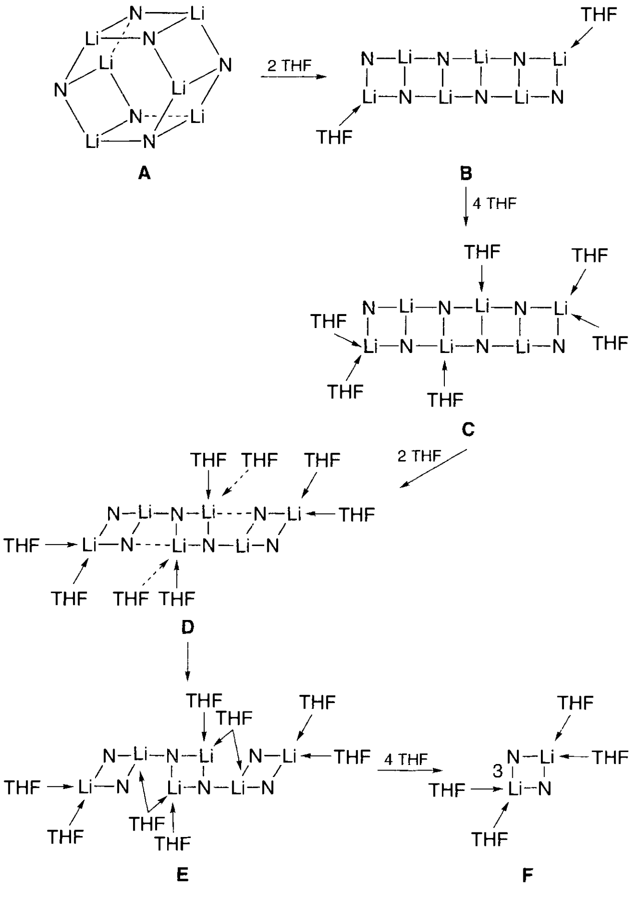


Fig. 1 (top) Molecular structure of the lithium anilide **1** without hydrogen atoms, showing selected numbering scheme. (bottom) Line drawing focussing on the three linked $(NLi)_2$ rings in the structure. Key dimensions (Å and °): Li(1)–O(1) 1.977(5), Li(1)–O(2) 1.936(5), Li(2)–O(4a) 2.217(5), Li(3)–O(3) 1.964(5), Li(3)–O(4) 2.058(4), Li(1)–N(1) 2.029(5), Li(1)–N(2) 2.066(5), Li(2)–N(1) 2.056(5), Li(2)–N(2) 2.011(5), Li(2)–N(3) 2.145(5), Li(3)–N(3) 2.199(5), Li–N(3a) 2.022(5); N(1)–Li(1)–N(2) 100.5(2), N(1)–Li(2)–N(2) 101.5(2), N(3)–Li(3)–N(3a) 104.2(2), Li(1)–N(1)–Li(2) 76.9(2), Li(1)–N(2)–Li(2) 77.1(2), Li(3)–N(3)–Li(3a) 75.8(2). Symmetry operator a: $1 - x, -y, 1 - z$ (inversion centre).

[{Bu^{t}N(H)Li}$_8$] is an octameric variant.[6] Irrespective of the precise starting structure, the first step in the dismantling process should be solvation of the 'terminal' Li$^+$ cations in the ladder ends. Monosolvation as illustrated in **B** was previously noted in the mixed dilithium disodium amide ladder [{[(PhCH$_2$)$_2$N]$_2$LiNa·OEt$_2$}$_2$][7] (solvent = diethyl ether). Terminal sites have the steric capacity to accommodate more solvent molecules so bis(solvation) (or its equivalent, bidentate solvation) is then possible, a precedent for which exists in [{[H$_2$C(CH$_2$)$_3$NLi]$_2$·TMEDA}$_2$] (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine).[1] To minimise crowding, the innermost Li sites would be the next preferred for further solvation, overall giving **C**. Support for **D** comes from the observation, discussed above, that the bridging THF in **1** forms a significantly shorter (by 0.159 Å) interaction with Li(3) than with Li(2a), implying that Li(3) was bis(solvated) beforehand. Either way, the pivotal step, insertion of the solvent molecule into the ladder framework, occurs next to give **E** as now established by the structure of **1**. Logically, the final step is complete fragmentation to tetra(solvated) dimers **F**. As yet the dimeric THF solvate has failed to crystallise (only solutions are obtained with THF : Li ratios greater than 2 : 1, implying that the dimer is appreciably more soluble than **1**). However, its existence has been indirectly proven by the isolation and crystallographic characterisation of the pyridine analogue [{PhN(H)Li·2py}$_2$], which adopts a standard transoid conformation.[6]



Scheme 1

In conclusion, the structural elucidation of a key model intermediate has shed unprecedented light on the way ladder structures dis-assemble into their constituent dimeric ring parts, a process of wide significance in lithium amide chemistry.

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Footnotes

† Yield of **1** (not refined), 53%. Satisfactory C, H, Li, N analyses were obtained. Mp 120–122 °C.

‡ *Crystal data* for **1**: $C_{68}H_{100}Li_6N_6O_8$, M = 1171.2, monoclinic, space group $P2_1/c$, a = 16.175(6), b = 10.637(3), c = 21.112(7) Å, β = 108.03(2)°, U = 3454(2) Å^3, Z = 2, D_c = 1.126 g cm^{-3}, $F(000)$ = 1264, T = 160 K. 5175 reflections were measured on a Stoe-Siemens diffractometer (Mo-Kα radiation, λ = 0.71073 Å, μ = 0.072 mm^{-1}, $2\theta < 47°$) with ω–θ scans and on-line profile fitting. Structure solution was by direct methods, and refinement by full-matrix least-squares methods on F^2 for all 5087 independent reflections. $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ = 0.1520 for all data, conventional R [on F values for 3292 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0470, goodness of fit = 1.046 on F^2 for all data and 416 refined parameters. All non-H atoms were refined with anisotropic displacement parameters, H atoms were subjected to riding model constraints. Programs: SHELXTL and SHELXL-93, G. M. Sheldrick, University of Göttingen, and local programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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