Regioselective solvation in a polymeric lithium amide: remarkable twisted ladder structure of $[\{[PhCH_2N(H)Li]_2\cdot H_2NCH_2Ph\}_\infty]$

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The hemi-benzylamine complex of lithium benzylamide exists in the crystal as an infinite, twisted-ladder structure of fused $(NLi)_2$ rings; curiously, one edge of the ladder is solvated by benzylamine molecules, while the other is solvent-free.

Lithium amide molecules can self-assemble by the process known as ‘ring-laddering’ to generate ladder structures, as most recently demonstrated by the cyclic octameric ladder structure of $[\{Bu^tN(H)Li\}_8]$.[1] This primary amide represents a special case in being oligomeric, on account of the bulky steric nature of its alkyl group. Generally, the absence of solvating ligands is thought to encourage continuous ladder growth rendering many lithium amide compounds polymeric. These infinite ladder structures can be broken down to smaller, partially solvated, ladders of a finite length, when exposed to certain solvating ligands. As a rule, this partial solvation takes place at the ladder ends (outer rungs), *e.g.* as found in the pyrrolidide $[\{[H_2C(CH_2)_3NLi]_2\cdot tmeda\}_2]$;[2] inner-rung solvation,[3] as studied theoretically by *ab initio* MO calculations on the model ladder tetramers $[(H_2NLi)_4\cdot nH_2O]$ (n = 0, 2 or 4),[2] has a destabilising influence. To the best of our knowledge, the possibility of donor molecules selectively ligating the ladder framework, along one edge only, has never been considered previously. In this paper we present experimental proof of such in the remarkable twisted-ladder structure of $[\{[PhCH_2N(H)Li]_2\cdot H_2NCH_2Ph\}_\infty]$ **1**. What is more, the selective solvation is achieved without interrupting the infinite nature of the ladder arrangement, so providing a rare example of a crystallographically characterised polymeric lithium amide (a lithium thiolate with an infinite ladder structure of Li–S rungs has been reported[4]). This study represents the first structural investigation of a lithium (mono) benzylamide species, and it is apt that it should provide such an important finding since it follows over a decade of activity in dibenzylamido systems[5] which has contributed significantly to our basic understanding of alkali metal amide structural chemistry.

Solubility problems necessitated the deliberate use of excess benzylamine in the reaction sequence producing **1**. Pure solvent-free, lithium benzylamide, prepared by treating freshly distilled benzylamine (10 mmol) with Bu^nLi (10 mmol) under standard inert-atmosphere conditions, precipitated as a pink slurry from hexane, and could not be dissolved on addition of toluene. However, dissolution was achieved by introducing a second equivalent of benzylamine (10 mmol) dropwise and strongly heating the mixture. Pink delicate platelets of **1** crystallised on cooling the resulting solution to *ca.* -30 °C for 1 d (yield of first batch, 40%). On isolation from solution, the crystals collapse to a melt in a matter of hours. While the synthesis proved reproducible, different batches of **1** were found to contain various amounts of benzylamine and occasionally toluene, suggesting that the loss of crystallinity is due to the product losing these solvents with time.†

An X-ray diffraction study‡ revealed that **1** adopts an infinite ladder structure of fused $(NLi)_2$ rings, only one Li centre of which is solvated by a benzylamine molecule [Fig. 1(*a*)]. Therefore one ladder edge has unsolvated, three-coordinate, pyramidal Li centres [Li(3), Li(4)], while the other has solvated, four-coordinate, distorted-tetrahedral ones [Li(1), Li(2)]. The pattern of N–Li bond lengths reflects this coordinative inequality. Rungs involving Li(3), Li(4) are distinctly shorter than those involving Li(1), Li(2) (respective mean values; 1.996, 2.102 Å); edge lengths are also generally shorter for the former atoms (mean value, 2.055 Å; *cf.* 2.116 Å for the latter atoms), the exception being N(3)–Li(3) which is longer than its opposite edge [N(4)–Li(1)] although the difference [0.012(7)Å] is not statistically significant. Alternating above and below the ladder framework along one edge, the benzylamine molecules form relatively long bonds to Li (mean length, 2.130 Å). By failing to

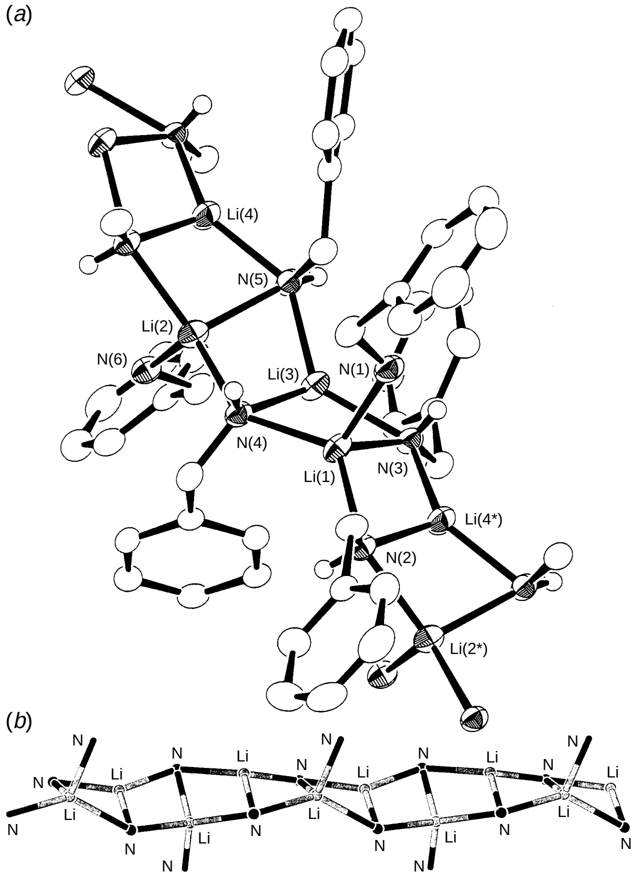

Fig. 1 (*a*) Section of the polymeric structure of **1** including the atom labelling scheme. Hydrogen atoms, apart from N–H ones, have been omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–Li(1) 2.135(5), N(2)–Li(1) 2.134(5), N(2)–Li(2*) 2.136(5), N(2)–Li(4*) 1.998(6), N(3) –Li(1) 2.102, N(3)–Li(3) 2.091(5), N(3*)–Li(4) 2.053(5), N(4)–Li(1) 2.079(5), N(4)–Li(2) 2.115(5), N(4)–Li(3) 1.993(5), N(5)–Li(2) 2.102(5), N(5)–Li(3) 2.060(5), N(5)–Li(4) 2.015(5) N(6)–Li(2) 2.125(5), N(2)–Li(1)–N(3) 104.4 (2), N(3)–Li(1)–N(4) 105.6(2), Li(1)–N(3)–Li(3) 69.7 (2), N(3)–Li(3)–N(4) 109.3 (2), N(4)–Li(3)–N(5) 104.0 (2), Li(1)–N(4)–Li(3) 72.0 (2), Li(2)–N(4)–Li(3) 73.5 (2), N(4)-Li(2)–N(5) 98.5 (2), N(5)–Li(2)–N(2*) 99.6 (2), Li(2)–N(5)–Li(3) 72.5 (2), Li(2)–N(5)–Li(4) 71.5 (2), N(5)–Li(4)–N(2*) 107.5 (2), N(2*)–Li(4)–N(3*) 111.4 (2), Li(2)–N(2*)–Li(4) 71.1 (2). (*b*) Stick drawing of a longer section of **1** emphasising the severe twisting within the ladder framework.

interrupt the laddering process and simply attaching itself to the ladder framework, this primary amine exhibits contrasting behaviour to that of the tertiary, chelating amines tmeda and pmdeta, which have been reported to break down (suspected) long ladders to finite ladders of limited length, *e.g.* as in $[\{[H_2C(CH_2)_3NLi]_2\cdot tmeda\}_2]$ and $[\{[H_2C(CH_2)_3NLi]_3\cdot pmdeta\}_2]$, respectively.[2] The four crystallographically distinct $(NLi)_2$ rings repeated throughout the ladder structure of **1** are non-planar. Two of them, Li(3)N(4)Li(2)N(5) and Li(2)N(5)-Li(4)N(2*), are much more distorted from planarity than the other pair, Li(1)N(2)Li(4*)N(3) and Li(1)N(3)Li(3)N(4) (respective summed bond angles: 348.5, 349.7, 356.6, 356.6°; respective mean rms deviations: 0.227, 0.212, 0.124, 0.123 Å); this factor contributes to the severe twisting within the ladder framework (symmetry code: $* = x + 1, y, z$). The twist is most pronounced at the solvated Li(2) centre [Fig. 1(*b*)]: considering only ladder framework N atoms, it is the most pyramidal of the Li centres [summed bond angle, 333.2°; *cf.* 337.9, 348.7 and 359.9° for Li(1), Li(3) and Li(4), respectively]; it also displays the smallest endocyclic N–Li–N bond angles (*i.e.* mean value, 99.1°; *cf.* range of others, 104.0–111.4°). Endocyclic angles at the N atoms cover a narrower range (69.7–73.5°) These five-coordinate N atoms have severely distorted trigonal bipyramidal geometries with the axial bonds positioned along the Li–N–Li ladder edges (range of axial bond angles, 137.0–143.3°). The benzylamine N atoms have distorted tetrahedral coordination geometries.

There is another unique feature to the ladder structure of **1**. The conformation of the bridging amido substituents $(PhCH_2, H)$ with respect to the four-membered $(NLi)_2$ rings, alternates between *cisoid* and *transoid*. In the octamer $[\{Bu^tN(H)Li\}_8]$[1] the conformation is exclusively *cisoid* (the bulky alkyl substituents all project *exo* from the N_8Li_8 framework), and it is this feature which dictates that the ladder turns in on itself and cyclises. However, most discrete lithium amide ring dimers exhibit *transoid* set-ups. In the laddering principle,[6] it is reasoned that ladder structures have their origin in the lateral association of two or more dimeric rings of formula $(R^1R^2NLi)_2$, but the possible ring conformations involved were not considered. The next goal is therefore to establish a correlation between the *cisoid/transoid* nature of the constituent $(NLi)_2$ rings and the final shape and size of the ladder.

We thank the EPSRC (studentship to A. R.) for sponsoring this research.

Footnotes and References

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† Satisfactory C, H, Li, N analyses. ^1H NMR (25 °C, 400 MHz, C_6D_6) δ −1.09 (t, NH), 0.30 (s, NH_2), 2.11 (s, CH_3, toluene) 3.67 (s, CH_2 amine), 4.18 (d, CH_2), 7.13 (br m, Ph).

‡ *Crystal data*: **1** $[C_{42}H_{50}Li_4N_6]_n$, monoclinic, space group $P2_1$, $a = 7.638(3)$, $b = 23.841(7)$, $c = 10.532(4)$ Å, $\beta = 92.78(3)°$, $U = 1915.6(10)$ Å^3, 7644 collected reflections, 6735 unique ($R_{merge} = 0.039$). Data collected at −150 °C on a Rigaku AFC7S diffractometer, $\lambda = 0.710\,69$ Å, $2\theta_{max} = 50°$. All reflections were collected with their Friedel mates. The absolute configuration could not be determined. Data was corrected for L_p effects only and then equivalent reflections were merged. Solution was by direct methods and Fourier techniques.[7] The H atoms bonded to N were refined isotropically but all other H atoms were placed in calculated positions. Final full-matrix least-squares refinement on F converged at $R = 0.0514$, $R_w = 0.0586$, $S = 1.80$ based on 5957 observations $[I > 2\sigma(I)]$ and 485 parameters. All calculations were performed using the teXsan package. TeXsan, Crystal Structure Analysis Package, Molecular Structure Corp., 1993. CCDC 182/668.

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Received in Cambridge, UK, 11th September 1997; 7/06615E