New Alkali Metal Primary Amide Ladder Structures Derived from *t*BuNH$_2$: Building Cisoid and Transoid Ring Conformations into Ladder Frameworks

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Abstract: Two novel alkali metal amide ladder complexes have been synthesised and crystallographically characterised. Derived from the same primary amine precursor (*t*BuNH$_2$), they represent important additions to the series of ladder arrangements previously established within secondary amide chemistry. Thus the sodium amide · amine complex $[\{[t\mathrm{BuN(H)Na}]_3 \cdot \mathrm{H_2N}t\mathrm{Bu}\}_\infty]$ forms an infinite wavelike ladder structure. Covering three nitrogen–sodium rungs, its curved sections display a cisoid conformation of amide substituents; but where these curved sections fuse, a transoid conformation is found. Every third sodium cation along the ladder framework is ligated by a *tert*-butylamine solvent molecule. In contrast, the heterobimetallic derivative, $[\{[t\mathrm{BuN(H)}]_2\mathrm{LiNa} \cdot \mathrm{tmeda}\}_2]$, adopts a finite oligomeric ladder structure limited to only four nitrogen–metal rungs in length. The central rungs contain lithium, while the outer rungs contain sodium. As in the all-sodium structure, the ladder is curved; there is a mixture of cisoid and transoid ring conformations within its framework. TMEDA solvent molecules complete the structure by chelating the sodium cations at the ladder ends.

Keywords: amides · ladder structures · lithium · sodium · structure elucidation

Introduction

The self-assembly of ladder structures,[1] a subject relevant to many different parts of the Periodic Table, is currently attracting considerable attention from chemists. As far as lithium amides and related compounds are concerned, the concept of ring-laddering began to develop in the mid-1980s.[2] To elaborate, polar compounds of this type have a pronounced tendency to self-associate, to maximise the number of electrostatic attractions; thus, it is thought that ladder structures have their origin in the lateral association of two or more dimeric rings of formula $(\mathrm{R^1R^2NLi})_2$.[3] In general, ladders can have an open or cyclic appearance and their lengths (as defined by the number of rungs) can vary. They are also not confined to the solid state, as their existence in solution has been confirmed by NMR spectroscopic studies.[4] An important point that appears not to have been addressed previously in this developing theme is considered here: the precursor dimeric rings from which the ladders are constructed can, in theory, start off with either a *cisoid* or *transoid* arrangement of amido substituents provided that $\mathrm{R^1} \neq \mathrm{R^2}$. Hitherto, most crystallographically characterised ladder complexes have failed to meet this condition on account of having equivalent R groups [e.g., as in the dibenzylamide **1**[5] and the bis(trimethylsilyl)phosphide **2**[6]] or R groups tied together as part of a heterocyclic ring (e.g., as in the hexamethyleneimide **3**,[7] the piperidide **4**,[8] the pyrrolide **5**,[9] and the pyrrolidide **6**[3]). We have circumvented this situation by preparing ladder complexes derived from primary amines (where $\mathrm{R^1} = \text{alkyl}$; $\mathrm{R^2} = \mathrm{H}$), thus opening the possibility of building cisoid and/or transoid conformations into ladder frameworks. Hence, this

$[\{[(\mathrm{PhCH_2})_2\mathrm{N}]_2\mathrm{LiNa} \cdot \mathrm{OEt_2}\}_2]$ **1** $[\{\mathrm{H_2C(CH_2)_4NLi} \cdot \mathrm{HN(CH_2)_4CH_2}\}_4]$ **4**

$[\{(\mathrm{Me_3Si})_2\mathrm{PLi}\}_6]$ **2** $[\{\mathrm{MeC(CMe)_3NNa}\}_\infty]$ **5**

$[\{\mathrm{H_2C(CH_2)_5NLi}\}_6]$ **3** $[\{[\mathrm{H_2C(CH_2)_3NLi}]_2 \cdot \mathrm{tmeda}\}_2]$ **6**

paper describes the novel sodium amide · amine polymeric ladder complex **7**, which features both conformations simultaneously in its wavelike structure. Also reported is the heterobimetallic derivative **8**, another curved ladder species,

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but a finite oligomer with a different combination of cisoid/transoid units to that found in **7**. Furthermore, adding these two new crystal structures to that previously described for **9**[10] not only completes the series of lithium, sodium, and mixed lithium–sodium structures of *tert*-butylamide, but it also establishes an unprecedented family of ladder compounds, each of which displays a unique rung size and architecture.

$[\{[t\mathrm{BuN(H)Na}]_3\cdot\mathrm{H_2N}t\mathrm{Bu}\}_\infty]$ **7**

$[\{[t\mathrm{BuN(H)}]_2\mathrm{LiNa}\cdot\mathrm{tmeda}\}_2]$ **8**

$[\{t\mathrm{BuN(H)Li}\}_8]$ **9**

Results and Discussion

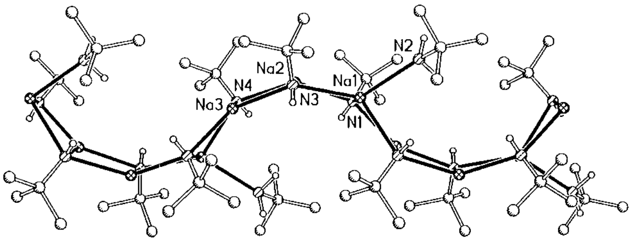

Figure 1. One-dimensional polymeric structure of **7**. Hydrogen atoms attached to carbon have been omitted for clarity.

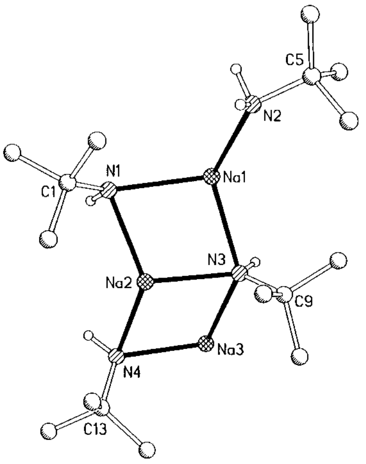

Figure 2. Section of **7** showing atom-labelling scheme. Selected bond lengths [Å] and angles [°]: Na1–N1 2.492(4), Na2–N3 2.346(4), Na3–N4 2.342(4), Na1–N3 2.498(4), Na1–N4A 2.489(4), Na2–N1 2.378(4), Na2–N4 2.428(4), Na3–N3 2.439(4), Na3–N1B 2.364(4), Na1–N2 2.567(5); N1-Na1-N3 99.16(13), N1-Na-N4A 98.65(13), N3-Na1-N4A 128.20(13), N1-Na1-N2 110.78(15), N3-Na1-N2 127.89(16), N4A-Na1-N2 89.01(15), N1-Na2-N3 107.06(13), N4-Na2-N3 104.38(12), N1-Na2-N4 130.55(16), N4-Na3-N3 104.19(12), N4-Na3-N1B 106.79(14), N3-Na3-N1B 141.78(14), Na1-N1-Na2 76.11(12), Na1-N1-N3A 76.00(11), Na2-N1-Na3A 138.75(17), Na2-N3-Na1 76.57(11), Na2-N3-Na3 75.49(11), Na1-N3-Na3 136.69(16), Na3-N4-Na2 75.78(11), Na3-N4-Na1B 76.48(10), Na2-N4-Na1B 133.81(15); symmetry codes: A = $-x$, $-1/2+y$, $1/2-z$; B = $-x$, $1/2+y$, $1/2-z$.

Figure 1 emphasises the curved, undulating nature of the extended structure of **7**, while Figure 2 focuses on its asymmetric unit. The curvature originates from the cisoid arrangement of amido substituents relative to the two $(\mathrm{NNa})_2$ ring planes within the $(\mathrm{NNa})_3$ ladder unit of Figure 2. This bending allows the bulky alkyl group to occupy the larger, more sterically accessible, exterior side of the curve, with the H atoms confined to the smaller interior side. Each individual cisoid $(\mathrm{NNa})_3$ subunit is turned upside-down with respect to its two adjacent cisoid $(\mathrm{NNa})_3$ subunits (successive subunits are related by a twofold screw rotation axis) to produce the alternating concave–convex pattern observed throughout the ladder framework. This inversion is attributed to the steric intrusion of the additional *tert*-butylamine molecules that ligate in sequence every third $\mathrm{Na^+}$ cation (Na1) along the polymer. As a consequence, where the cisoid subunits fuse (along the edge bonds, Na1–N4′ and Na3–N1′), the conformation of the amido substituents changes to a transoid set-up. This contrasts with the situation found in the lithium analogue **9**, [10] where the lack of solvent ligands leads to an exclusively cisoid conformation; this results in a closed cyclic structure comprising eight N–Li rungs.

Bond dimensions within the ladder framework of **7** are also strongly influenced by the selective solvation, as this gives rise to different metal coordination numbers (3 for Na2/Na3; 4 for Na1). There are alternating short and long N–Na rungs (mean lengths, 2.344 and 2.492 Å), the latter involving solvated Na1. Edge bonds come in three distinct pairs: adjacent long ones (Na1–N3, Na1–N4; mean length 2.494 Å), adjacent short ones (Na2–N1, Na3–N1; mean length 2.372 Å) that lie directly opposite the first pair, and intermediate ones (Na2–N4, Na3–N3; mean length 2.433 Å) that face each other across the ladder. Without the complication of solvent molecules, the bond length pattern is much simpler in the only other crystallographically characterised sodium amide polymeric ladder **5**:[9] one rung type of intermediate length with alternating short and long edge bonds (respective lengths: 2.411, 2.351 and 2.694 Å). The longest N–Na bonds in **7** [2.566(5) Å] are the dative ones involving the amine molecules. Turning to angular dimensions, the four-membered $(\mathrm{NNa})_2$ rings making up the ladder framework are essentially planar (root mean square deviations 0.082, 0.032 and 0.113 Å). Endocyclic angles show little variation at N (mean value, 76.1°), but substantial variation at Na (mean values at Na1, 98.9°; at Na2/Na3, 105.6°) due to the aforementioned coordination differences. The obtuse bond angles along the edges of the ladder cover a wide range [128.21(13)–141.79(14)°], again with less variation at N than Na. Positioned at the centre of the three-runged cisoid unit, Na2 possesses significantly greater pyramidal character than Na3 (sum of bond angles: 342.0° and 352.8° respectively) because Na3 lies at the juncture of the convex–concave pattern, while Na1 adopts a distorted tetrahedral geometry (bond angles 89.0–128.2°). The five-coordinate N centres have a distorted trigonal bipyramidal coordination, with the axial N–Na bonds lying along the ladder edges; the planarity of the N(H)C units is consistent with sp^2-hybridisation.[11]

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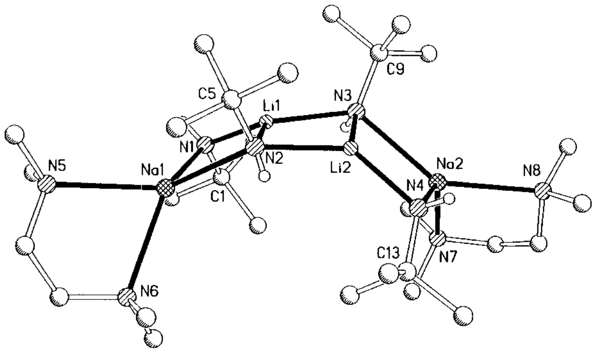

Figure 3. Convex structure of **8** showing atom-labelling scheme. Hydrogen atoms attached to carbon have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Na1–N1 2.341(7), Na1–N2 2.481(7), Na2–N3 2.441(7), Na2–N4 2.312(7), Na1–N5 2.571(7), Na1–N6 2.537(7), Na2–N7 2.509(7), Na2–N8 2.508(7), Li1–N1 1.952(13), Li1–N2 2.048(14), Li1–N3 2.083(14), Li2–N2 2.095(14), Li2–N3 2.019(14), Li2–N4 1.961(14); N1-Na1-N2 89.7(2), N5-Na1-N6 71.6(2), N1-Na1-N5 120.7(6), N2-Na1-N5 129.9(2), N1-Na1-N6 129.5(3), N2-Na1-N6 120.8(2), N3-Na2-N4 90.0(2), N7-Na2-N8 74.3(2), N3-Na2-N7 112.4(2), N4-Na2-N7 132.7(3), N3-Na2-N8 140.9(2), N4-Na2-N8 114.1(3), N1-Li1-N2 116.6(7), N2-Li1-N3 107.3(6), N1-Li1-N3 130.0(7), N2-Li2-N3 107.9(6), N3-Li2-N4 115.2(7), N2-Li2-N4 130.2(7), Na1-N1-Li1 79.3(4), Na1-N2-Li1 74.3(4), Li1-N2-Li2 71.4(5), Na1-N2-Li2 131.5(4), Li1-N3-Li2 72.2(5), Li2-N3-Na2 75.2(4), Li1-N3-Na2 129.9(5), Li2-N4-Na2 79.4(4).

Significantly, the cisoid arrangement of the *t*Bu/H substituents in the all-lithium cyclic ladder **9**[10] is maintained in the central $(NLi)_2$ section of the mixed lithium–sodium open ladder structure **8** (Figure 3). A switch to a transoid conformation occurs within its outer (NLiNNa) rings. TMEDA molecules chelate the Na^+ ions at the ladder ends to prevent the possibility of increasing the number of rungs beyond four. Ether molecules perform a similar function in the secondary amide ladder structure **1**, which features the same arrangement of N–Na and N–Li rungs as in **8**;[5] however, in a major departure, these rungs are accommodated within a stepladder, as opposed to a curved, convex framework. Bond dimensions in **8** conform to the same pattern previously found in **1**: N–Li bond lengths increase in the order outer-edge < rung < inner-edge; the largest difference is 0.143 Å, and the N–Na edges are on average 0.134 Å longer than N–Na rungs. As in **7**, each $(N-metal)_2$ ring in **8** is essentially planar, its three-coordinate metal centres (Li in this case) are pyramidal (mean total bond angle, 353.6°), and its four-coordinate Na centres are distorted tetrahedral (mean bond angle, 110.6°). The curvature within **8** is relatively smooth as indicated by the similar NLiN and LiNNa edges angles (mean values: 130.1° and 130.7°, respectively). This contrasts with the asymmetrical edge angles (at Li, 132.1°; at N, 145.9°) accompanying the step motif in **1**. Discussion on the geometry of the amide and amine ligands is precluded by the limited precision of the structure.

Conclusions

In summary, we have shown that it is possible to construct new alkali metal amide ladder structures containing different combinations of cisoid- and transoid-arranged amido substituents by metalating the primary amine *tert*-butylamine.

Experimental Section

Compound 7: A chilled suspension of *n*-butylsodium (10 mmol in hexane) in a Schlenk tube under argon, was treated with *tert*-butylamine (10 mmol). Warming to room temperature gave a viscous, white precipitate which failed to dissolve on further heating. Excess amine (20 mmol) was subsequently added to produce a golden solution on gentle warming. Controlled cooling of the solution back to room temperature afforded colourless crystals. On isolation these turned opaque and degraded to a powder. Yield: 53%. M.p. 262–265 °C.

Compound 8: *tert*-Butylamine (20 mmol) was introduced to a stirred, chilled mixture of *n*-butyllithium and *n*-butylsodium (10 mmol each) in hexane. Following a vigorous reaction, a white precipitate was obtained, and the mixture was allowed to warm up to room temperature. Complete dissolution was achieved on adding TMEDA (10 mmol). Freezer cooling (to about −30°C) of the resultant orange solution afforded large, colourless, cuboidal crystals. Yield: 33%. M.p. 79–81 °C.

Satisfactory C, H, Li, N, Na analyses for both compounds. Single crystals suitable for X-ray crystallography were selected direct from the mother liquors and mounted under an inert oil prior to examination.

Crystallography: 7: $C_{16}H_{41}N_4Na_3$, $M_r = 358.5$, crystal dimensions $0.80 \times 0.60 \times 0.39$ mm, monoclinic, $P2_1/c$, $a = 9.687(2)$, $b = 11.832(3)$, $c = 20.641(4)$ Å, $\beta = 95.310(5)^\circ$, $V = 2355.7(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.011$ g cm^{-3}, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $T = 160$ K, $\mu = 0.11$ mm^{-1}. 9568 (3086 unique, $2\theta < 45^\circ$, $R_{int} = 0.1442$) data were collected on a Stoe-Siemens four-circle diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values for all data (G.M. Sheldrick, SHELXTL manual, Siemens Analytical X-ray Instruments Madison, WI, 1994, version 5) to give $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2671$, conventional $R = 0.0949$ for F values of 2718 reflections with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.105$ for 266 parameters. Disorder was resolved and refined for one *t*Bu group; isotropic H atoms were constrained/restrained, other atoms were anisotropic. Residual electron density extremes were +0.50 and −0.47 e Å^{-3}.

8 : $C_{28}H_{74}Li_2N_8Na_2$, $M_r = 582.8$, crystal dimensions $0.56 \times 0.52 \times 0.47$mm, monoclinic, $P2_1/n$, $a = 10.939(2)$, $b = 28.149(4)$, $c = 12.996(2)$ Å, $\beta = 90.022(3)^\circ$, $V = 4001.7(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 0.967$ g cm^{-3}, $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $T = 160$ K, $\mu = 0.08$ mm^{-1}. 16836 (5237 unique, $2\theta < 45^\circ$, $R_{int} = 0.1184$) data were collected on a Siemens SMART CCD diffractometer. The structure was solved and refined as for **7**, to give $R_w = 0.3509$, conventional $R = 0.1268$ (4318 reflections), $S = 1.178$ for 424 parameters. There was considerable disorder, resolved successfully only for the TMEDA ligand. Residual electron density extremes were +0.30 and −0.39 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100560. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: Int. code + 441223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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