The Laddering Principle in Lithium Amide Chemistry: the Crystal and Molecular Structure of the Pyrrolididolithium Adduct $[H_2\overline{C(CH_2)_3N}Li]_3 \cdot MeN(CH_2CH_2NMe_2)_2$

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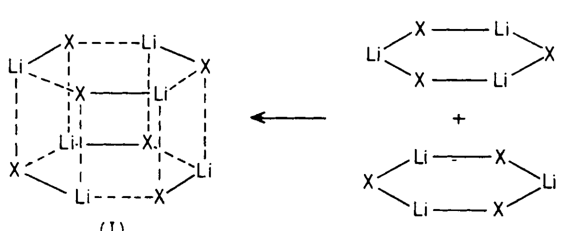
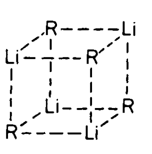
The title compound, $\{[H_2\overline{C(CH_2)_3N}Li]_3 \cdot PMDETA\}_n$, (**1**) (PMDETA = pentamethyldiethylenetriamine), is shown to be the first example of an organonitrogen–lithium laddered structure, consisting in the solid ($n = 2$) of two attached $(NLi)_2$ rings, or alternatively four (N–Li) rungs, with two terminal NLi units complexed by PMDETA, so preventing further association; cryoscopic and ^7Li n.m.r. spectroscopic studies imply that extension of the ladder framework can occur in arene solutions of (**1**), and these results, together with those from *ab initio* m.o. calculations on model systems, suggest that similar compounds of type $(RR'NLi \cdot x donor)_n$, but of various ladder lengths, should be preparable.

We recently noted that the metal–nitrogen distances in iminolithium hexamers $(R'R''C{=}NLi)_6$, [(I); X = $R'R''C{=}N$] allow these molecules to be regarded as stacked pairs of cyclic trimers $(R'R''C{=}NLi)_3$, (II).[1] Such stacking raises the metal and nitrogen co-ordination numbers [the metal atoms are only 2-co-ordinate in (II)] converting three 2-centre NLi bonds in each trimer into 3-centre NLi_2 bonds in the hexamer, and is facilitated by the coplanarity of the substituents R′ and R″ with the $(NLi)_3$ ring system of (II). In lithium alkyl chemistry, similar stacking of dimers $(RLi)_2$ or trimers $(RLi)_3$, with exclusively 3-centre CLi_2 bonds, can be used to account for the prevalence of tetramers $(RLi)_4$ [(III)] and hexamers [(IV)], with exclusively 4-centre CLi_3 bonds.[2] Indeed such stacking can extend beyond pairs of rings: the dodecamer $(Bu^tC{\equiv}CLi)_{12} \cdot (THF)_4$ (THF = tetrahydrofuran) contains a column of six $(CLi)_2$ rings.[3] Such structures reflect the strong tendency for lithium to achieve the maximum co-ordination number compatible with steric constraints; cyclic systems $(RLi)_2$ or $(RLi)_3$ are expected only when ring stacking is prevented by the bulk of the substituents R, or by Lewis bases.

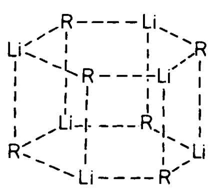


(I)

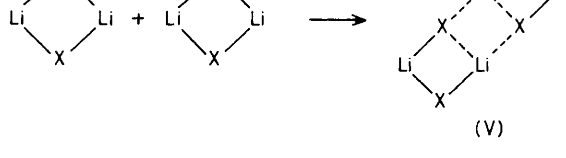
(II)



(III)



(IV)



(V)

Lithium amides $(R'R''NLi)_n$ by contrast cannot adopt such stacked structures, because in cyclic dimers or trimers such as $[(Me_3Si)_2NLi]_2$[4] or $[(PhCH_2)_2NLi]_3$[5] the substituents R project above and below the $(NLi)_{2\text{ or }3}$ ring plane, inhibiting close approach of the rings vertically. Instead, however, the strong tendency to associate can be realised (provided the substituents R are not *too* bulky) by *lateral* association to form ladder structures such as (V) (X = $R'R''N$). This is exemplified by the subject of the present paper, the pyrrolididolithium–pentamethyldiethylenetriamine (PMDETA) adduct, $[(PyrrolididoLi)_3 \cdot PMDETA]_2$, (**1**).

Reaction of pyrrolidine with one equivalent of n-butyllithium in hydrocarbon solvents produces a white, insoluble powder. In the presence of PMDETA (1 or ⅓ molar equiv.) in toluene, warming to *ca.* 60 °C gives a pale yellow solution which on cooling provides (in 89% yield, based on Bu^nLi) very pale yellow needles (m.p. 118—120 °C) of $\{[H_2\overline{C(CH_2)_3N}Li]_3 \cdot PMDETA\}_n$, (**1**).†

An *X*-ray diffraction study shows that (**1**) is dimeric ($n = 2$) in the solid. The structure, shown in Figure 1,‡ consists of four central amido-N–Li rungs [this portion can alternatively be viewed as being comprised of two attached $(NLi)_2$ rings], with in addition two terminal N–Li units each complexed by PMDETA. This inhibits further association. The central unit, $\overline{N(1)Li(1) \cdot N(1')Li(1')}$, is strictly planar and the N atoms of the outer rungs [N(2),N(2′)] are essentially in this same plane (within 0.006 Å). However, the corresponding Li atoms [Li(2),Li(2′)] deviate by ±0.71 Å, presumably owing to the steric effects of the terminal groups. The ladder framework of (**1**) can best be viewed as forming by lateral association of two $(NLi)_2$ rings. This requires the available electrons to be spread over more centres, converting one electron-precise N–Li bond within each isolated dimer into a 3-centre N–Li_2 interaction involving an N–Li rung (an 'intradimer' contact) and a new N–Li edge connecting the dimers. This view is confirmed on inspection of the dimensions of (**1**) (Figure 2). The above-

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† Satisfactory elemental analyses (C, H, Li, N) were obtained for (**1**). ^1H N.m.r. data: distorted singlet, centred δ 3.30 [12H, 3 × $(CH_2)_2$ of pyrrolidide ligand]; complex multiplet, δ 2.30—1.70 [35H, 3 × $(CH_2)_2$ of pyrrolidide ligand + 23 PMDETA protons].

‡ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

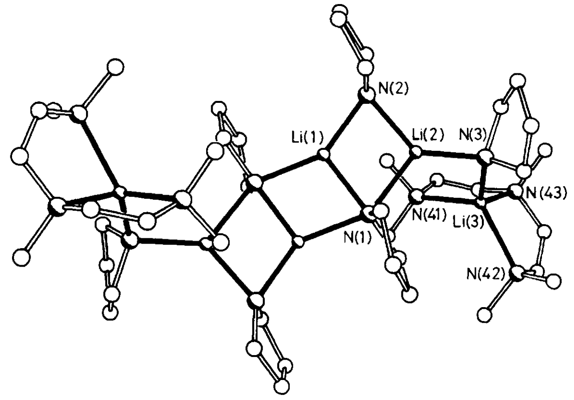

Figure 1. Molecular structure of $\{[H_2\overline{C(CH_2)_3N}Li]_3{\cdot}PMDETA\}_2$, (**1**). *Crystal data* for (**1**): $C_{42}H_{94}Li_6N_{12}$, $M = 808.9$, monoclinic, $C2/c$, $a = 20.746(2)$, $b = 16.927(2)$, $c = 17.695(2)$ Å, $\beta = 119.00(1)°$, $Z = 4$ dimers, $\mu = 0.41$ mm^{-1} for Cu-K_α radiation ($\lambda = 1.541\,84$ Å). From 2054 reflections with $F > 4\sigma(F)$ and $2\theta \leqslant 130°$, solution and refinement with anisotropic thermal parameters and with H atoms in calculated positions gave $R = 0.093$.

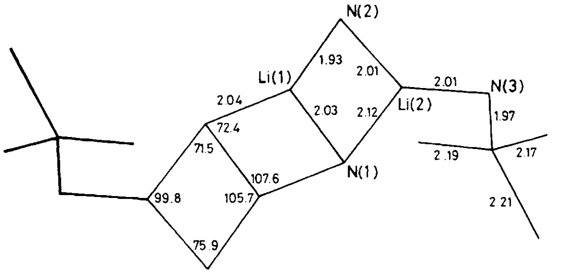

Figure 2. N–Li bond lengths (Å) and Li–N–Li, N–Li–N ring angles (°) in the N–Li skeleton of (**1**): e.s.d.'s are 0.01 Å and 0.1°.

mentioned N–Li lengths are 2.03 [*e.g.*, N(1)Li(1)] and 2.04 Å [*e.g.*, N(1)Li(1′)] respectively. The third bond per central N atom is a formally electron-precise one, as in the isolated dimer. An indication of its expected length in the absence of distortions due to terminal NLi·PMDETA units [*e.g.*, N(1)Li(2), 2.12 Å] is given by the extremely short value for N(2)Li(1), 1.93 Å. An *ab initio* optimisation of $(H_2NLi)_4$ (6–31G basis set), corresponding to the central (but undistorted, planar symmetry assumed) portion of (**1**), gives N–Li distances of 2.16, 2.06, and 1.97 Å for central rungs, connecting inter-dimer contacts, and intra-dimer ladder edges, respectively.

Somewhat similar features are apparent (though they were not interpreted in terms of a ladder model) in the structure of $[Li_2(\mu_3\text{-}Bu^t{}_2P){\cdot}(\mu_2\text{-}Bu^t{}_2P){\cdot}THF]_2$,[6] which consists of two attached $(PLi)_2$ rings with just one THF molecule at each end of the four-rung (PLi) ladder.

The behaviour of compound (**1**) in arene solutions can be analysed on the basis of the ladder model. Although the 25 °C ^{7}Li n.m.r. spectra (139.96 MHz) of $[^2H_8]$toluene solutions of (**1**) consist of single resonances due to rapid exchange, the −95 °C spectrum of a concentrated solution (0.18 mol dm^{-3}, with molarity expressed relative to empirical formula, $n = 1$, of formula mass 404) consists of just three resonances of equal integrals, assignable to the three types of Li atoms in dimeric (**1**) itself; two of these are close together (at δ −0.08 and −0.33 p.p.m. relative to external PhLi in toluene) with the third quite separate (δ −1.49 p.p.m.), and so correspond to the two sets of 3-co-ordinate Li atoms within the ladder and to the 4-co-ordinate, PMDETA-complexed Li atoms respectively. On dilution, complex equilibria are observed, apparently involving further linear association of (**1**) along the existing ladder framework. For example, cryoscopic relative molecular mass (r.m.m.) measurements on benzene solutions of (**1**) give typical values of *ca.* 2630 (*n ca.* 6.5, 0.065 mol dm^{-3}), *ca.* 2290 (*n ca.* 5.7, 0.050 mol dm^{-3}), and *ca.* 1360 (*n ca.* 3.4, 0.030 mol dm^{-3}). Commensurate with these results, the ^{7}Li n.m.r. spectra of solutions of comparable concentrations now show many complex resonances as well as the three due to dimeric (**1**) noted above. These features imply amendment of the role of the PMDETA ligands (but not their complete dissociation, when n would always be <2).

Ab initio m.o. optimisations on an $(H_2NLi)_4$ tetramer have been used to probe further the structural preferences of amidolithium oligomers. Three possible models were considered: (i) a cubane-like structure (D_{2d}) formed by stacking two $(H_2NLi)_2$ rings [type (III), R = H_2N], (ii) an open eight-membered ring (D_{4h}) analogous to that found for $[Me_2\overline{C(CH_2)_3CMe_2N}Li]_4$,[7] and (iii) a ladder structure (C_{2h}) analogous to the central portion of (**1**) and formed by lateral association of two $(H_2NLi)_2$ rings [type (V), X = H_2N]. Previous calculations had shown (ii) to be more stable than (i) by 9—12 kcal mol^{-1} (1 kcal = 4.184 kJ) depending on the basis set used.[8] Our 6–31G calculations confirm this, the energy difference being 11.4 kcal mol^{-1}, but also show that structure (iii) is a local minimum of intermediate stability, only 7.4 kcal mol^{-1} less stable than (ii). In practical systems $(RR'NLi)_4$, where R,R′ ≠ H, this preference for (ii) or (iii) over (i) should be enhanced by the steric demands of R,R′ groups. For (ii) *vs.* (iii), these results, and those given above specifically for compound (**1**), imply that ladders (iii) with 4-membered ring units will be favoured when R,R′ groups are small and tied together, while (ii), with its 8-membered ring, will be preferred by ligands with larger, more substituted groups. It is also implicit in these results that, given suitable choice of such groups, different length ladders may be obtainable by using varying donor : Li ratios.

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