Three Model Structural Types in Lithium Amide Chemistry: the Crystal and Molecular Structures of Dimeric $[Ph(Me)NLi{\cdot}TMEDA]_2$ (TMEDA = $Me_2NCH_2CH_2NMe_2$) and Monomeric Ph(naphthyl)NLi·PMDETA [PMDETA = $MeN(CH_2CH_2NMe_2)_2$], and of $[Ph(naphthyl)NLi{\cdot}TMEDA]_2$, a 'Loose Dimer'

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The crystal structures of three amidolithium complexes are reported, those of $[Ph(Me)NLi{\cdot}TMEDA]_2$ (TMEDA = $Me_2NCH_2CH_2NMe_2$), (**1**), and Ph(naphthyl)NLi·PMDETA [PMDETA = $MeN(CH_2CH_2NMe_2)_2$], (**2**), whose Li atoms are all four-co-ordinate, confirming predicted structural types, while a new structural option is found for $[Ph(naphthyl)NLi{\cdot}TMEDA]_n$, (**3**), whose monomeric (n = 1) molecules, each containing a three-co-ordinate Li atom, are prompted to associate loosely in pairs (n = 2) *via* intermolecular Li · · · phenyl interactions.

Amidolithium compounds, $(RR'NLi)_n$, and complexes, $(RR'NLi{\cdot}xL)$, L = a Lewis base, are important proton abstraction reagents in organic syntheses,[1] and as such are commonly prepared, then used, *in situ*. Recently, however, such reagents have been isolated and examined in their own right as a preliminary to understanding how they actually operate, and several structural types have been predicted[2] or, indeed, have emerged.[2,3] Here we help to stress that the structural options available to such species reflect a balance between the steric requirements of their ligands and the electronic requirements of their lithium centres. We do this by reporting the crystal structures of three related complexes: those of $[Ph(Me)NLi{\cdot}TMEDA]_2$ (TMEDA = $Me_2NCH_2CH_2NMe_2$), (**1**), and Ph(naphthyl)NLi·PMDETA, [PMDETA=$MeN(CH_2CH_2NMe_2)_2$] (**2**), both containing four-co-ordinate metal atoms, ratify two expected structural options, while that of $[Ph(naphthyl)NLi{\cdot}TMEDA]_n$, (**3**), pinpoints a new one in that, although n formally equals 1, the thereby co-ordinatively unsaturated (three-co-ordinate) lithium then engages in loose inter-monomer association, so acquiring further electron density from CH– units within a neighbouring monomeric molecule.

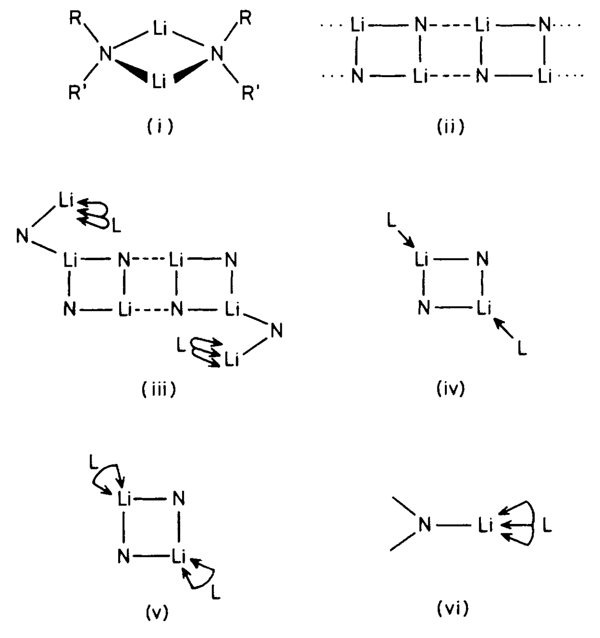

Figure 1. Some known or expected structures in amidolithium chemistry.

The three complexes noted above were synthesised† and structurally characterised in the hope of realising some hitherto unobserved structural types, and of clarifying what further structural options might be available. Figure 1 illustrates some amidolithium structures identified or expected. The key unit is a $(NLi)_n$ ring [Figure 1(i), for n = 2] whose R,R' groups straddle the ring plane so precluding vertical association (or 'stacking').[4] When R,R' are bulky, the merely two-co-ordinate Li atoms of such rings must remain as such, *e.g.*, n = 2 for gaseous $[(Me_3Si)_2NLi]_2$,[5] n = 3 for $[(PhCH_2)_2NLi]_3$,[6] and n = 4 for $[Me_2C(CH_2)_3CMe_2NLi]_4$.[2] More usually, however, these rings associate further giving ladder-like polymeric structures [Figure 1(ii)], fragments of which can occur on treatment with Lewis bases, *e.g.*, the base-deficient complex $\{[H_2C(CH_2)_3NLi]_3{\cdot}PMDETA\}_2$, [Figure 1(iii)].[7] When the Li : L ratio is 1 : 1, ladders cannot persist and one expects then their constituent rings or their individual (monomeric) rungs. The former have so far been of the type (NLi·monodentate L)$_2$ [Figure 1(iv)], *e.g.* $[(PhCH_2)_2NLi]_3$ forms complexes $[(PhCH_2)_2NLi{\cdot}L]_2$, L = Et_2O, hexamethylphosphoramide (HMPA).[6] While in principle attachment of a second monodentate donor per Li or of a single bidentate one per Li [Figure 1(v)] should be favoured, as thereby Li reaches four-co-ordination, in practice so far further complexation, abetted by bulky R groups, has led to monomers, as in $[Bu^t_3C_6H_2(H)NLi{\cdot}OEt_2]_2$[8] becoming $Bu^t_3C_6H_2(H)NLi{\cdot}TMEDA$[5] (though, significantly, the then formally only three-co-ordinate Li seems to interact intramolecularly with the NH unit). However, this expected option has now been found in the structure of $[Ph(Me)NLi{\cdot}TMEDA]_2$, (**1**) [Figure 2(a)],‡ whose small (Me) and flat (Ph) amide groups allow lithium's four-co-ordination preference to be achieved. A final structural type predicted[2] is that of a monomeric complex with a tridentate donor like PMDETA [Figure 1(vi)]. This too has now been found, for Ph(naphthyl)NLi·PMDETA, (**2**), [Figure 2(b)];‡ the fact that Ph(Me)NLi·PMDETA is also monomeric[9] [*cf.* (**1**)] implies that it is the denticity of this donor, independently of the bulk of the amido ligand, which dictates this structural preference.

Given the results on (**1**) and (**2**), the complex of especial interest became $[Ph(naphthyl)NLi{\cdot}TMEDA]_n$, (**3**), the key question being whether n would equal 2, as in (**1**), or whether

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† Syntheses by 1 : 1 : 1 amine : Bu^nLi : L reactions in hexane, followed by product recrystallisation from toluene; satisfactory elemental analyses were obtained for all three complexes.

‡ 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.

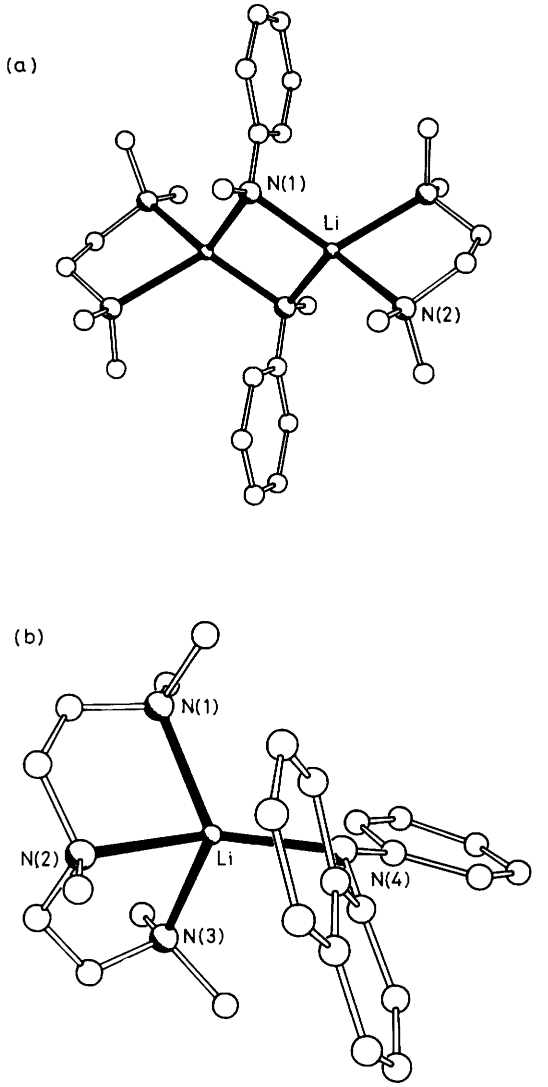

Figure 2. (a) Molecular structure of [Ph(Me)NLi·TMEDA]$_2$, (**1**). Orthorhombic, *Pnnm*, $a = 7.936(1)$, $b = 13.792(2)$, $c = 13.420(1)$ Å, $U = 1468.9$ Å^3, $Z = 2$. $R = 0.081$ for 708 reflections with $F > 3\sigma(F)$ and $2\theta \leq 45°$ (Mo-K_α radiation, $\lambda = 0.71069$ Å). Molecular site symmetry C_{2h} (2/*m*). Key dimensions: Li–N(1) 2.082(6), Li–N(2) 2.296(7), Li · · · Li 2.74(2) Å; N(1)–Li–N(1a) 97.6(4)°. (b) Molecular structure of Ph(naphthyl)NLi·PMDETA, (**2**). Orthorhombic, $P2_12_12_1$, $a = 8.7773(5)$, $b = 16.4168(9)$, $c = 16.7655(8)$ Å, $U = 2418.5$ Å^3, $Z = 4$. $R = 0.076$ for 2197 reflections with $F > 3\sigma(F)$ and $2\theta \leq 110°$ (Cu-K_α, $\lambda = 1.54184$ Å). Key dimensions: Li–N(1) 2.18(1), Li–N(2) 2.21(1), Li–N(3) 2.22(1), Li–N(4) 2.00(1) Å.

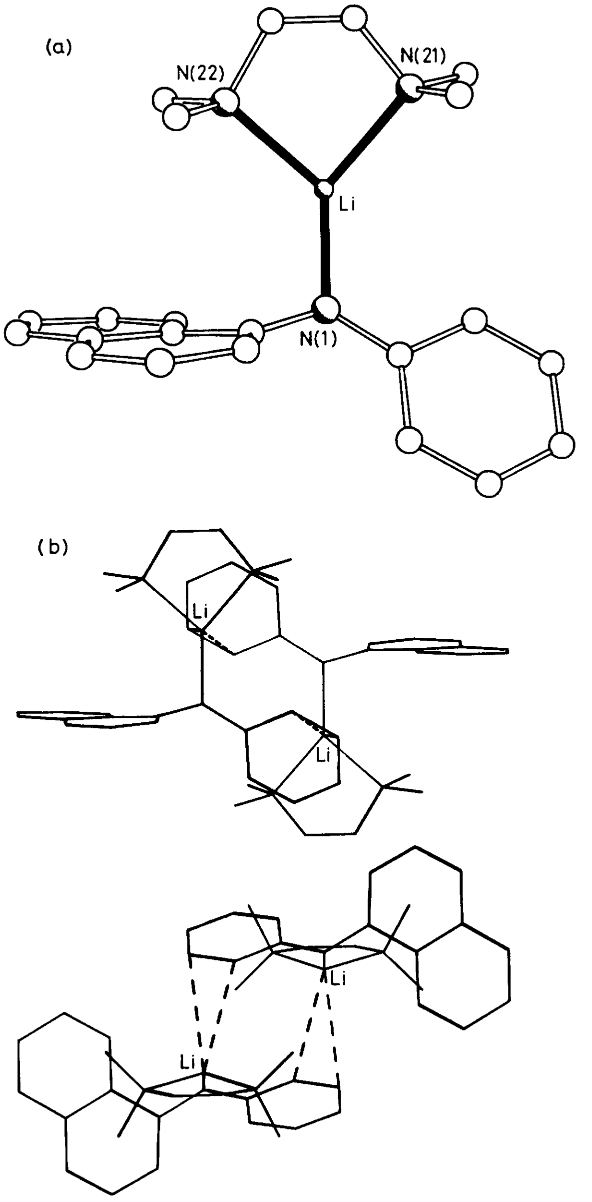

Figure 3. The crystal structure and molecular structure of [Ph(naphthyl)NLi·TMEDA]$_n$, (**3**). (a) The monomeric unit ($n = 1$). Monoclinic, $P2_1/c$, $a = 9.713(1)$, $b = 11.612(1)$, $c = 18.234(1)$ Å, $\beta = 95.612(7)°$, $U = 2046.7$ Å^3, $Z = 4$. $R = 0.101$ for 1495 reflections with $F > 3\sigma(F)$ and $2\theta \leq 115°$ (Cu-K_α). Key dimensions: Li–N(1) 1.97(1), Li–N(21) 2.12(1), Li–N(22) 2.13(1) Å; N(1)–Li–N(21) 132.0(6), N(1)–Li–N(22) 125.9(5), N(21)–Li–N(22) 86.6(4)°, deviation of Li from plane of 3N atoms = 0.451(3) Å. (b) The loosely-associated pairs of monomers in the crystal structure.

replacement of Me by naphthyl would demand, sterically, a monomeric structure akin to (**2**). Figure 3‡ provides the answer, but it is a surprising one since (**3**) is neither just a monomer, not just a dimer, but rather it is a novel combination of both. The basic unit is a monomer [Figure 3(a)]. However, the amide substituents adopt very different orientations, naphthyl having the expected roughly perpendicular aspect to the N(1)Li bond axis [as in (**2**)], but phenyl running alongside this axis. Such features permit pairs of these monomers to come together in 'slipped' vertical association, each displaced molecule running in the opposite direction to the other and so allowing each formally three-co-ordinate Li to interact *inter*molecularly (*cf.* ref. 5) with one *ortho* and one *meta* CH unit of the neighbouring phenyl group [Figure 3(b)]. Although loose (Li · · · C′ distances being 3.12 and 3.15 Å respectively) such association is clear cut, the displacement of just every two molecules towards each other being emphasised by all of the Li · · · C′ distances beyond each 'dimer' exceeding 5.2 Å.

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9 The complex mentioned has had its basic structure established, though the structure needs further refinement at low temperature; W. Clegg, unpublished observations.