Dimers of thf-solvated lithium anilide and lithium pentafluoroanilide: basic building blocks of lithium amide ladder structures

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Representing the elementary constituents in the dis-assembling process of lithium amide ladder arrangements, the tetrasolvated dimers $[C_6H_5N(H)Li{\cdot}2thf]_2$ and $[C_6F_5N(H)Li{\cdot}2thf]_2$ are isolated and cryo-crystallographically characterised, which, based on the unexpected geometries in the solid-state structures, lead to the unaccustomed classification of nitrogen tending to sp^2 hybridisation in the planar $(LiN)_2$ four-membered rings.

Organonitrogen–lithium compounds, and lithium amides (RR′NLi) in particular, are valuable reagents in organic and organometallic synthesis.[1] Owing to their lower nucleophilic character compared with C–Li reagents, these bases efficiently favour proton abstraction over addition reactions, and often stand out due to their high regio- *and* stereo-selectivity. In the recent past, the investigation of structural aspects became the focus of interest, and a general concept rationalising the lateral association in lithium amides has been developed.[2] In contrast to ring-stacking in lithium imides, ladder frameworks are formed upon edge-to-edge linking of $(LiN)_2$ rings as a consequence of the tetrahedral geometry at the amide N centre. As has been emphasised again in a recent publication, solvation of the lithium atoms is the determining factor regarding the ladder $\longleftrightarrow$ dimer transformation:[3] Clegg *et al.* described the solid-state structure of a *model* intermediate, $[\{PhN(H)Li_6\}{\cdot}8thf]$, in the stepwise dis-assembling process of unsolvated laterally connected lithium anilide to tetrasolvated dimeric lithium anilide, initiated by thf solvation. Herein we report on the isolation and analysis of the final fragmentation product in this process $[PhN(H)Li{\cdot}2thf]_2$ **1**, and its pentafluorinated analogue $[C_6F_5N(H)Li{\cdot}2thf]_2$ **2**, providing the structural link to further support the proposed mechanism. Special care was necessary during preparation of both compounds for the X-ray structure analysis, as they not only react vigorously with air and moisture but also proved to be unstable at ambient temperature (mp of **1** = −20 °C, solutions of **2** gradually decompose at temperatures above −30 °C). Applying inert-oil techniques using a low temperature crystal mounting device[4] we finally succeeded in mounting the single crystals on the diffractometer.

Lithiated aniline **1**† was synthesised in pure thf to achieve maximum solvation of the lithium atoms favouring the formation of $(LiN)_2$ dimers over higher aggregated species. Crystallisation at −43 °C yielded transparent blocks, suitable for crystal structure analysis.

A four-membered $(LiN)_2$ ring, planar by crystallographic imposition, forms the centre of the dimeric structure of **1**‡ [Fig. 1(*a*)]. In addition to the anilido ligands, two thf molecules complete the coordination sphere of each lithium atom inhibiting further association of lithium anilide moieties. The endocyclic ring angles at nitrogen (76.8°) and lithium (103.2°) are well within the range of corresponding values in related dimers.[2b] An unprecedented structural feature, however, is the asymmetric bridging of lithium by the anilido N centres [N(1)–Li(1) 1.989 Å, N(1)–Li(1a) 2.087 Å] and the planar environment of nitrogen§ which deserve particular attention (sum of angles at nitrogen disregarding the longer N–Li bond = 358°). Previously, alternating Li–N distances in lithium amides have been observed in laterally connected $(LiN)_n$ ring systems with $n > 2$ only. The different bond lengths have been attributed to stronger two- and weaker three-centre interactions between lithium and sp^3-hybridised nitrogen. Consequently, according to the ring-laddering principle, four bonds of equal length {as observed in the lithiated aniline $[PhN(Me)Li{\cdot}tmeda]_2$[5]} would be expected in *isolated* four-membered rings, in contrast to the situation ascertained in **1** which could alternatively be described as a donor–acceptor complex between two monomeric units. In addition, the position of the lithium atom almost within the plane of the anilide ligand contradicts the assumption of sp^3 hybridisation at nitrogen [Fig. 2(*a*); torsion angle Li(1)–N(1)–C(1)–C(2) 14.3°]. If the nitrogen atom was sp^3 hybridised an orientation of the aromatic plane intersecting the Li(1)–N(1)–Li(1a) angle would be predicted which corresponds to the

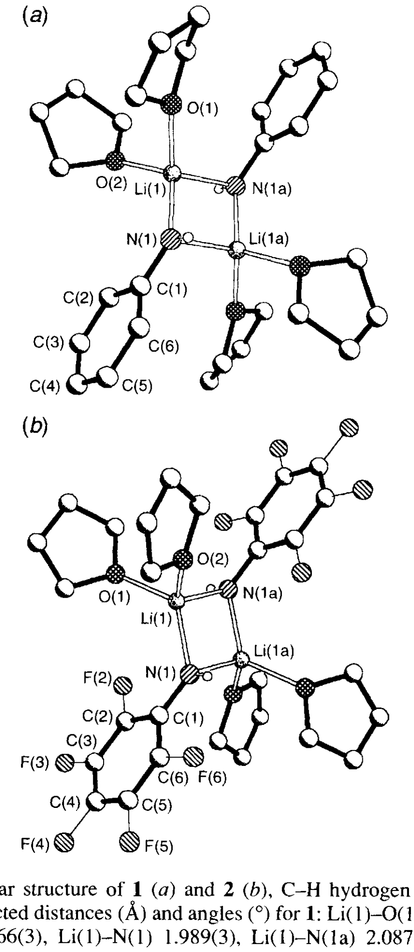

Fig. 1 Molecular structure of **1** (*a*) and **2** (*b*), C–H hydrogen atoms not displayed. Selected distances (Å) and angles (°) for **1**: Li(1)–O(1) 2.001(3), Li(1)–O(2) 1.966(3), Li(1)–N(1) 1.989(3), Li(1)–N(1a) 2.087(3), N(1)–C(1) 1.365(2), N(1)–Li(1)–N(1a) 103.2(1), Li(1)–N(1)–Li(1a) 76.8(1); for **2**: Li(1)–O(1) 1.982(9), Li(1)–O(2) 1.982(8), Li(1)–N(1) 2.006(7), Li(1)–N(1a) 2.067(7), N(1)–C(1) 1.351(5), N(1)–Li(1)–N(1a) 101.9(3), Li(1)–N(1)–Li(1a) 78.1(3).

sterically most favourable position of the phenyl group between the thf ligands. This is clearly not the case. Evidently, bonding in **1** is described more appropriately based on an sp^2-hybridised nitrogen atom. Two sp^2 orbitals are involved in σ-bonding of the hydrogen and the *ipso*-carbon atom, while the free electron pairs occupy the remaining hybrid orbital and the unhybridised p orbital which is oriented orthogonal to the anilide plane. The short N(1)–Li(1) distance is due to the interaction of lithium with the sp^2 lone pair, the weak interaction with the nitrogen p orbital is reflected by the longer N(1)–Li(1a) distance. The approximate coplanarity of the phenyl group with the plane defined by Li(1), N(1) and H(1) can be rationalised in terms of a π interaction of the aromatic system with the nitrogen p orbital. This may also explain the rather short N(1)–C(1) distance (1.365 Å) compared to 1.394 Å in $[(C_6H_2Bu^t{}_3\text{-}2,4,6)N(H)Li{\cdot}Et_2O]_2$[6] and 1.39 Å (average value) in aniline[7] (both N–C distances refer to higher temperature data; an even greater divergence is to be expected after correction for libration). It remains speculation, however, to what extent Li···C–N interactions contribute to the tilted arrangement of the anilide ligand, as has been postulated for dimeric $[SCNLi{\cdot}tmpda]_2$[8] (tmpda = tetramethylpropylenediamine).

As in **1**, the solid-state structure‡ of the pentafluorinated derivative **2** consists of isolated dimeric associates with central planar $(LiN)_2$ rings [Fig. 1(*b*)]. However, the phenyl groups are located in an intermediate position between the two positions expected for an sp^2 and sp^3 hybridised nitrogen. In addition, the deviation from planarity at the nitrogen atom is more noticeable [sum of angles at nitrogen disregarding the longer N(1)–Li(1a) bond = 348°], as is the twisting of the aromatic plane with respect to the Li(1)–N(1) bond [torsion angle Li(1)–N(1)–C(1)–C(2) 40.2°]. This tendency is even more prominent in $[(C_6H_2Bu^t{}_3\text{-}2,4,6)N(H)Li{\cdot}Et_2O]_2$[6] indicating that steric effects (substitution of hydrogen with fluorine at the phenyl group) are important here. Although, compared to **1**, the preference for sp^2 hybridisation at nitrogen appears less pronounced in **2**, the corresponding geometric effects are nevertheless apparent as established by the different N–Li distances [N(1)–Li(1) 2.006, N(1)–Li(1a) 2.067 Å].

The unexpected structural parameters of **1** and **2** suggest that the electronic configuration of nitrogen can not be categorised as purely sp^3 hybridisation. Moreover, the crystal structure of dimeric sodium anilide $[PhN(H)Na{\cdot}pmdeta]_2$[9] also exhibits divergent Na–N distances within the central ring as well as an arrangement of the metal cation coplanar with the closest anilido ligand. This is quite understandable now, particularly since the increased cation radius should facilitate an interaction with the nitrogen p orbital as shown clearly for rubidium and caesium.[10] Apparently, an intermediate state between sp^2 and sp^3 hybridisation of nitrogen offers a more appropriate description of the electronic configuration in amide–LiN ring systems. The structural contrast between **1** and its methylated derivative $[PhN(Me)Li{\cdot}tmeda]_2$[5] demonstrates that steric impositions play an important role in determining the extent of sp^2 and sp^3 contributions. An accurate model, however, can not be derived from geometric parameters of crystal structures alone, but needs to be substantiated by MO calculations provided that symmetry constraints are chosen accordingly. Likewise, it remains a subject of interpretation to connect the variance of Li–N distances in lithium amide ladder frameworks with a partial sp^2 hybridisation at nitrogen.

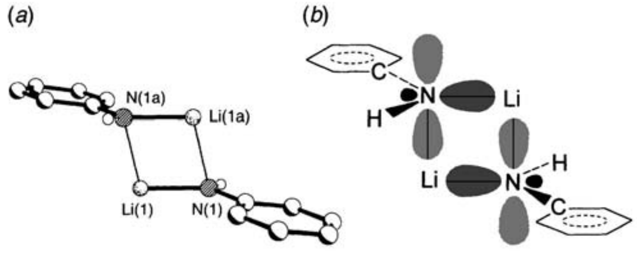

Fig. 2 View perpendicular to the $(LiN)_2$ planar ring of **1** (*a*) and schematic representation of the electronic configuration based on sp^2 hybridised nitrogen (*b*). C–H hydrogen atoms and thf ligands have been omitted for clarity.

Footnotes

† Yield of **1**: 36%; mp −20 °C. NMR data ($[^2H_8]$thf, 25 °C): ^1H δ 2.54 (s, 1 H, NH), 5.82 [dd, 1 H, *p*-CH, $^3J(H_pH_m)$ 7.1, $^4J(H_pH_o)$ 1.1 Hz], 6.23 [dd, 2 H, *o*-CH, $^3J(H_oH_m)$ 8.4, $^4J(H_oH_p)$ 1.1 Hz], 6.63 [dd, 2 H, *m*-CH, $^3J(H_mH_o)$ 8.4, $^3J(H_mH_p)$ 7.1 Hz]; ^{13}C δ 108.0 (s, *p*-CH), 116.3 (s, *o*-CH), 129.0 (s, *m*-CH), 165.5 (s, CN); ^7Li δ 0.94(s). Yield of **2**: 42%; mp 46 °C (decomp.). NMR data ($[^2H_8]$thf, −30 °C): ^1H δ 2.83 (br, NH); ^{19}F δ −8.4 (br, 4F, *o,m*-CF), −34.7 (br, 1F, *p*-CF); ^7Li δ 0.59(s).

‡ *Crystal data* for **1**, $[C_{14}H_{22}LiNO_2]_2$, colourless, crystal dimensions 1.2 × 0.7 × 0.5 mm, $M = 486.53$, monoclinic, space group $P2_1/c$, $a = 8.518(4)$, $b = 17.594(9)$, $c = 10.041(5)$ Å, $\beta = 110.70(4)°$, $U = 1407.7(12)$ Å^3 (from 70 reflections, $10 < \theta < 12.5°$), $Z = 2$, $D_c = 1.148$ g cm^{-3}, $\mu = 0.074$ mm^{-1}, $F(000) = 528$, 3909 reflections collected ($4.06 \leqslant \theta \leqslant 27.51°$) at 153(2) K, 3211 independent ($R_{int} = 0.059$), 3209 used in the structure refinement; $R1 = 0.050$ [$I > 2\sigma(I)$], $wR2 = 0.141$ [all data], GOF = 1.061 for 204 parameters and 190 restraints, largest difference peak, hole = 0.224, −0.275 e Å^{-3}.

For **2**, $[C_{14}H_{17}F_5LiNO_2]_2$, colourless, crystal dimensions 0.4 × 0.4 × 0.3 mm, $M = 666.45$, triclinic, space group $P\bar{1}$, $a = 8.564(3)$, $b = 10.315(3)$, $c = 10.882(3)$ Å, $\alpha = 113.089(11)$, $\beta = 94.93(2)$, $\gamma = 112.375(10)°$, $U = 785.9(4)$ Å^3 (from 58 reflections, $10 < \theta < 12.5°$), $Z = 1$, $D_c = 1.408$ g cm^{-3}, $\mu = 0.131$ mm^{-1}, $F(000) = 344$, 2729 reflections collected ($4.11 \leqslant \theta \leqslant 22.50°$) at 200(2) K, 2052 independent ($R_{int} = 0.022$), 2050 used in the structure refinement; $R1 = 0.072$ [$I > 2\sigma(I)$], $wR2 = 0.210$ [all data], GOF = 1.052 for 221 parameters and 147 restraints, largest difference peak, hole = 0.437, −0.273 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/115.

§ The amide hydrogen atom which is part of the planar environment of nitrogen was located by difference Fourier synthesis and refined isotropically; no constraints or restraints were applied.

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