Unusual Molecular Structures of Some Sterically Hindered Lithium Amides: Electron Diffraction Results on Gaseous $[Li\{N(SiMe_3)_2\}]_2$ and *X*-Ray Data on Crystalline Monomeric Li(NHAr)(tmeda) (Ar = $C_6H_2Bu^t{}_3$-2,4,6; tmeda = $Me_2NCH_2CH_2NMe_2$)†

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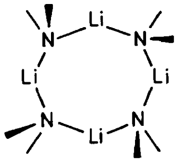
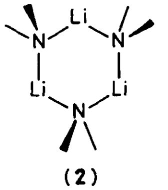
Gaseous bis(trimethylsilyl)amidolithium at *ca.* 403 K is a cyclic LiNLiN dimer of D_2 symmetry, with Li–N 1.99(3) Å and ∠ NLiN 100(3)° assuming the bridging $\bar{N}(SiMe_3)_2$ ligands to be orthogonal to the LiNLiN plane; crystalline 2,4,6-tri-t-butylanilido(*N,N,N′,N′*-tetramethylethylenediamine)lithium is a monomer at ambient temperature with lithium in a trigonal planar environment, Li–NHAr 1.895(8), average $Li–NMe_2$ 2.15(1) Å, ∠ $LiNC_{Ar}$ 155.6(4)°, and a rather short Li· · ·H(N) distance of 2.08(4) Å.

The structures of lithium amides are a topic of current experimental[1—3] and theoretical[4] interest. We now present diffraction results on two compounds, each of which is without precedent. For one of these, $[Li\{\mu\text{-}N(SiMe_3)_2\}]_2$, the data (Figure 1) represent the first for a gaseous alkali metal amide. The other, $Li(NHC_6H_2Bu^t{}_3\text{-}2,4,6)(Me_2NCH_2CH_2NMe_2)$ (Figure 2), demonstrates a rare crystalline monomeric alkali metal amide, with the shortest recorded Li–N bond length.

Some key parameters are presented in Table 1 and compared with published data on lithium amides; the skeletal structural types are represented schematically by (**1**)—(**7**), with (**3**) and (**5**) being those derived from the present study (Figures 1 and 2, respectively). For each of the crystalline compounds $[Li\{\mu\text{-}NCMe_2(CH_2)_3CMe_2\}]_4$ (**1**),[1] $[Li\{\mu\text{-}N(SiMe_3)_2\}]_3$ (**2**),[5] $[Li\{\mu\text{-}N(SiMe_3)_2\}(OEt_2)]_2$,[1,2] and $[Li\{\mu\text{-}NHC_6H_2Bu^t{}_3\text{-}2,4,6\}(OEt_2)]_2$ (**4**),[3] the co-ordination geometry at each of the bridging nitrogen atoms approximates to tetrahedral. From mass spectrometry and u.v. photoelectron spectroscopy it was inferred that gaseous bis(trimethylsilyl)-amidolithium is a dimer.[6]

Calculations for monomeric $Li(NH_2)$ showed a planar C_{2v} molecule with a significant $\ddot{N}\!\rightharpoonup\!Li$ π-component to the NLi bond, and an Li–N bond length in the range 1.715—1.754 Å depending on the choice of basis set.[4] For Li_2NH_2, there is little energy difference between a planar C_{2v} and a tetrahedral (at N) C_{2v} structure, *l*(Li–N) being 1.808 and 1.871 Å, respectively.


(**1**)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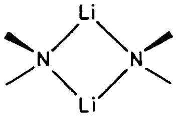
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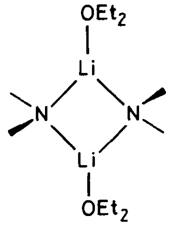
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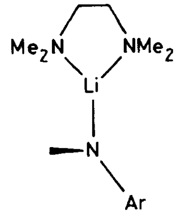
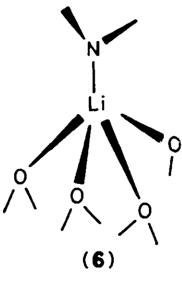
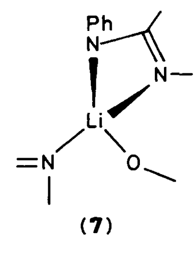

(**5**)


(**6**)


(**7**)

We now find that gas-phase electron diffraction (g.e.d.) data (for experimental details, see ref. 7) on bis(trimethylsilyl)amidolithium vapour, at a nozzle temperature of *ca.* 403 K, are consistent with a model including only dimers, although small percentages of higher oligomers or the monomer cannot be excluded. Assuming the bridging $\bar{N}(SiMe_3)_2$ ligands to be perpendicular to the planar LiNLiN ring and the overall molecular geometry to be D_2, the

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† No reprints available.

Table 1. Some structural parameters for lithium amides [R = $SiMe_3$, Ar = $C_6H_2Bu^t{}_3$-2,4,6, tmeda = $Me_2N(CH_2)_2NMe_2$].

Empirical formula	Degree of molecular aggregation: crystal (vapour)	Co-ordination number of Li	Co-ordination number of amido N	Li–N$_{av}$ (Å)	Si–N$_{av}$ (Å)	∠Li–N–Li$_{av}$ (°)	∠Si–N–Si (°)	Ref.
Li{$NCMe_2(CH_2)_3CMe_2$}[a]	Tetramer, (**1**)	2	4	2.00(2)	—	101.5(3)	—	1
Li(NR_2)[a,b]	Trimer, (**2**)	2	4	2.00(2)	1.729(4)	92(2)	118.6(9)	5
Li(NR_2)[a]	(Dimer), (**3**)	2	4	1.99(3)	1.712(7)	80(3)	129.8(1.7)	This work
Li(NR_2)(OEt_2)[a,c]	Dimer, (**4**)	3	4	2.055(5)	1.705(2)	75.1(2)	121.2(2)	1, 2
Li(NHAr)(OEt_2)[a]	Dimer, (**4**)	3	4	2.041(6)	—	77.8(2)	—	3
Li(NHAr)(tmeda)[d,e]	Monomer, (**5**)	3	3	1.895(8)	—	[∠Li–N–C$_{Ar}$ 155.6(4)°]	— —	This work
Li(NR_2)(12-crown-4)	Monomer, (**6**)	5[f]	3	1.965(4)	1.681(2)	—	123.5(1)	12
Li{N(2-C_5H_4N)Ph}(L)(L′)[g]	Monomer, (**7**)	4	3	2.091(7)	—	—	—	13

[a] The $(LiN)_n$ ring conformation is invariably planar; in the bis(diethyl ether) compounds the two O atoms are also coplanar. [b] A similar structure has recently been found for crystalline $[Li\{N(CH_2Ph)_2\}]_3$, but with close CH · · · Li interactions.[11] [c] Similar structures have recently been found for $[Li\{N(CH_2Ph)_2\}(L)]_2$ [L = OEt_2 or $P(O)(NMe_2)_3$].[11a] [d] In Li(NHAr)(tmeda) the $N_2LiNC_6C_3$-2,4,6 framework is planar. [e] This is a new compound, prepared from $[\{Li(\mu\text{-}NHAr)(OEt_2)\}_2]$[3] in PhMe and tmeda at 25 °C; δ [^7Li, C_6D_6, in p.p.m. rel. to $LiNO_3$ (1.0 mol dm^{-3} in D_2O)], −1.32 ($w_{\frac{1}{2}}$ 103.0 Hz); *X*-ray quality crystals were obtained by low temperature crystallisation from n-C_6H_{14}. [f] The four LiO distances are 2.393(3), 2.332(4), 2.108(4), and 2.094(4) Å.[12] [g] L = N{C_5H_4(NHPh)-2}, L′ = $OP(NMe_2)_3$.

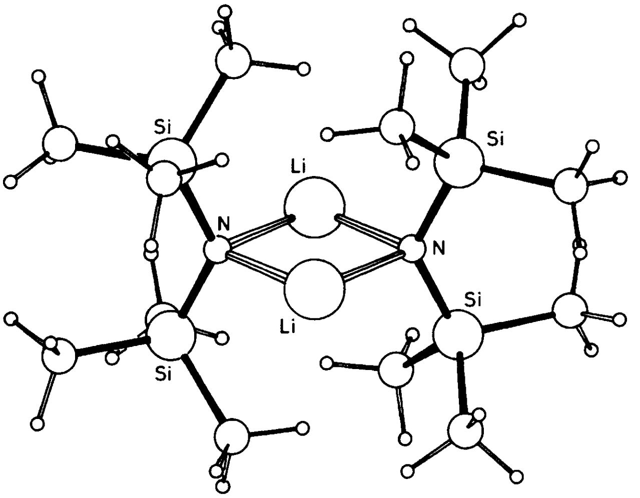

Figure 1. Molecular model of $[Li\{N(SiMe_3)_2\}]_2$, as determined by gas-phase electron diffraction. Selected bond lengths (Å) and angles (°): Li–N 1.99(3), Si–N 1.712(7), Si–C 1.889(4), C–H 1.108(8); Li–N–Li 80(3), Si–N–Si 129.8(1.7), N–Si–C 112.2(0.9), Si–C–H 114.3(2.5).

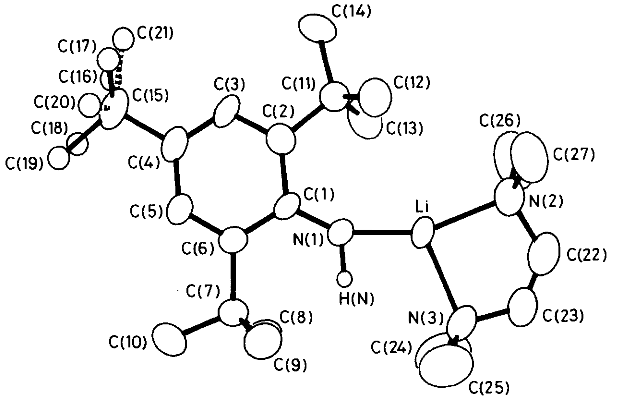

Figure 2. *X*-Ray crystal structure of $Li(NHC_6H_2Bu^t{}_3$-2,4,6)($Me_2NCH_2CH_2NMe_2$). Numbering scheme and selected bond lengths (Å) and angles (°): Li–N(1) 1.895(8), Li–N(2) 2.137(9), Li–N(3) 2.165(9), N(1)–H(N) 1.03(4), Li · · · H(N) 2.08(4); C(1)–N(1)–Li 155.6(4), N(1)–Li–N(2) 159.0(5), N(1)–Li–N(3) 114.7(4), N(2)–Li–N(3) 86.2(3), Li–N(1)–H(N) 85(2), C(1)–N(1)–H(N) 119(2). [C(16), C(17), and C(19) or C(18), C(20), and C(21) are the alternative positions for a disordered Bu^t group].

structure is that illustrated in Figure 1. The $SiMe_3$ groups of each $\bar{N}(SiMe_3)_2$ ligand are close to staggered with respect to each other when viewed along the Si · · · Si vector, whereas the methyl groups are twisted *ca.* 25° (mean value) away from their staggered reference positions. This arrangement is close to that found for gaseous $NH(SiMe_3)_2$.[8] However, the Si–C bonds in the lithium amide, 1.889(4) Å, are significantly longer than those in $NH(SiMe_3)_2$, 1.876(1) Å; this may be regarded as compensating the shorter Si–N bonds in the amidolithium, *cf.*, 1.738(5) Å in $NH(SiMe_3)_2$. These effects may arise from the fact that inter-ligand C · · · C and H · · · H interactions are a feature only in the dimeric lithium amide, and shorter Si–N bonds tend to increase intra-ligand interactions. An alternative (or complementary) explanation is that the lithium amide is more ionic than $NH(SiMe_3)_2$ and hence has a greater partial negative charge on the amido N. In support of the latter proposition, we note similar contrasts in two linear species $[(Me_3Si)_3C\text{–}Li\text{–}C(SiMe_3)_3]^-$ and $[(Me_3Si)_3C\text{–}Hg\text{–}C(SiMe_3)_3]$: the average bond lengths Si–C(1) [1.82 and 1.887(4) Å, respectively] may be compared with the average Si–C(Me) distances [1.95 and 1.871(3) Å, respectively].[9]

Crystal data: $C_{24}H_{46}LiN_3$, monoclinic, space group $P2_1/n$, a = 10.299(1), b = 19.614(3), c = 12.939(2) Å, β = 101.38(2)°, Z = 4. The crystal was sealed in a capillary and did not show any signs of decomposition during the data collection. However, there were virtually no high angle data, and hence the data set is rather limited.‡

The structure of crystalline Li(NHAr)(tmeda) (tmeda = $Me_2NCH_2CH_2NMe_2$), Figure 2, was refined using 1283 reflections [$I > \sigma(I)$], measured on an Enraf-Nonius CAD 4 diffractometer with Mo-K_α radiation, to give a final residual of R = 0.090 (R' = 0.113). The hydrogen atom H(N) was located on a difference map and refined in the least squares procedures.

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‡ The atomic co-ordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The atoms C(1) to C(6), N(1) to N(3), Li and H(N) form an extended approximately co-planar arrangement (maximum deviation 0.14 Å). The co-ordination about the Li atom is distorted trigonal with a very large N(1)–Li–N(2) angle of 159.0(5)°. The bonding about the atom N(1) is also distorted trigonal with a very large C(1)–N(1)–Li angle of 155.6(4)°. The small Li–N(1)–H(N) angle of 85(2)° leads to a rather short Li · · · H(N) distance of 2.08(4) Å which may indicate some interaction between the two. The Li–N(tmeda) distances (average 2.15 Å) are significantly longer than the Li–NHAr bond [1.895(8) Å]. The latter represents the shortest Li–N distance yet recorded; the previous lower limit appears to have been that found in $[C_5H_4N\text{-}2\text{-}(Li)C(SiMe_3)_2]_2$, 1.936(6) Å.[10] The short Li–NHAr bond reflects some degree of $\ddot{N}\overset{\curvearrowright}{-}Li$ π-bonding. In the crystal the molecules pack in layers perpendicular to the *b* axis. The rather large angular distortions from regular geometry at N(1) and Li are just those that are required to minimise intra-molecular steric strain if the molecule has to have the planar arrangement seen.

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