Structural Chemistry of Lithium Hydrazides☆

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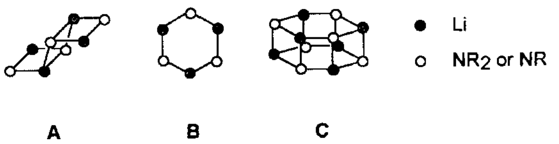
Deprotonation of NH protons of four diorgano-, organo(trimethylsilyl)- and bis(trimethylsilyl)hydrazines by *n*-butyllithium in hexane led to the following lithium hydrazides: $[Et(Li)N-N(H)Et]_6$ $(\mathbf{1})_6$, $[Me_3Si(Li)N-N(Li)SiMe_3]_4$ $(\mathbf{2})_4$, $[Me_3Si(Li)N-N(Li)SiMe_3 \cdot (Me_3Si)_2N-N(Li)SiMe_3]_2$ $(\mathbf{3})_2$, and $[Ph(Li)N-N(Li)SiMe_3]_4$, $(\mathbf{4})_4$, respectively. The structure determination by X-ray methods at low temperature reveals butterfly-shaped Li_2N_2 structural monomeric units which associate through "laddering" to the observed oligomers thereby generating penta- and hexacoordinated Li centers. N−N bonds lengths of up to 1.556 Å suggest that negative charge accumulates at the nitrogen atoms of $(\mathbf{1})_6$, $(\mathbf{2})_4$, and $(\mathbf{3})_2$. An amazing structure shows the red compound **4** where two Li ions are π-sandwiched between two phenyl groups each. The compound can be looked at as a new type of a lithium lithiate complex, $Li_2[Li_6N_8Ph_4(SiMe_3)_4]$, but short N−C and N−N bonds in the Li_6N_8 core indicate that its negative charge is transferred to the phenyl groups.

Alkali metal amides MNR_2 are important reagents[1] and some of them are commercially available. Their structural chemistry has been explored extensively, and results have been summarized in several reviews[2]. Typical structural features are "laddering" and ring formation of the units as depicted in structures **A** and **B** while "stacking" (**C**) is more typical for imino lithium compounds. Coordination numbers for the nitrogen atoms are usually four and five, but three[3] occurs also in some instances. Similarly, the Li centers exhibit tri- and tetracoordination, but "agostic" Li···H interactions lead to a better steric shielding of the Li centers. Bonding between Li and N centers is obviously characterized by high polarity[2c].



More recently, *N*-substituted lithium amides[4] have been investigated in more detail, and these studies have been focused on lithium silyamides[5], and also the structural chemistry of lithium hydrazides is developing[4−8] as shown by examples such as $[Li_2N_2(SiMe_2tBu)_2]$[6], $[LiN_2(SiMe_3)_3]$[6], or $[Li(H)N-N(H)SiMe_2tBu]_6$[7]. We have extended our studies into the structural chemistry of organo- and silyl-substituted lithium hydrazides, compounds that we are using as synthons for the preparation of various kinds of boryl-substituted hydrazines[9]. In the course of these investigations we obtained four different lithium hydrazides in the form of single crystals which we studied by X-ray and NMR methods.

Lithium *N,N'*-Diethylhydrazide (1)

Lithium *N,N'*-diethylhydrazide (**1**) was prepared by allowing butyl lithium to react with *N,N'*-diethylhydrazine in a 1:1 molar ratio in hexane as described by eq. (1).

$$Et(H)N-N(H)Et + BuLi \rightarrow \underset{\mathbf{1}}{Et(H)N-N(Li)Et} + BuH \qquad (1)$$

The compound crystallized from a hexane solution in well-formed single crystals suitable for an X-ray structure analysis. As shown in Figure 1 this compound is *hexameric* in the solid state. The unique building block consists of an N_2Li triangle, and six such units constitute the molecule $(\mathbf{1})_6$. From each of these six triangles an N−Li atom pair joins to form a distorted "hexagonal prism" by laddering. The nitrogen atom of the Et(H)N group of each N_2Li triangle bridges neighboring N and Li atoms from the upper and lower deck of the "hexagonal prism". A view on top of the hexameric molecule is depicted in Figure 2, and this plot demonstrates that the symmetry of the molecule is close to point group S_6 as revealed by the same sense in which the NH groups (as well as the ethyl groups) are oriented.

The fairly unusual structure of $(\mathbf{1})_6$ reveals tetracoordination for all lithium centers. The nitrogen atoms of the Li_6N_6 core are pentacoordinated while the N atoms of the NHEt groups are tetracoordinated. Every pair of LiN units, which are part of the "lower" and "upper" deck, is bridged by the N atom of EtNH groups. We observe a range of N−Li atom distances [2.038(3)−2.121(3) Å] for the penta-

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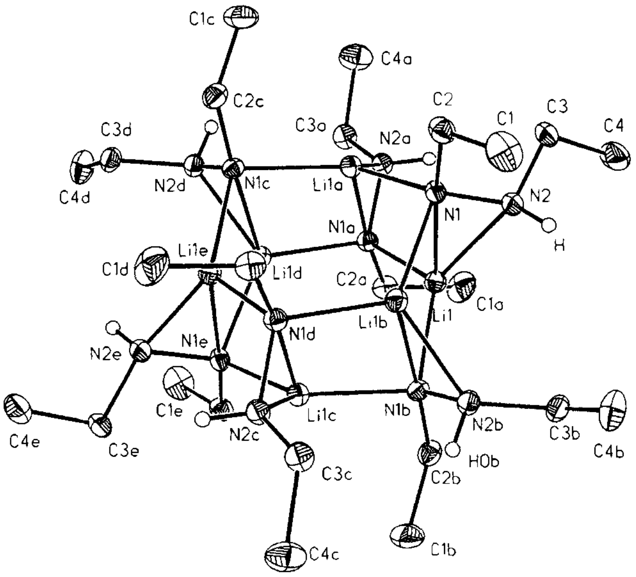
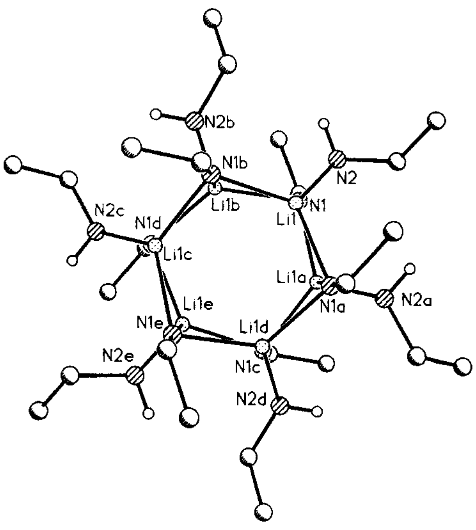
coordinated atom N1 while the Li−N bond for the tetracoordinated atom N2 is 2.020(3) Å. This is consistent with the well-known fact that the bond length increases as the coordination number increases. In spite of this, we find an N1−N2 bond length of 1.465(2) Å which corresponds with those bond lengths found for hydrazine itself and organo-substituted hydrazines[10]. A consequence of the molecular structure of $(\mathbf{1})_6$ are two distinctly different Li···Li atom distances, short ones with 2.479(4) Å across the four-membered Li_2N_2 rings, and long ones with 3.252(4) Å across the six-membered ring. It is worth noting that there are no "agostic" Li···H−C interactions.

Figure 1. ORTEP-type representation of the molecular structure of $(\mathbf{1})_6$; hydrogen atoms omitted for clarity; thermal ellipsoides are drawn on a 25% probability scale; estimated standard deviations in parentheses; selected bond lengths [Å] and angles [°]: N1−N2 1.465(2), N1−Li1 2.121(3), N1−Li1a 2.038(3), N1−Li1b 2.057(3), N1−C2 1.464(2), N2−Li1 2.020(3), N2−C3 1.460(2), Li1···Li1a 2.479(4), Li1···Li1c 3.252(4), Li1−N1b 2.037(3); C2−N1−N2 111.5(1), N2−N1−Li1a 111.5(1), N2−N1−Li1b 111.2(1), C2−N1−Li1 174.2(1), Li1a−N1−Li1 73.2(1), Li1a−N1−Li1b 105.2(1). N2−N1−Li1 65.61(9), Li1b−N1−Li1 72.8(1), N1−N2−C3 115.6(1), N1−N2−Li1 65.61(9), N1−N2−Li1 73.0(1), Li1−N2−N1 115.8(1), Li1−N2−C3 130.3(1), N1−Li1−N2 41.36(7), N1−Li1−N1a 105.6(1), N1a−Li1−N1b 123.4(1), N1−Li1−N1b 106.5(1), N1b−Li1−N2 117.8(1)



Will the hexameric structure of Et(H)N−N(Li)Et be retained in solution? The answer to this question can be given by NMR spectra in [D$_8$] toluene solution. Both, the ^{1}H- and the ^{13}C-NMR spectra show signals for four different ethyl groups and these show an intensity ratio of 2:2:3:3. Thus, there are two pairs each, and this indicates the presence of two different species in solution. This is ascertained by the presence of two ^{7}Li-NMR signals at $\delta = 2.00$ and 1.59, and these signals show also a 2:3 intensity ratio. Heating the solution to 65°C results in a single ^{7}Li-NMR signal at $\delta = 1.94$, and the ^{1}H-NMR spectrum at this temperature exhibits only signals for two different ethyl groups in a 1:1 ratio. The straightforward interpretation of these data could be the assumption of a monomer-hexamer equilibrium as in eq. (2).

Figure 2. View on top of molecule $(\mathbf{1})_6$ demonstrating the symmetry which is close to point group S_6 (C-bound hydrogen atoms omitted for clarity)



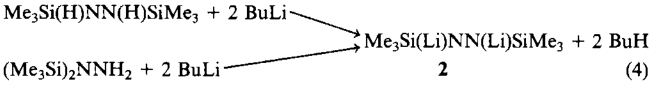
$$6\ \mathrm{Et(H)N{-}N(Li)Et} \rightleftharpoons [\mathrm{Et(H)N{-}N(Li)Et}]_6 \tag{2}$$

$$3\ [\mathrm{Et(H)N{-}N(Li)Et}]_2 \rightleftharpoons [\mathrm{Et(H)N{-}N(Li)Et}]_6 \tag{3}$$

However, the breakdown of the hexamer into a dimer as described by eq. (3) with a symmetry as observed for $[(Me_3Si)_2N{-}N(SiMe_3)Li]_2$[6] is the more realistic alternative because fewer bonds must be ruptured in this case. This kind of degradation is reasonable also from the point of view that there are pairs of alternating Li−N bond lengths in the hexamer which suggests a dissoziation into dimeric units[11]. This situation will certainly be favored over the formation of a monomer, which would require low-coordinate Li atoms in a nonpolar solvent. Attempts to obtain information on the fragmentation of $(\mathbf{1})_6$ in the gas phase by mass spectrometry failed because $(\mathbf{1})_6$ could not be volatilized without severe decomposition.

Dilithium *N,N'*-Bis(trimethylsilyl)hydrazide 2

The hydrazide **2** is readily prepared according to eq. (4) by allowing butyllithium to react with a mixture of isomers of *N,N*- and *N,N'*-bis(trimethylsilyl)hydrazine in hexane in a 2:1 molar ratio. Since **2** is formed almost quantitatively the reaction proceeds with migration of one Me_3Si group[12] to finally form the Li derivative of the isomer $Me_3Si(H)N{-}N(H)SiMe_3$.



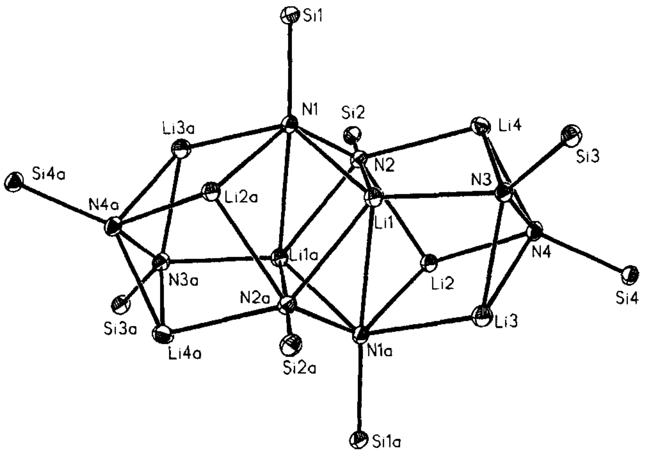
$$\left.\begin{array}{l}\mathrm{Me_3Si(H)NN(H)SiMe_3 + 2\ BuLi}\\ \mathrm{(Me_3Si)_2NNH_2 + 2\ BuLi}\end{array}\right\} \longrightarrow \underset{\mathbf{2}}{\mathrm{Me_3Si(Li)NN(Li)SiMe_3}} + 2\ \mathrm{BuH} \tag{4}$$

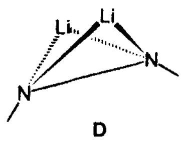
The lithium hydrazide **2** is slightly soluble in pentane, hexane, benzene and toluene, and excellently in THF. Single crystals separated from hexane solutions.

The molecular structure of **2** as revealed by an X-ray structure analysis is depicted in Figure 3. It shows the compound to be present as a *tetramer* $(\mathbf{2})_4$ in the solid state with a crystallographically imposed C_i symmetry. There are two types of lithium atoms, six Li centers of coordination number 3 and two with coordination number 5. Four nitrogen atoms are pentacoordinated and four additional ones show hexacoordination (by N and Li). There are two ways to describe the formation of tetrameric **2** from the monomeric molecules **2** with side-on coordinated lithium atoms (Formula **D**).

a) By joining three of these butterfly-shaped molecules in such a way that each Li atom becomes tricoordinate by interaction with one N atom each increasing the coordination at the N atoms from 4 to 5. It should be noted that there are two types of these butterfly Li_2N_2 units, one with a folding angle of 105.5° at the N1–N2 bond, and two with a folding angle of 140.2° at the N3–N4 and N3a–N4a bond. The trimeric unit that forms is shown in Figure 4a. This trimer adds a fourth monomeric molecule of **2** having *terminal* lithium atoms (depicted by dashed lines thus generating four pentacoordinated Li and four hexacoordinated N atoms in the final structure.

Figure 3. ORTEP-type plot of the structure of molecule $(\mathbf{2})_4$; hydrogen atoms omitted; thermal ellipsoides are drawn on a 25% probability level; estimated standard deviations are given in parentheses; selected bond lengths [Å] and angles [°]: N1–Si1 1.719(2), N1–N2 1.570(3), N1–Li1 2.070(5), N1–Li3a 2.072(5), N1–Li1a 2.255(5), N2–Si2 1.713(2), N2–Li1 2.155(5), N2–Li1a 2.132(5), N2–Li2 2.102(5), N2–Li4 1.985(5), Li1–N3 2.000(5), Li2–N4 1.985(5), Li2–N1a 2.088(5), N3–Li3 1.925(5), N3–Li4 1.982(5), N3–N4 1.549(3), N3–Si3 1.716(5), N4–Si4 1.707(2), N4–Li3 2.045(5), N4–Li4 1.925(5); N2–N1–Li1 71.1(2), N2–N1–Li1a 64.9(2), N2–N1–Li3a 107.6(2), Li1–N1–Li3a 133.5(2), Li3a–N1–Li2a 73.2(2), N2–N1–Li2a 128.4(2), L1–N1–Li1a 68.5(2), N1–N2–Li2 130.2(2), N1–N2–Li4 111.8(2), Li2–N2–Li4 70.8(2), N1–N2–Li1a 73.3(2), Li2–N2–Li1a 71.8(2), Li1a–N2–Li4 132.7(2), N1–N2–Li1 65.3(2), Li2–N2–Li1 69.6(2), Li1–N2–Li4 71.1(2), N3–Li1–N1 133.2(3), N1–Li1–N2 43.5(1), N3–Li1–N1a 99.2(2), N2a–Li1–N1a 41.8(1), N3–Li1–N2a 127.2(2), N3–Li1–N2 103.1(2), N2a–Li1–N2 110.6(2), N1–Li1–N1a 111.5(2), N1a–Li2–N2 99.0(2), N4–Li2–N1a 105.7(2), N4–Li2–N2 104.3(2), Li3–N3–Li4 121.4(2), Li1–N3–Li3 78.1(2), Li1–N3–Li4 77.8(2), N4–N3–Li3 71.2(2), N4–N3–Li1 104.6(2), N4–N3–Li4 64.7(2), N3–N4–Li2 100.9(2), N3–N4–Li4 68.6(2), N3–N4–Li3 63.0(2), N3–Li3–N4 45.8(1), N3–Li3–N1a 108.5(2), N1a–Li3–N4 104.1(2), N3–Li4–N4 46.7(1), N3–Li4–N2 104.8(2), N4–Li4–N2 104.8(2)





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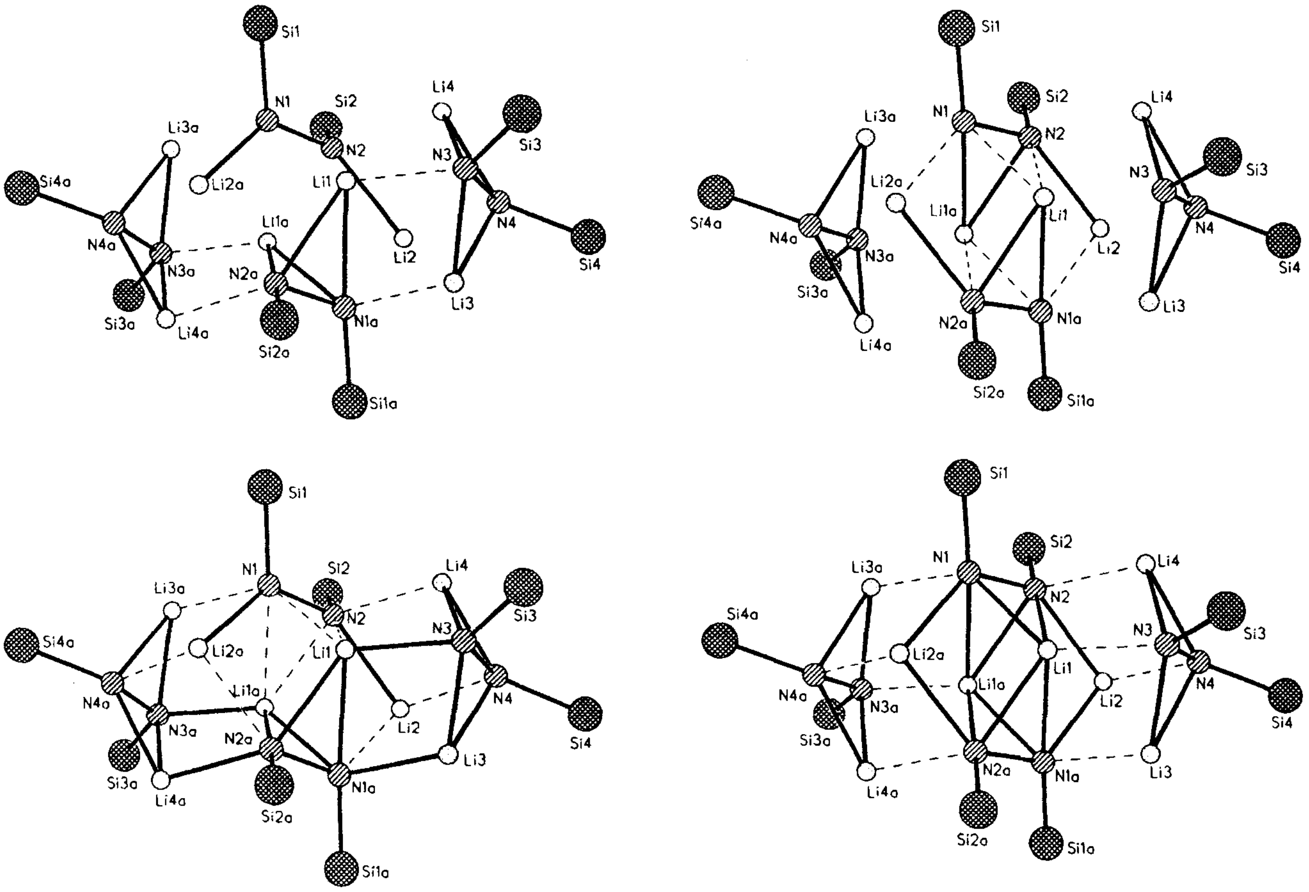
b) A different way to construct $(\mathbf{2})_4$ is to join first the central part of the tetramer from two dilithium hydrazide units which are structurally composed of hydrazine units carrying each a side-on and a terminally bonded Li atom. To these units, see Figure 4b, two more molecules of **2** having only side-on bonded Li centers add from each side to generate teterameric **2** [= $(\mathbf{2})_4$]. Li–N bond lengths from atoms Li3 and Li4 range from 1.925(5)–2.144(5) Å while the Li–N atom distances for the pentacoordinated Li center Li1 span lengths of 2.000(5)–2.255(5) Å. Atom Li1 exhibits a distorted trigonal coordination with atoms N1, N2a and N3 constitution the "trigonal plane" (sum of bond angles 359°), while the additionally coordinated atoms N2 and N1a form a bond angle of 92.4(2)°. Once again the average Li–N atom distances are longer for the higher coordinated Li centers, and this is true also for the nitrogen centers. The N–N bond length for the hexacoordinated atoms N1 and N2 of a hydrazide unit is 1.570(3) Å but for the pentacoordinated N atoms N3 and N4 it is only 1.549(3) Å. The most acute bond angles (41.8–45°) are found for the N–Li–N angle of the LiN_2 three-membered rings while the bond angles at the nitrogen atoms of this ring range from 64.7–68.6°. Atom distances between lithium centers (Li1–Li2a and Li2–Li1a) that are part of a four-membered Li_2N_2 ring are 2.483(6) Å while the Li1–Li1a distance is 2.440(9) Å. Surprisingly, the Li···Li distances are much *shorter* for Li atoms with a *higher* coordination sphere, and this finding is compatible with highly polar Li–N interactions. Li atoms which are surrounded by three nitrogen atoms show one "agnostic" Li···H interaction[13]. Finally, it should be noted that the compound $Me_3C(Li)N-N(Li)SiMe_3$ is, in principle, isostructural with $(\mathbf{2})_4$, but due to Me_3C/Me_3Si disorder it is not advisable to discuss its structure in more detail[13].

^7Li-NMR data of $(\mathbf{2})_4$ in [D$_8$] toluene at 25°C show three signals in a 1:2:1 ratio. This would be in accord with the presence of tetrameric **2** in solution because $(\mathbf{2})_4$ contains three different Li centers (Li1, Li2 and Li3 + Li4). Although three ^{29}Si-NMR signals are expected for the structure shown in Figure 3 only two signals are observed. Four pairs of signals showing approximately equal intensities are found in the ^1H-NMR spectrum of $(\mathbf{2})_4$, and the ^{13}C-NMR spectrum also reveals eight resonances. Thus, the ^1H- and ^{13}C-NMR data do not reflect the symmetry of $(\mathbf{2})_4$ with freely rotating Me_3Si groups. We therefore assume hindered rotation of these groups. This assumption is justified because at 107°C there is a single signal in both the ^1H- and ^{29}Si-NMR spectra. Therefore, dynamic processes make the Me_3Si groups equivalent, while there are still two ^7Li resonances but now in a 3:1 ratio. These interesting phenomena are worthy a more detailed study. Obviously and in contrast to $(\mathbf{1})_6$ the molecular structure of $(\mathbf{2})_4$ remains intact at elevated temperatures. Actually, the Li_8N_8 "cluster" does not even break down by THF coordination as shown by Klingebiel et al. for $(\mathbf{2})_4 \times 2$ THF[8].

Figure 4. Two ways of constructing the molecule $(2)_4$: a) by joining three "side on" coordinated Li_2N_2 units with an "end-on" coordinated Li_2N_2 units with an "end-on" coordinated $Li_2N_2(SiMe_3)_2$ molecule (left); b) by joining two side-on coordinated Li_2N_2 units to a central Li_4N_4 core (right)



[Monolithium Bis(trimethylsilyl)hydrazide]−[Dilithium Bis(trimethylsilyl)hydrazide] (3)

Since the degree of association of lithium hydrazides will be influenced by the steric demand of the *N* substituent, we were interested in the hydrazide $Me_3Si(H)N-N(Li)SiMe_3$ because we expected to learn from the structures of $(\mathbf{1})_6$ and $[Me_3Si(H)N-N(Li)SiMe]_n$ how *n* changes when Et groups are replaced by the more bulky $SiMe_3$ groups. For this purpose we treated a mixture of isomers $(Me_3Si)_2N_2H_2$ with BuLi in a 1:1 ratio, expecting to obtain $Me_3Si(Li)N-N(H)SiMe_3$[15] as show in eq. (5).

$$(Me_3Si)_2N_2H_2 + BuLi \rightarrow Me_3Si(Li)N-N(H)SiMe_3 + BuH \quad (5)$$

The reaction, performed in boiling pentane or hexane, yielded, however, crystals of a "mixed" compound composition $(Me_3Si)_2N-N(Li)H \cdot Me_3Si(Li)N-N(Li)SiMe_3$ (**3**)[8b] in almost quantitative yield. They separated from hexane as single crystals.

The result of the structure determination of **3** is shown in Figure 5. Once again the molecule is centrosymmetric and proves to be a dimer of **3** [= $(\mathbf{3})_2$] with four hydrazide units in the molecular unit similar to $(\mathbf{2})_4$. There are two types of Li atoms in $(\mathbf{3})_2$, four with coordination number 3 and two which are tetracoordinated. The nitrogen atoms which carry two trimethylsilyl groups are tetracoordinated, while the N2 and N2a atoms, to which a hydrogen atom is bonded, are pentacoordinated as are atoms N3 and N3a. Hexacoordination is present at the atoms N4 and N4a. Therefore, the structure of $(\mathbf{3})_2$ is more complex than the structures previously described. Li−N bond lengths from atom Li1 are 1.999 Å to atom N3, 2.003 Å to N2, and 2.218 Å to N4a. Li2−N atom distances range from 1.953−2.087 Å, and those to atom Li3 have distances of 1.974, 2.024, 2.048 and 2.139 Å. On average, the Li−N bond lengths are shorter for the tricoordinated Li1 atom and longer for the two tetracoordinated atoms Li2 and Li3 although the shortest of all Li−N distances is found at atom Li3. The influence of coordination is also demonstrated for the N1−N2 bond length of 1.528 Å involving tetra- and pentacoordinated N atoms while the N3−N4 bond between a penta- and a hexacoordinated N atom shows a bond length of 1.556 Å. On the other hand it is worthwhile noting that the N4−Si4 bond is shorter (1.711 Å) than the Si−N bonds to the tetracoordinated atom N1 (1.751 and 1.754 Å) in spite of the fact that atom N4 is hexacoordinated. Finally, it must be noted that there is additional steric shielding at atom Li1 by two "agostic" interactions with hydrogen atoms [Li1···H−C9a (2.25 Å), Li1···H−C2 (2.42 Å)] as indicated in Figure 5, while two Li···H atom distances at atom Li2 are much longer (>2.78 Å).

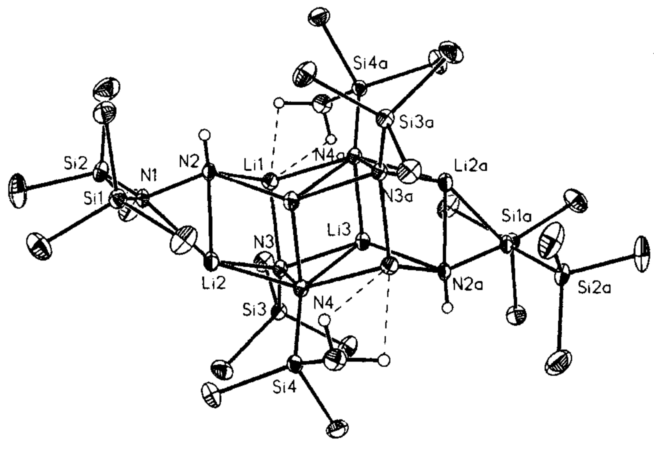


Figure 5. ORTEP-type plot of the molecular structure of compound **(3)**$_2$; hydrogen atoms omitted except those which show agostic interaction with Li centers; thermal ellipsoides are drawn on a 25% probability level; estimated standard deviations are given in parentheses; selected bond lengths [Å] and angles [°]: N1−Si1 1.751(2), N1−Si2 1.754(2), N1−Li2 2.087(3), N1−N2 1.528(2), N2−Li1 2.003(4), N2−Li2 2.004(4), N2−Li3a 2.024(3), N3−Li1 1.999(4), N3−Li2 1.953(3), N3−Si3 1.715(2), N3−N4 1.556(2), N4−Si4 1.711(2), N4−Li2 2.061(3), N4−Li3 2.048(4), N4−Li1a 2.218(3), Li1−H9a 2.25(3); Si1−N1−Si2 126.85(9), Li2−N1−N2 65.2(1), Li1−N2−Li3a 70.7(1), Li1−N2−Li2 74.9(1), N2−Li1−N3 102.9(3), N2−Li1−N4a 98.6(2), N3−Li1−N4a 100.9(2), N1−Li2−N4 143.6(2), N2−Li2−N3 87.5(1), N2−Li2−N4 105.5(2), N3−Li2−N4 45.50(9), N3−Li3−N4 45.45(9), Si4−N4−N3 125.2(1), Si4−N4−Li2 103.0(1), Si4−N4−Li3a 127.8(1), Si4−N4−Li3 136.2(1), Si3−N3−Li1 131.9(1), Si3−N3−N4 126.0(1), Li1−N3−N4 101.4(1), Li1−N3−Li3 77.2(1), N4−Li3−N4a 96.5(1), N3−Li3−N4 45.45(9), N4a−Li3−N2a 102.0(1)

Bond angles at the nitrogen atoms span a wide range: on N1 from 65.2−126.8°, on N2 from 70.6−128.7°, on N3 from 76.1−131.9°, and on N4 from 63.5−140.8°. On the other hand the N−Li−N angles of side-on coordinated Li atoms are always close to 45°. There are two features in **(3)**$_2$ which seem to be typical of lithium hydrazides. Thus, the $Me_3Si(Li)N-N(Li)SiMe_3$ unit exhibits a butterfly structure as already described with a folding angle at N3−N4 of 142.5°, while the $(Me_3Si)_2N-N(H)Li$ unit features terminal Li atoms. The butterfly units are joined in a manner that resembles the laddering of lithium dialkylamides. Atoms Li2 and Li2a remain dicoordinated in this formal built-up procedure and become tricoordinated by adding the $(Me_3Si)_2N-NHLi$ units with its $(Me_3Si)_2N$ nitrogen atom, and atoms Li1 and Li1a join to the nitrogen atoms N3, N4a, N3a, and N4. This association of the subunits generates Li···Li contacts across the four-membered rings, ranging from 2.329 Å (Li1−Li3a) over 2.436 Å (Li1−Li2) to 2.478 Å (Li1−Li3), while the Li3···Li3a distance is long with 2.789(6) Å. All four-membered rings are not planar, the folding angle at N2−N3 is 15.4°, at Li1−Li3 26.4°, and at N2a−N4a 24.9°. As expected from the geometry of the molecule the Li2···Li3 atom distance is even longer (3.502 Å).

NMR spectra recorded of [D$_8$] toluene solutions of **(3)**$_2$ show no temperature dependence up to 90°C. There are more ^{1}H-NMR signals for the Me_3Si groups than expected from the solid-state structure of the molecule. However, two ^{7}Li-NMR signals in a 2:1 ratio would be in accord with the structure depicted in Figure 5. However, eight signals found in the ^{27}Si-NMR spectrum seem not to be compatible with the molecular symmetry of a point group C_i.

Dilithium *N*-Phenyl-*N'*-trimethylsilylhydrazide (4)

N-Phenyl-*N'*-trimethylsilylhydrazine can be doubly deprotonated by butyllithium in boiling hexane solution as described by eq. (6).

$$\mathrm{Ph(H)N-N(H)SiMe_3 + 2\ BuLi \rightarrow} \qquad \mathbf{4} \qquad \mathrm{Ph(Li)N-N(Li)SiMe_3 + 2\ BuH} \qquad (6)$$

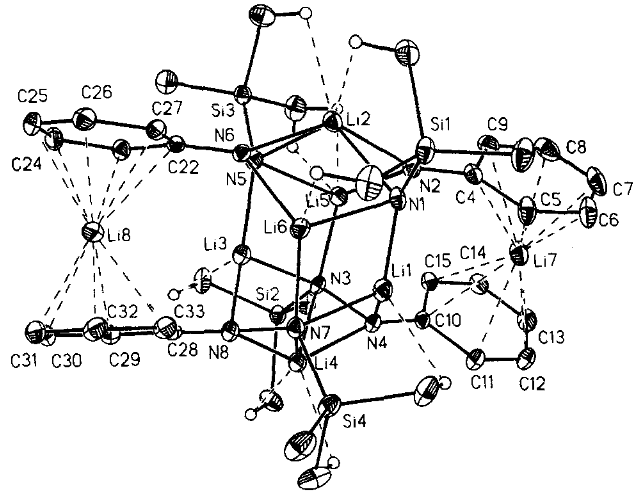
In contrast to the colorless lithium hydrazides **(1)**$_6$, **(2)**$_4$ and **(3)**$_2$ crystals of compound **4** are red. This points already to the conclusion that its structure may differ considerably from those previously described.

As demonstrated by Figure 6, which presents the molecular structure of **4** in the solid state, the arrangement of atoms is indeed unusual and unprecedented for lithium hydrazides. We not only note that the molecular unit consists of tetrameric **4** [= **(4)**$_4$] but that two lithium atoms are sandwiched by pairs of phenyl rings which act as η^6 ligands. Consequently, the remaining six lithium and eight nitrogen atoms form the core of a lithium hydrazide cluster. In this cluster we find 4 nitrogen atoms with coordination number five and four that are tetracoordinated, the former are carrying the Me_3Si groups, while the latter have a phenyl group as an external substituent. Similarly, there are four tetracoordinated Li atoms, besides "agostic" Li-H contacts, e.g. Li1−H36 (2.34 Å, Li2−H3a (2.16 Å), Li4−H35b (2.18 Å), Li7−H17a (2.29 Å), and Li6−H2c (2.32 Å).

The Li−N bond lengths in the Li_6N_8 cluster of **(4)**$_4$ span a fairly narrow range, 1.950−2.118 Å and Li···Li atom distances cover 2.440−2.547 Å which are on the long side as compared with the previously described examples. The fairly small differences in bond lenghts hold also for the N−N bonds which fall between 1.492 and 1.509 Å and can be considered as equal on the basis of the 3σ criterion of estimated standard deviations.

A closer view on the Li_6N_8 cluster part of the molecule (see Figure 7) reveals approximately C_2 point group symmetry with the twofold axis passing through atoms Li2 and Li4. Each of these atoms are capping a chair-shaped, distorted Li_2N_4 hexagon. The core structure of the Li_6N_8 unit consists of six four-membered rings which are joined by three-membered rings. Out of the four-membered rings the Li1−N4−Li4−N7 ring and its symmetry-related ring are almost planar (largest deviation from the ideal plane is 0.025 Å) while the Li1−N7−Li6−N1 ring (plane 1) is significantly folded (folding angle between Li1−N7−Li6 and Li1−N1−Li6 14.6°). The Li1−N7−Li6 plane forms an angle of 47.4° with plane 1. Also, the four-membered ring

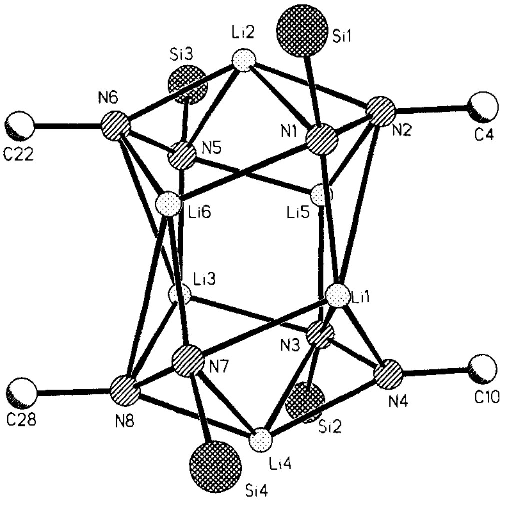
Figure 6. ORTEP-type plot of the molecular structure of compound **(4)**$_4$; hydrogen atoms omitted for clarity except those which show Li···H−C interactions; thermal ellipsoids are drawn on a 20% probability level; estimated standard deviations are given in parentheses; selected bond lengths [Å] and angles [°]: N1−N2 1.509(4), N1−Li1 1.981(6), N1−Li6 2.082(6), N1−Li2 2.100(7), N2−C4 1.345(4), N2−Li2 1.982(6), N2−Li5 2.055(6), N3−N4 1.500(3), N3−Li5 2.003(6), N3−Li3 2.104(6), N3−Li4 2.124(6), N4−C10 1.344(3), N4−Li4 1.968(6), N4−Li1 2.052(6), N5−N6 1.500(3), N5−Li3 1.988(6), N5−Li5 2.081(6), N5−Li2 2.088(6), N6−Li2 1.964(6), N6−Li6 2.060(6), N7−N8 1.501(4), N7−Li6 1.987(6), N7−Li1 2.075(6), N7−Li4 2.082(6), N8−Li4 1.947(6), N8−Li3 2.070(7), Li7−C 2.292(7)−2.528(6); N2−N1−Li1 96.5(2), N2−N1−Li2 64.2(2), Li1−N1−Li2 119.5(3), Li6−N1−Li2 74.6(2), C4−N2−N1 115.0(3), N1−N2−Li2 72.5(2), N1−N2−Li5 104.9(2), Li2−N2−Li5 75.2(2), N4−N3−Li3 124.8(2), Li5−N3−Li3 73.9(2), N4−N3−Li4 63.0(2), Li5−N3−Li4 124.7(3), C10−N4−N3 116.4(2), N3−N4−Li4 74.2(2), N3−N4−Li1 98.7(2), Li4−N4−Li1 77.1(2), N6−N5−Li3 97.2(2), N6−N5−Li2 63.9(2), Li3−N5−Li2 120.1(3), Li5−N5−Li2 72.4(2), N5−N6−Li2 72.7(2), N5−N6−Li6 105.9(2), Li2−N6−Li6 78.0(2), N8−N7−Li6 101.1(2), N8−N7−Li1 124.0(2), Li6−N7−Li1 73.6(2), N8−N7−Li4 63.4(2), Li1−N7−Li4 74.2(2), N7−N8−Li3 101.0(2), Li4−N8−Li3 77.5(2), N7−N8−Li6 46.0(2), Li3−N8−Li6 71.0(2), N1−Li1−N4 133.9(3), N1−Li1−N7 105.5(3), N4−Li1−N7 102.9(3), N6−Li2−N2 132.4(3), N6−Li2−N5 43.3(2), N2−Li2−N5 106.9(3), N6−Li2−N1 104.8(3), N2−Li2−N1 43.3(2), N5−Li2−N1 111.4(3), N5−Li3−N8 131.9(3), N5−Li3−N3 104.6(3), N8−Li3−N3 102.6(3), N8−Li4−N4 134.4(3), N8−Li4−N7 43.6(2), N4−Li4−N7 105.6(3), N8−Li4−N3 106.2(3), N4−Li4−N3 42.8(2), N7−Li4−N3 108.2(3), N3−Li5−N2 124.7(3), N3−Li5−N5 105.0(3), N2−Li5−N5 104.5(2), N7−Li6−N6 127.9(3), N7−Li6−N1 104.9(3), N6−Li6−N1 102.0(3)



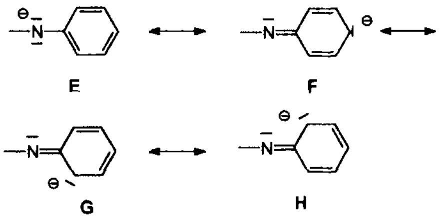
N1−Li2−N6−Li6 is not planar (largest derivation from the mean plane is 0.048 Å, folding angle at N1−N6 4.4°). The phenyl groups are twisted by 9.2° (C4−C9/C10−C15) and 6.2° (C22−C27/C28−C33) and the Li atoms are 1.90(1) Å above and below these planes.

Finally, there is another point to be noted, the lenghts of the N−C bonds to the phenyl groups. Bond lengths between 1.347 and 1.363 Å are compatible only with a high degree of C−N double bond character as found in conjugated nitrogen heterocyclic compounds[16]. This points to the conclusion that resonance structures of type **E** and especially **F**, **G**, and **H** contribute to the ground state is reasonable because this would lead to a strengthening of

Figure 7. Core of the formal $Li_6N_8(SiMe_3)_4Ph_4$ anion



the η^6 bonding of the phenyl rings with the π-complexed Li ion[17].



Discussion

Lithium organohydrazides or lithium silylhydrazides are useful synthetic reagents for the preparation of many organoelement-substituted hydrazines, e.g. of cyclic and noncyclic borylhydrazines[9], Cp_2Ti−hydrazines[18], silylhydrazines[19] and many others.

Early work by N. Wiberg et al.[15] has shown that the lithium trimethylsilylhydrazides $LiN_2(SiMe_3)_3$ and $Li_2N_2(SiMe_3)_2$ are associated in solution. The dimeric state of $LiN_2(SiMe_3)_3$ as found for solutions has been ascertained for the solid state as well[6]. $Li_2N_2(SiMe_2tBu)_2$ proved to be a tetrameric molecule in the solid state[7], and this holds also for the monolithium hydrazide $LiN_2H_3(SiMe_2tBu)$[6]. The present study adds four more structurally characterized examples, hexameric Et(Li)N−N(H)Et [**(1)**$_6$], tetrameric Me_3Si(Li)N−N(Li)$SiMe_3$ [**(2)**$_4$], dimeric [Me_3Si(Li)N−N(Li)$SiMe_3$ · $(Me_3Si)_2N$−N(H)Li] [**(3)**$_2$], and finally tetrameric Ph(Li)N−N(Li)$SiMe_3$ [**(4)**$_4$]. In addition, Klingebiel et al. have characterized [Me_3Si(Li)N−N(Li)$SiMe_3$] · 2 THF[10]. This latter compound has practically the same structure as **(2)**$_4$ in spite of the fact that two of the eight Li centers are coordinated to THF. This demonstrates strong bonding in the Li_nN_m clusters of the lithium hydrazides, evidence for the fact that the degree of association in not too strongly polar and basic solvents (ether, THF, glyme) remains the same as determined for the solvent-free molecular structure in the crystal.

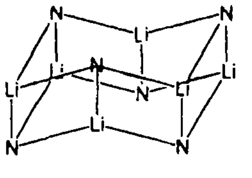
As demonstrated, $t\mathrm{BuMe_2Si(H)N{-}NH_2}$ can be readily metalated to $t\mathrm{BuMe_2Si(H)N{-}NHLi}$[7] and this is also true for $\mathrm{Et(H)N{-}N(H)Et}$. However, we failed to substitute only a single hydrogen atom by a lithium atom in the mixture of isomers $\mathrm{(Me_3Si)_2N_2H_2}$ which should give rise to $\mathrm{(Me_3Si)_2N{-}NHLi}$ or $\mathrm{Me_3Si(Li)N{-}N(H)SiMe_3}$. The product that actually forms is the dimer of the 1:1 mixed hydrazide, $\mathrm{Me_3Si(Li)N{-}N(Li)SiMe_3 \cdot (Me_3Si)_2N{-}NHLi}$ (**3**)[20].

This result stands in contrast to the finding of N. Wiberg et al.[15] who reported the formation of $\mathrm{(Me_3Si)_2N_2HLi}$ by monolithiation of the mixture of isomers $\mathrm{(SiMe_3)_2N_2H_2}$ in ether and pentane. It should be noted, however, that the C/H/N analytical data are not only acceptable for the reported "$\mathrm{(Me_3Si)_4N_4H_2Li_2}$" [here written as the dimer of $\mathrm{(Me_3Si)_2N_2HLi}$], but are also consistent with the composition $\mathrm{(Me_3Si)_4N_4HLi_3}$ (= **3**).

The consequence of this study is that the metalation of a mixture of isomers $\mathrm{(Me_3Si)_2H_2N_2}$ results in $\mathrm{Me_3Si(Li){-}N{-}N(Li)SiMe_3}$, obviously because deprotonation of the isomer $\mathrm{Me_3Si(H)N{-}N(H)SiMe_3}$ occurs with comparable rate on both NH protons, while the first deprotonation of $\mathrm{(Me_3Si)_2N{-}NH_2}$ is of the same rate as in the other isomer, but much slower for the second step. This results in the formation of **3** which is only slightly soluble in pentane or hexane. However, no monolithiation is possible by the above-mentioned reaction, because the solution after addition of BuLi in a 1:1 ratio still contains the isomer mixture of the starting hydrazines.

The structures of the lithium hydrazides so far reported are more complex than those of lithium amides. However, the triangular array of $\mathrm{LiN_2}$ units, either of monolithium hydrazides[6] or of dilithium hydrazides is the characteristic structural feature of this class of compounds, and this has also been found in several theoretical studies[7,8,21].

These units oligomerized to di-, tetra- and hexamers with formation of new Li···N interactions, and concomitant increases of the coordination at Li and N atoms. Dimerization of $\mathrm{(Me_3Si)_2N{-}N(Li)SiMe_3}$ corresponds with the first step of the "laddering" of lithium amides[2]. This is extended in the structure of $(\mathbf{1})_6$ which results in the formation of a distorted "hexagonal prism" (see **1**). This kind of atomic arrangement also occurs in the trimer of $t\mathrm{BuMe_2Si(Li)N{-}N(Li)SiMe_2}t\mathrm{Bu}$[6] which requires the association of three butterfly units.



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A combination of "laddering" as depicted for Li amides and joining of "butterfly units" is present in the structures of $(\mathbf{2})_4$[17] and $(\mathbf{4})_4$ (see Figure 4). The "laddering" can be readily recognized in Figures 1, 5 and 7.

The $\mathrm{Li_6N_8}$ core of compound $(\mathbf{4})_4$ shows another interesting point, namely comparatively short N−N bond lengths [1.500(3)−1.509(4) Å]. This supports the assumption of charge transfer to the phenyl groups, which is further supported by the fact that the C−C bond length of the *ipso*-C atom to the C atoms in *ortho* position are definitely longer (averaging 1.43 Å) than the remaining bond lengths (approx. 1.38 Å). On the other hand, the Li centers are shifted away from the *ipso*-C atoms towards the *p*-C atoms which, on average, form the shortest Li···C contact (2.30 Å). This kind of coordination of Li centers with phenyl rings is, to our knowledge, yet unprecedented in organometallic compounds of lithium[22].

There is no doubt that the structural chemistry of alkali metal hydrazides is quite variable. The degree of association is at the moment hard to predict. Nevertheless, the butterfly arrangement in lithiohydrazines seems to be responsible for reactions of lithium hydrazides with electrophiles leading to isomers as observed by Klingebiel et al. in a number of interesting reactions with silyl halides[19c,d].

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Experimental

All reactions were performed under rigorous exclusion of moisture under dinitrogen or in vacuo. Glassware was dry-flamed in vacuo. The hydrazines used were prepared according to literature procedures[23]. BuLi in hexane solution was used as supplied (Chemetall GmbH). − NMR: Jeol 270 [^{1}H, ^{7}Li (39.76 MHz), ^{13}C (67.94 MHz), ^{29}Si (53.67 MHz)], with internal TMS (^{13}C, ^{29}Si) and saturated LiCl solution (external) as standards. Positive δ values refer to resonances at lower field than the standard. − X-ray: Siemens P4 four-circle diffractometer [$(\mathbf{1})_6$, $(\mathbf{2})_4$, $(\mathbf{3})_2$]; Nicolet R3 diffractometer [$(\mathbf{4})_4$], low-temperature attachment. Samples were mounted in glass capillaries by using perfluoro ether oil, and Mo-K_α radiation with a graphite monochromator was used. All calculations were performed by using the SHELXL PLUS PC version package and in the final refinement the SHELXL 93 programs[24]. Details of the structure determinations are deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Dokumentation, 76344 Eggenstein-Leopoldshafen, and may be obtained by quoting the depository number CSD-401188−401192, the names of the authors, and the literature citation.

Lithium N,N'-Diethylhydrazide (**1**): BuLi (8.1 ml, 1.56 M, 12.6 mmol) was slowly added to a stirred and boiling solution of $\mathrm{Et(H)N{-}N(H)Et}$ (1.1 g, 12.7 mmol) in 60 ml of hexane. Gas evolution commenced immediately. After 3 h, the flask was placed in an ice bath. Clear crystals separated from the solution within a few hours. Yield: 1.08 g (91%), m.p. 94−96°C. − NMR ([D$_8$] toluene) at 25°C: δ (^{1}H) = 0.96 (t, 3H, CH$_3$), 0.98 (t, 3H, CH$_3$), 1.09 (t, 3H, CH$_3$), 1.11 (t, 3H, CH$_3$), 2.63 (br., 2H, CH$_2$), 3.20 (br., 4H, CH$_2$ + NH), 3.29 (br., 2H, CH$_2$), 3.44 (br., 2H, CH$_2$); δ(^{7}Li) = 1.59, 2.00 (3:2); δ(^{13}C) = 13.92, 14.01, 14.16, 15.69 (4 CH$_3$ groups), 42.07, 43.00, 44.11, 45.67 (4 CH$_2$ groups). − NMR at 65°C: δ(^{1}H) = 0.98 (3H, CH$_3$), 1.09 (3H), 2.63 (3H, CH$_2$ + NH), 3.30 (2H, NCH$_2$); δ(^{7}Li) = 1.94. − IR (nujol mull): 3204.9 cm^{-1} (s, NH), 2968.4 (s), 2788.7 (s), 2639.3 (m), 1447.2 (s), 1375 (s), 1360.3 (s), 1327 (s), 1073.2 (s), 1023 8s), 956 s, 932 (s), 797.6 (s), 578 (s), 532.3 (s).

X-ray Structure Determination of $(\mathbf{1})_6$: Formula $\mathrm{C_4H_{11}LiN_2}$; M_r = 94.09; colorless rhombus with dimensions 0.5 × 0.6 × 0.6

mm; $a = b = 18.592(3)$, $c = 9.605(2)$ Å; hexagonal; space group $R\bar{3}$; $Z = 18$ (three hexameric units); $d_{calcd.} = 0.978$ Mg/m^3; $\mu = 0.059$ mm^{-1}. – Data collection: $T = 173$ K; $2\Theta = 4.4-4.8°$ in $0 < h < 18$, $-21 < k < 0$, $-10 < l < 10$; ω scans; scan range 1.24°, scan speed 4–60°/min; 2015 reflections collected; 1004 unique reflections with $F > 4\sigma(F)$; $R_{int} = 0.0497$. – Structure solution and refinement: Direct methods; nonhydrogen atoms were refined anisotropically; hydrogen position were taken from a Fourier map and refined with fixed adapted U_i parameters; full-matrix least-squares refinement on F^2; 97 parameters refined; data-to-parameter ratio 10.3:1; $R = 0.0406$; $R = 0.060$ for all data; $wR2 = 0.099$ (on F^2); $GOOF = 1.046$; largest diff. peak/hole 0.128/–0.132 eÅ^{-3}.

Dilithium N,N'-Bis(trimethylsilyl)hydrazide (**2**): A BuLi solution in hexane (11.1 ml, 1.56 M, 17.2 mmol) was added with stirring to a boiling solution of a mixture of bis(trimethylsilyl)hydrazine isomers (1.52 g, 8.63 mmol). After 2 h, the solution was allowed to cool to ambient temperature. This caused crystals of **2** to settle from the solution, many of them as single crystals. The crystals ignited when brought into contact with air. Yield: 1.51 g (93%), m.p. 113–115°C. – NMR ([D$_8$] toluene) at 25°C, 270 MHz: $\delta(^1H) = 0.06$, 0.10, 0.22, 0.25, 0.26, 0.27, 0.29, 0.31 (SiMe$_3$); $\delta(^7Li) = 1.92$, 1.76, 1.59 (ratio 1:2:1); (67.94 MHz): $\delta(^{13}C) = -1.31$, 0.29, 1.09, 1.23, 1.20, 1.26, 4.08 (br.) (SiMe$_3$ groups); $\delta(^{29}Si) = 4.16$, -7.67; at 107° C: $\delta(^1H) = 0.22$; $\delta(^7Li) = 1.96$, 1.74 (ratio 3:1); $\delta(^{13}C) = -6.04$.

X-ray Structure Determination of $(\mathbf{2})_4$: Formula $C_6H_{18}Li_2N_2Si_2$; $M_r = 188.28$; colorless cube with dimensions $0.2 \times 0.2 \times 0.4$ mm; $a = 9.965(2)$, $b = 10.110(3)$, $c = 12.625(3)$ Å; $\alpha = 68.27(2)$, $\beta = 84.55(2)$, $\gamma = 73.50(2)°$; $V = 1132.8(5)$ Å^3; triclinic; space groups $P\bar{1}$; $Z = 8$ (two tetrameric units); $d_{calcd.} = 1.104$ Mg/m^3; $\mu = 0.263$ mm^{-1}; $F(000) = 408$. – Data collection: $T = 183$ K; scan range 1.7°; scan speed 4–60°/min; $2\Theta = 3.5-55°$ in $-1 < h < 12$, $-11 < k < 12$, $-16 < l < 16$; 5211 reflections collected; 5016 unique reflections with $F > 4\sigma(F)$; $R_{int.} = 0.050$. – Structure solution and refinement: Direct methods; nonhydrogen atoms refined anisotropically, hydrogen positions found in difference Fourier map; positions of all atoms refined freely, H atoms with fixed, adapted U_i parameters; $R = 0.0485$; $R = 0.0786$ for all data; $wR2 = 0.1123$ (on F^2); $GOOF = 0.985$; largest diff. peak = 0.390 e/Å^3.

[Lithium N,N-Bis(trimethylsilyl)hydrazide]–[Dilithium N,N'-Bis(trimethylsilyl)hydrazide] (**3**): To a boiling solution of a mixture of bis(trimethylsilyl)hydrazine isomers (1.63 g, 9.24 mmol) in 40 ml of hexane was added slowly and with stirring a solution of BuLi (5.9 ml, 1.56 M, 9.20 mmol) in hexane. After 2 h, the solution was allowed to cool to ambient temperature. Colorless, well-shaped crystals separated within a day. Yield: 1.09 g (96%) of **3**, m.p. 107–109°C (decomp.). – NMR ([D$_8$] toluene): $\delta(^1H) = 0.06$, 0.10, 0.22, 0.25, 0.26, 0.27, 0.29, 0.31 (SiMe$_3$); $\delta(^7Li) = 1.74$, 1.57 (ratio 2:1); $\delta(^{13}C) = -1.31$, 0.30, 2.09, 1.22, 1.25, 1.27, 1.30, 2.00, 3.12, 3.68, 4.02, 4.16 (SiMe$_3$); $\delta(^{29}Si) = -8.20$, -7.67, -0.38, 0.06, 3.58, 4.16, 5.27, 5.56.

X-ray Structure Determination of $(\mathbf{3})_2$: Formula $C_{12}H_{37}Li_3N_4Si_4$; $M_r = 370.64$; colorless cube-shaped crystals of dimensions $0.4 \times 0.5 \times 0.6$ mm; $a = 9.903(2)$, $b = 11.465(3)$, $c = 11.912(2)$ Å; $\alpha = 76.36(1)$, $\beta = 67.28(1)$, $\gamma = 74.86(1)°$, $V = 1190.3(4)$ Å^3; triclinic; space group $P\bar{1}$ (No. 2 of Intern. Tables); $Z = 2$; $d_{calcd.} = 1.034$ Mg/m^3; $\mu = 0.25$ mm^{-1}; $F(000) = 404$. – Data collection: $T = 183$ K; $2\Theta = 3.7-57.5°$ in $1 < h < 11$, $-14 < k < 14$, $-14, < l < 15$; ω scans; scan range 1.2°; scan speed 1–60°/min; 5975 reflections collected; 5138 observed reflections with $I > 4\sigma(I)$; $R_{int.} = 0.0637$. – Structure solution and refinement: Direct methods; full-matrix least-squares refinement, nonhydrogen atoms refined with anisotropic temperature factors, hydrogen atoms refined freely with fixed isotropic U parameters; 5138 data $[F > 4\sigma(F)]$; $R = 0.0428$; $wR2 = 0.1081$ (on F^2); $GOOF = 1.035$ on F^2; largest diff. peak = 0.518 eÅ^{-3}.

Dilithium N-Phenyl-N'-trimethylsilylhydrazide $(\mathbf{4})_4$: A hexane solution of BuLi (9.25 ml, 1.56 M, 14.4 mmol) was added dropwise to a vigorously stirred solution of Ph(H)N–N(H)SiMe$_3$ (1.30 g, 7.2 mmol) in 40 ml of hexane. The solution turned orange as the reaction proceeded and a yellow solid of $(\mathbf{4})_4$ settled. The solid was removed by filtration and deep orange to red single crystals formed in the filtrate at ambient temperature within a week. Yield: 1.23 g (89%), m.p. 109–112 cm^{-1}. – NMR (C_6D_6) at 25°C: $\delta(^1H) = -0.16$, 0.13 (ratio 1:2), 0.38 (9 H for the 3 signals; ratio ca. 1:2:6), 5.40–7.38 (5 H, Ph); $\delta(^7Li) = -7.63$ (2 Li, complexed by Ph groups), -0.03 (2 Li; Li2, Li4), 1.31 (4 Li; Li1, Li3, Li5, Li6); $\delta(^{13}C) = -1.10$, 2.06, 2.20, 2.36 (SiMe$_3$), 161.8 (NC), 129.7 (br.), 112.9, 109.0 (both br.), 100.8 (*p*-C); $\delta(^{29}Si) = -7.95$, 8.13, two additional weak signals at $\delta = -6.59$ and 12.16.

X-ray Structure Determination of $(\mathbf{4})_4$: Formula $C_{18}H_{28}Li_4N_4Si_2$; $M_r = 384.4$; red single crystal; size $0.4 \times 0.5 \times 0.5$ mm; monoclinic; $a = 11.576(2)$, $b = 13.217(2)$, $c = 15.252(4)$ Å; $\beta = 103.46(2)°$; $V = 2267.7(8)$ Å^3; space group $P2_1$, $d_{calcd.} = 1.126$ Mg/m^3; $\mu = 0.164$ mm^{-1}; $F(000) = 816$. – Data collection: $T = 200$ K; $2\Theta = 3.6-41.7°$ in h, $\pm k$, $\pm l$, ω-scans; scan range 1.2°; scan speed 3–30°/min; 6678 reflections collected; 6347 independent and 5635 observed reflections with $I > 4\sigma(I)$. – Structure solution and refinement: Direct methods; full-matrix least-squares refinement; nonhydrogen atoms anisotropically refined; H atoms in calculated position and refined with riding model and fixed, adapted U_i; $R = 0.0337$; $R1 = 0.0474$ (all data); $wR2 = 0.0770$; $GOOF = 1.031$ on F^2; largest diff. peak/hole = 0.15/–0.21 eÅ^3.

☆ Dedicated to Professor *Ernst Biekert* on the occasion of his 70th birthday.

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