Structural Chemistry of Alkali Metal Phenylhydrazides☆

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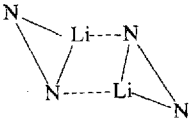
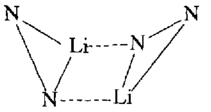
The crystal and molecular structures of a series of *N*-phenyl-substituted lithium hydrazides were determined in order to investigate possible Li···Ph π interactions. These are pronounced when there are no donor molecules present to solvate the Li centers. An η^6-Li···Ph interaction is particularly distinct in tetrameric $(Me_3Si)_2N-N(Ph)Li$ but also in trimeric $Ph_2N-N(SiMe_3)Li$. Deprotonation of *N*,*N'*-diphenylhydrazine with butyllithium in ether resulted in the formation of $Ph(Li)N-N(Ph)Li \cdot 2\ LiNPh_2 \cdot 2\ OEt_2$ with phenyl group migration and N–N bond cleavage by a redox process. An increase of the size of the cations, as shown for $Ph(Me_3Si)N-N(Ph)Na \cdot NH_3$ and the caesium salt $(Me_3Si)_2N-N(Ph)Cs \cdot n$THF, results in increased coordination of the metal ion to the phenyl group. The caesium compound forms a three-dimensional network. Channels along the *c* axis are partially filled with THF molecules.

The structural chemistry of lithium diorganylamides $LiNR_2$ is well-developed[1]. More recently many structures of *N*-functionalized lithium amides[2] have been determined. These deviate to some extent from those of the amides MNR_2 due to the donor properties of the functional group. Amongst these compounds are the alkali metal hydrazides, particularly those of lithium[3]. Here new structural patterns emerged which are characterized by three-membered arrays of the unit LiN_2 which are differently arranged in the oligomeric compounds. So far the most simple way how the dicoordinated lithium atom of the LiN_2 unit attains coordination saturation is by dimerization and formation of a four-membered Li_2N_2 ring as shown by formulae **A** and **B**. *N*,*N'*-Dilithium hydrazides, on the other hand, show the topological pattern depicted in formula **C**. This unit is butterfly-shaped and associates to dimers, trimers, and tetramers[3].



A



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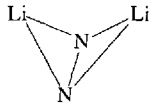
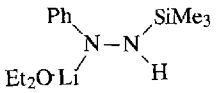


C

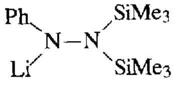
The most unusual structure observed so far is the tetrameric $Ph(Li)N-N(Li)SiMe_3$: It consists of a $Li_6N_8^{2-}$ cluster, and two Li^+ ions are sandwiched between pairs of phenyl groups, each in an η^6 manner[3e]. This requires that four phenyl groups are arranged in two parallel oriented pairs which π-complex these two Li ions. This unexpected behavior required a sytematic study of the preparation and structure of alkali metal phenylhydrazides and those of lithium in particular.

Preparation of Metal Phenylhydrazides

The alkali metal phenylhydrazides were prepared by conventional routes: a) by deprotonation of a phenylhydrazine with butyllithium in hexane or pentane, b) by reaction of a phenylhydrazine with $NaNH_2$ in refluxing toluene, c) by allowing a metal to react with a phenylhydrazine in the presence of tetrahydrofuran (THF). By one of these methods the phenylhydrazides **1** to **7** were obtained.



1



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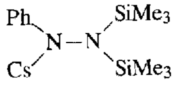

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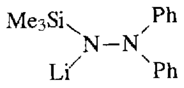

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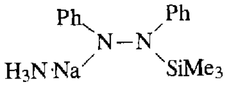

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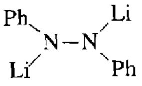

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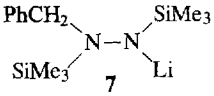
$Ph(Li)N-N(Li)Ph \cdot 2\ LiNPh_2 \cdot 2\ OEt_2$

6a



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Since it is well-known that silyl group migration[4] may happen during the preparation of a specific lithium (trimethylsilyl)hydrazide no prediction can be made which of the possible isomers will result. To give two examples: $LiN_2(SiMe_3)_2Ph$ can exist as two isomers **8** and **9** in the form of

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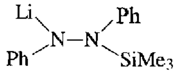
monomeric units, while monomeric $LiHN_2Ph(SiMe_3)$ can provide three monomeric isomers (**10**−**12**).



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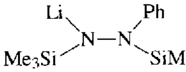

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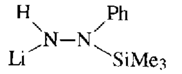

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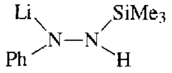

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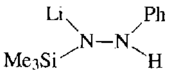

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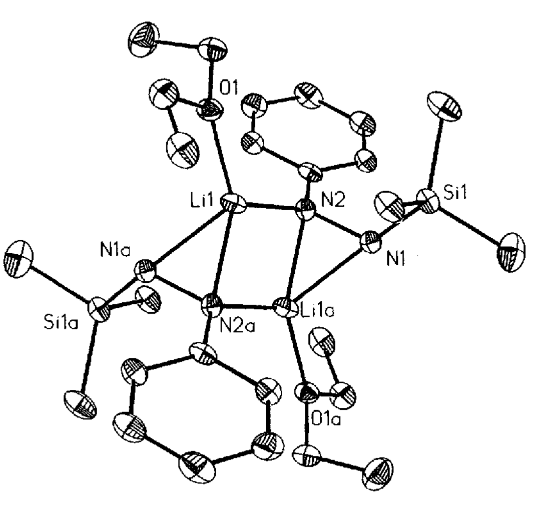
Conceivably, the number of possible isomers increases rapidly with oligomerization of these monomers.

Crystal and Molecular Structures

The structure of lithium phenylhydrazides in solution is often difficult to be reliably interpreted on the basis of NMR data. However, ^{7}Li-NMR data furnished evidence for the coordination sphere at the Li atom and are, therefore, helpful to suggest possible structural environments (v.i.). Helpful in this respect is the direct information on the structure of the compounds under consideration, e.g. in the solid state. Therefore, their molecular structures in the solid state had to be determined by X-ray crystallography.

The hydrazide $Ph(Li)N-N(SiMe_3)H$ could not be properly crystallized solvent-free in contrast to the ether adduct **1**. The yellow-colored crystals of **1** belong to the triclinic system, space group $P\bar{1}$. There are four molecules in the unit cell as *two* independent dimers, each possessing a crystallographic center of inversion. Figure 1 represents one of the two dimeric molecules[5].

Figure 1. ORTEP representation of dimeric $[Me_3Si(H)N-N(LiOEt_2)Ph]_2$ (**1**). Only one of the two independent molecules is shown. Data for the second molecules are deposited[15]. Thermal ellipsoids correspond to 25% probability. Selected bond lengths and atom distances [Å] (standard deviations in parentheses): N1−N2 1.469(5), N1−Si1 1.749(4), N1−Li1a 2.091(8), N2−Li1 1.98(1), N2−Li1a 2.02(8), N2−C4 1.374(6), Li1−O1 1.977(9), Li1−Li1a 2.45(2). − Bond angles [°]: Si1−N1−N2 118.6(3), Si1−N1−Li1a 134.1(3), N2a−Li1−N1a 41.8(2), N1−N2−C4 113.5(4), N1−N2−Li1 115.6(4), C4−N2−Li1 127.4(4), C4−N2−Li1a 139.1(4), N1−N2−Li1a 71.7(3), Li1−N2−Li1a 75.4(4), N2a−Li1−Li1a 51.6(3), N2−Li1−N1a 123.1(4); N2−Li1−N2a 104.6(4), N2−Li1−O1 122.1(4), O1−Li1−N2a 131.7(5), O1−Li1−N1a 109.5(5)



Each Li atom of compound **1** is tetracoordinated by an oxygen atom and three nitrogen atoms with Li−N distances ranging from 1.98(1) to 2.091(8) Å. However, the coordination sphere at the Li atom deviates strongly from a tetrahedron due to the acute N1a−Li1−N2a bond angle of 41.8(2)°, and the "open" O1−Li1−N2 bond angle of 122.1(4)° adds to this. If one takes the plane made of atoms O1, N2 and the midpoint of the N1−N2 bond, then the Li1 atom lies almost in the center of a trigonal plane. This pattern shows the typical "side-on" coordination of the Li atom to the dinitrogen unit of the hydrazide.

The Li−O atom distances [1.977(9), 1.952(9) Å] for O1 and O2 seem to be slightly smaller than the Li−N distances. Both oxygen atoms reside in an almost planar surrounding because the sum of bond angles subtending at these atoms is 357.5° for O1 and 356.1° for O2. A twist of 22.7° is found for the C11−O1−C12 plane against the four-membered Li_2N_2 plane. In addition, there is one Li···H distance of 2.75 Å to Li1, and there are two similar ones (2.78 and 2.68 Å) to Li2. More notable are the short N−C bond lengths. These are similar to those found in benzamides[6]. It should also be noted that the phenyl group is only slightly twisted out of the N2, N1, Li1 plane (21.9°) while the interplanar angle PhN1N2/N2N1Si1 is 93.3°. However, the analogous twisting is only 44.7° in the second independent molecule of **1** in the solid state.

The compound $(Me_3Si)_2N-NPhLi$ (**2**) is dark green and crystallizes in the orthorhombic system, space group *Pbca*, with 16 molecules in the unit cell. These are arranged in four tetrameric units $\mathbf{2}_4$, and one tetrameric molecule is shown in Figure 2. The most remarkable feature is that each Li atom of the two independent Li atoms (Li1, Li2) is coordinated to a phenyl ring of an adjacent monomeric unit in an η^6 manner. The Li···C atom distances vary from 2.31(1) to 2.60(1) Å. Most of them are, however, in the closer range of 2.31 to 2.45 Å. Since each Li atom is coordinated to an N atom, the Li centers can be considered as being essential heptacoordinated.

The two independent Li−N distances are 1.883(9) and 1.881(9) Å and can be considered as being comparatively short[1]. On the other hand, the N−N bond lengths [1.493(5), 1.486(5) Å] represent long N−N single bonds. All nitrogen atoms reside in an essentially planar environment with Si−N−Si bond angles of 130.7(2)° at N4 and 132.1(2)° at N1. The Li−N−C bond angles are even wider with 138.3(4)° at N1 and 138.7(4)° at N4. Fairly short N−C bonds [1.346(5) Å at N1 and 1.349(5) Å at N3][6] are also typical of this molecule. Another feature worthy of note are the interplanar angles $LiN_2C/SiNSi$ (87.6 and 92.3°) as well as the interplanar angle between the N_2Li plane and the phenyl group, e.g. 4.9° for Li2N3N4. There are no short intramolecular Li···H contacts, and, surprisingly, there exists no side-on coordination of the Li centers to the N_2 units of molecule $\mathbf{2}_4$ as observed for $[LiN(SiMe_3)-N(SiMe_3)_2]_2$[3c].

Surely, the tetrameric structure of **2** is unexpected, and even more complex structures can be envisaged for the heavier alkali metal salts, particularly for the caesium salt

Figure 2. ORTEP representation of the molecular structure of the tetrameric unit of (Me$_3$Si$_2$N−N(Ph)Li (**2**) (hydrogen atoms omitted). Thermal ellipsoids are drawn on a 25% probability scale. Selected bond lengths [Å] and bond angles [°] with estimated standard deviations in parentheses. Bond lengths: N1−N2 1.493(5), N1−C7 1.346(5), N1−Li 1.883(9), N2−Si1 1.736(4), N2−Si2 1.733(4), Li−C30a 2.31(1), Li1−C29a 2.31(1), Li1−C31a 2.369(9), Li1−C32a 2.455(9), Li1−C28a 2.41(1), Li1−C27a 2.557(9), N3−N4 1.486(5), N3−C27 1.349(6), N3−Li2 1.877(9), N4−Si3 1.731(4), N4−Si4 1.738(4), Li2−C9 2.32(1), Li2−C10 2.35(1), Li2−C8 2.418(9), Li2−C11 2.430(9), Li2−C7 2.604(9), Li2−C12 2.537(9). − Bond angles: N2−N1−Li1 107.6(4), N2−N1−C7 113.7(3), Li1−N1−C7 138.3(4), N1−N2−Si1 118.5(3), Si1−N2−Si2 132.1(2), N1−N2−Si2 108.4(3), N1−Li1−C39a 141.3(5), N1−Li1−C9a 126.6(4), N1−Li1−C31a 160.0(5), N1−Li1−C28a 128.0(4), N1−Li1−C32a 157.4(5), N4−N3−Li2 108.2(4), C27−N3−Li 138.7(4), C27−N3−N4 113.0(3), N3−N4−Si3 109.0(3), N3−N4−Si4 118.5(3), Si3−N4−Si4 130.7(2), N3−Li2−C9 126.7(5), N3−Li2−C10 141.1(5), N3−Li2−C8 126.3(4), N3−Li2−C11 162.3(5), N3−Li2−C7 139.5(4), N3−Li2−C12 159.7(5)

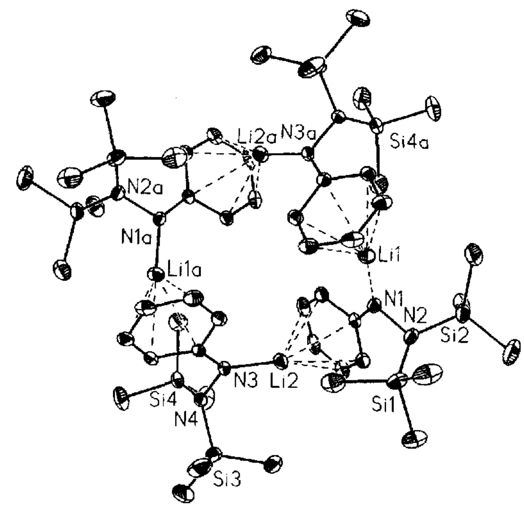
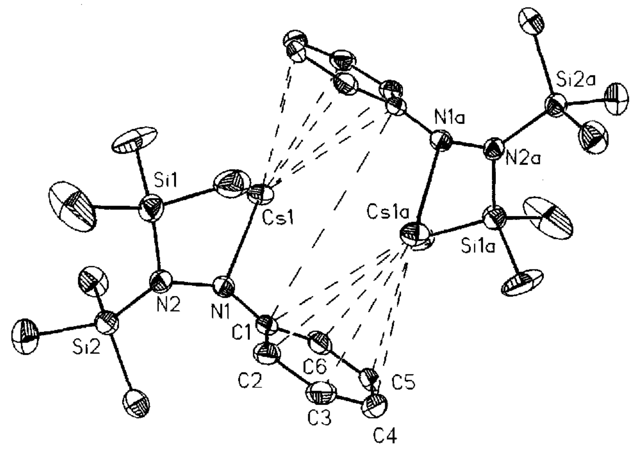


Figure 3. The molecular unit of (Me$_3$Si)$_2$N−N(Ph)Cs (**3**). Thermal ellipsoids are represented at a 25% probability level. Selected bond lengths or atom distances [Å] and bond angles [°] with estimated standard deviations in parenthesis. N1−N2 1.501(8), Cs1−N1 2.991(6), N1−C1 1.351(9), N2−Si1 1.735(7), N2−Si2 1.724(6), Cs1···C1a, Cs1···C2a 3.621(7), Cs1···C3a 3.396(8), Cs1···C4a 3.403(9), Cs1···C5a 3.590(8), Cs1···C6a, Cs1···C1b 3.775(7), Cs1···C2b 3.748(8), Cs1···C3b 3.615(8), Cs1···C4b 3.523(9), Cs1···C5b 3.541(8), Cs1···C6b 3.666(8). − Bond angles: N1−N2−Si1 114.5(4), N1−N2−Si2 105.4(4), Si1−N2−Si2 129.7(4), Cs1−N1−C1 122.4(4), C1−N1−N2 111.8(5)



due to the larger effective radius of the caesium ion. The caesium salt **3** contains non-coordinated THF molecules. Compound **3** crystallizes in orange prisms which belong to the rhombohedral system, space group $R\bar{3}$ with $Z=18$. The molecular structure in the asymmetric unit is depicted in Figure 3.

It can be noted that there is only a single Cs···N interaction in the "monomeric" unit with a distance of 2.991(6) Å. Thus, the nitrogen atom N2 is not involved in coordination to Cs. The sum of bond angles at atom N2 is 349.6° corresponding to a flat pyramid. However, four hydrogen atoms are in proximity to the Cs atom, thus increasing the steric shielding of the Cs center. The N1−N2 bond length is rather long with 1.501(8) Å, and the N−C bond to the phenyl group is short with 1.351(9) Å[6]. It is also immediately evident from Figure 3 that the Cs center is coordinatively unsaturated. A more realistic pattern of the coordination sphere around Cs in the crystal is shown in Figure 4. It reveals that the Cs atom in addition to its coordination to the N1 atom and to three hydrogen atoms has contacts to two phenyl rings of two additional (Me$_3$Si)$_2$N−N(Ph)Cs molecules. These contacts are of an unsymmetrical η^6 type. Therefore, each phenyl group is coordinated to two symmetry equivalent Cs centers, and this *subunit* forms a slightly distorted hexagonal bipyramid with two Cs atoms as apex atoms. Therefore, each Cs center has altogether 16 atoms as neighbors (12 C, 1 N, 3 H atoms).

A stereoscopic view of the unit cell on the [001] plane is depicted in Figure 5. It shows channels along the *c* axis, which contain THF molecules. Refinement of the site occupation factors for these THF molecules reveals the presence of approximately 4 THF molecules in the unit cell of the sample under investigation. THF solvent is readily lost, and the clear orange crystals separating from THF solutions become rapidly turbid in vacuo.

Compound Ph$_2$N−N(SiMe$_3$)Li (**4**) forms bright orange crystals of the monoclinic system, space group $P2_1/c$. Figure 6 depicts the molecular structure of this molecule. There are four trimeric molecules **4**$_3$ in the unit cell.

Inspection of Figure 6 demonstrates that the three Li centers are in different environments: atom Li1 is tetracoordinated, and atoms Li3 and Li5 are pentacoordinated. The N−N bond lengths in **4**$_3$ are significantly different as shown by the atom distances 1.454(5), 1.474(5), and 1.441(5) Å. This, of course, reflects the different coordination of the Li centers which are unusual in the sense that some of these correspond to a side-on-coordinated LiN$_2$ unit. Moreover, there are different contacts of the Li centers to the C atoms of the phenyl rings: namely contacts of Li1 to *two* carbon atoms of two *different* phenyl groups. Atom Li3 interacts with *two* C atoms of one phenyl group and *one* C atom of a different phenyl group, and the same coordination is found for atom Li5.

The N atoms of the three Ph$_2$N units are in planar environment. The N−N−Si bond angles [114.4(3), 106.9(2), 107.1(2)°] lead to the conclusion that these N atoms can be considered as sp^3-hybridized. N−Li−N bond angles for Li1

Figure 4. Association of three molecules of the caesium hydrazide 3 demonstrating two phenyl groups η^6-π-bonded to a Cs ion

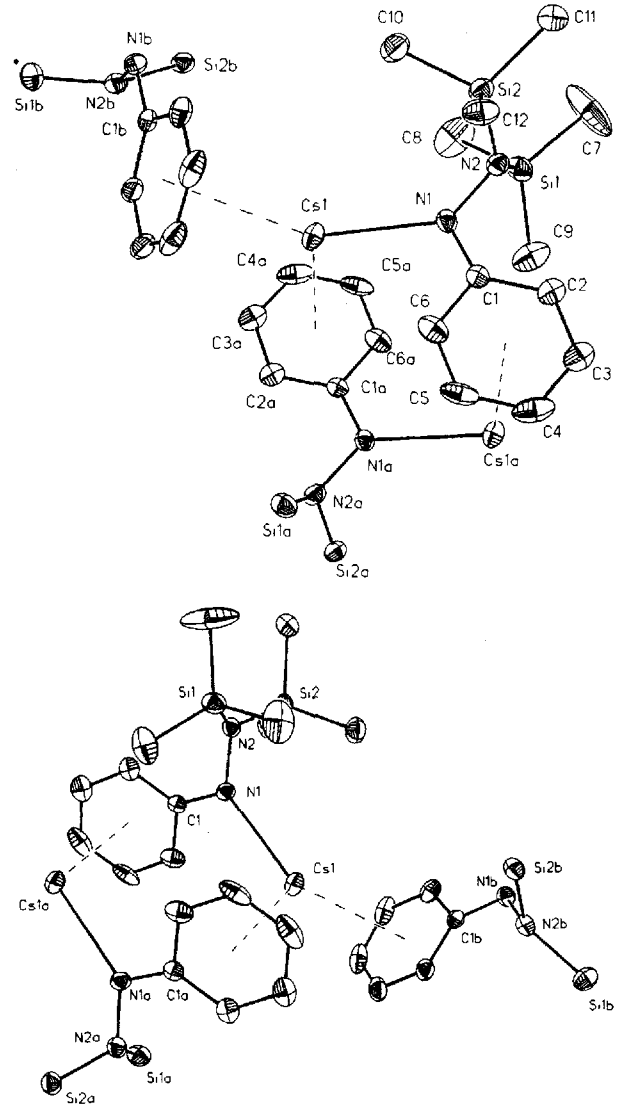
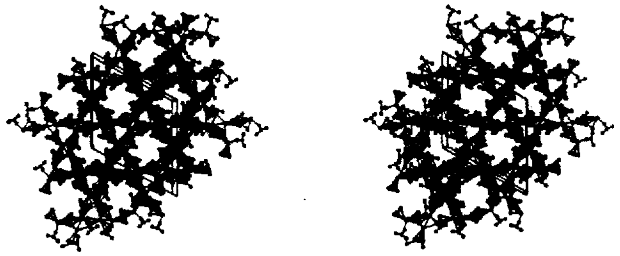
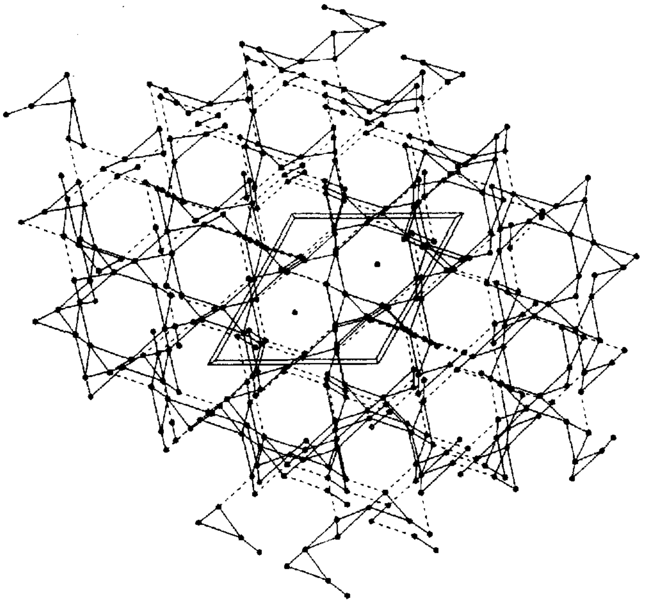


Figure 5. Stereoview on the [001] face of the unit cell to show the channels running along the *c* axis. These are partially filled with THF molecules



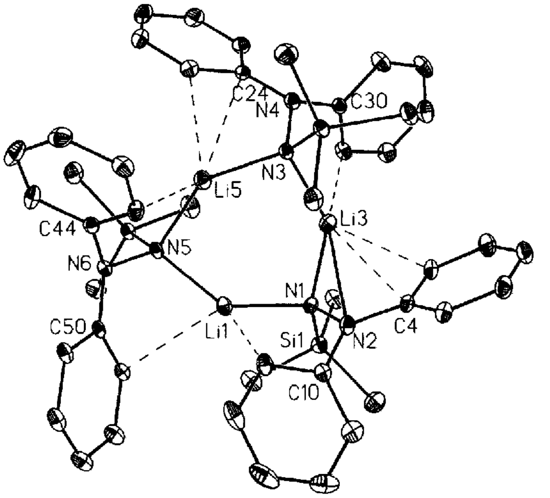


[139.1(5)°], for Li3 [138.7(4)°] and for Li5 [143.9(5)°] are significantly different although the Li−N bond lengths remain comparable, and the same holds for Li−N−Li bond angles [139.1(5) at N1, 138.7(4)° at N3, and 143.0(5)° at N5]. The six-membered ring of $\mathbf{4}_3$ can be regarded as having a chair conformation. On the other hand, the C−N bond lengths to the phenyl groups are short [1.384(6) to 1.441(6) Å] and similar to those of the other phenylhydrazides. This is also reflected by larger differences of the Li−N atom distances in this compound. The Li···C interaction is primarily determined by the orientation of the phenyl rings to one another (ranging from 43.4 to 116.1° for adjacent phenyl groups).

Figure 7 depicts the molecular structure of compound $Ph(Me_3Si)N{-}N(Ph)Na \cdot NH_3$ (**5**). The colorless crystals are monoclinic, space group $P2_1/c$ with $Z=4$. Two molecules each are associated to a dimeric unit $\mathbf{5}_2$ whereby a central four-membered Na_2N_2 ring is formed. The point group symmetry of this dimeric unit is C_2 due to a crystallographic twofold axis passing through the center of this ring. Each N_2 unit coordinates side-on to a Na center with atom distances Na−N = 2.386(2) and 2.421(2) Å. In addition, each Na atom binds an ammonia molecule with an Na1−N2 bond length of 2.354(2) Å. Each Na atom has also contacts to three carbon atoms of the phenyl group. Due to the different orientation of the phenyl rings there is only one contact to the phenyl group at N2 with a "short" atom distance of Na1−C25 = 3.043(3) Å, while there are two contacts to the other phenyl group with distances of 3.036(8) and 3.115(3) Å, respectively. Finally, a hydrogen atom of the methyl group at C1 is only 3.04 Å apart from Na1, raising the coordination number at the sodium atom to eight.

The nitrogen atoms in compound $\mathbf{5}_2$ are tetracoordinated. If one neglects the Na1a−N1 contact, then the geometry at N1 is strictly planar. This would correspond with sp^2 hybridization at N1. It is, however, more difficult to estimate the hybridization at atom N2. The sum of bond angles (C25−N2−N1, Na1−N2−N1, C25−N2−Na1) is 340.6°, corresponding to a pyramidal coordination at N2. On the other hand, the C25−N2−N1 bond angle (113.0°)

Figure 6. ORTEP representation of the trimeric unit of molecule $\mathrm{Ph_2N{-}N(SiMe_3)Li}$ (**4**) in the crystal (hydrogen atoms omitted). Selected bond lengths [Å] and bond angles [°], standard deviations in parenthesis. Bond lengths and atom distances: N1−N2 1.454(5), N3−N4 1.474(5), N5−N6 1.491(5), N1−Si1 1.745(4), N3−Si2 1.745(4), N5−Si3 1.736(4), N1−Li3 1.979(9), N1−Li1 1.985(8), N2−Li3 2.411(9), N3−Li3 1.988(9), N3−Li5 1.987(8), N5−Li1 2.001(9), N5−Li5 2.004(9), Li1···Li5 2.95(1), Li1···Li3 2.02(1), Li3···Li5 2.99(1), N2−C10 1.415(6), N6−C50 1.402(5), N6−C44 1.435(5), N4−C24 1.384(5), N2−C4 1.96(5). Atom distances: Li1···C15 2.765(9), Li3···C4 2.606(9), Li5···C49 2.652(9), Li1···C51 2.716(9), Li3···C5 2.563(9), Li3···C35 2.629(9), Li5···C25 2.51(1), Li5···C24 2.780(9). − Bond angles: Si−N1−N2 114.4(3), Si1−N1−Li1 103.3°, Si1−N1−Li3 135.8(3), N2−N1−Li1 116.0(3), N2−N1−Li3 87.8(3), N4−N3−Si2 106.9(2), N4−N3−Li3 111.0(3), N4−N3−Li5 103.4(3), Si2−N3−Li5 128.3(3), Si−N3−Li3 108.8(3), N6−N6−Li1 119(3), N6−N5−Li5 111.4(3), N6−N5−Si3 107.1(2), Si3−N5−Li1 120.8(3), Li1−N5−Li5 94.8(3)



is close to the C11−N1−N2 bond angle (115.7°), and this would also be a good guess for suggesting an sp^2-type N2 atom. This is further corroborated because the two phenyl groups (C11 to C16, C21 to C26) are almost orthogonal to one another, allowing optimal repulsion of the lone pairs of electrons at the N atoms.

The N−N bond length [1.458(2) Å] is rather similar to the molecules described previously, and this is also true for the fairly short C−N bond lengths [1.376(3), 1.399(3) Å]. The latter bond lengths indicate that the nitrogen atoms have to be considered as being sp^2-hybridized.

Deprotonation of *N,N'*-diphenylhydrazine with butyllithium in ether provided orange-colored prisms crystallizing in the monoclinic systems in space group *C*2/*c*. They turned out not to be Ph(Li)N−N(Li)Ph (**6**) but to be Ph(Li)N−N(Li)Ph · 2 $\mathrm{LiNPh_2}$ · 4 $\mathrm{OEt_2}$ (**6a**) as revealed by X-ray structure analysis. Figure 8 represents the molecular unit. There is a crystallographic center of inversion at the midpoint of the N−N bond of the *N,N'*-diphenylhydrazide unit which proved to be disordered. The description of the structure will ignore this situation at the moment and will be focussed to one orientation only.

Atom Li1 is tricoordinated by O1, N1, and N2. The Li1−X atom distances are 1.930(6) to O1, 2.009(8) Å to N1, and 2.026(6) Å to atom N2. In contrast to atom Li1,

Figure 7. ORTEP representation of the molecular structure of $\mathrm{[Ph(Me_3Si)N{-}N(Ph)Na \cdot NH_3]_2}$ (**5**$_2$). Thermal ellipsoids represent a 25% probability. Selected bond lengths [Å] and bond angles [°]. Bond lengths: N1−N2 1.458(2), N1−Si1 1.759(2), N1−C11 1.399(3), N2−C25 1.376(3), Na1−N3 2.354(2), Na1−N2 2.421(2), Na1−Na2 2.386(2), Na1−N1a 2.840(2), Na1−C11a 3.036(2), Na1−C16a 3.115(3), Na1−C25 3.043(3), Na1−H1A 3.036(2). − Bond angles: Si1−N1−C11 125.4(1), Si1−N1−N2 118.8(1), C11−N1−N2 115.7(2), Si1−N2−Na1A 127.75(9), C11−N1−Na1 84.2(1), C25−N2−N1 113.0(2), Na1−N2−N1 124.6(1), Na1A−N2−N1 92.1(1), C25−N2−Na1 103.0(1), C15−N2−Na1A 143.7(2), N3−Na1−N2 125.79(8), N3−Na1−C25 99.82(8), N3−Na1−C16A 75.43(8), N3−Na1−C11A 76.33(8), N3−Na1−N2A 127.56(8), N2−Na1−N2A 98.74(7), Na1−N2−Na1A 92.1(1)

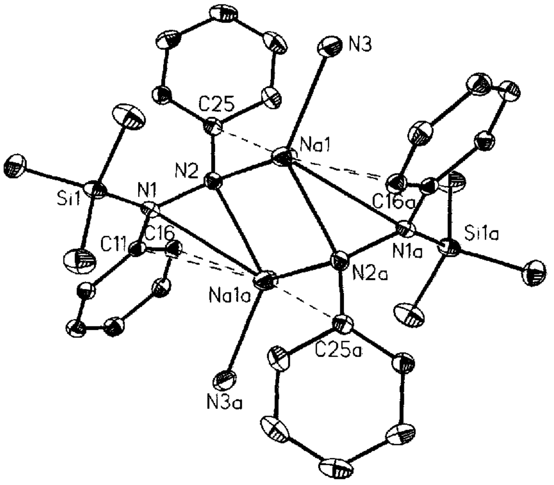
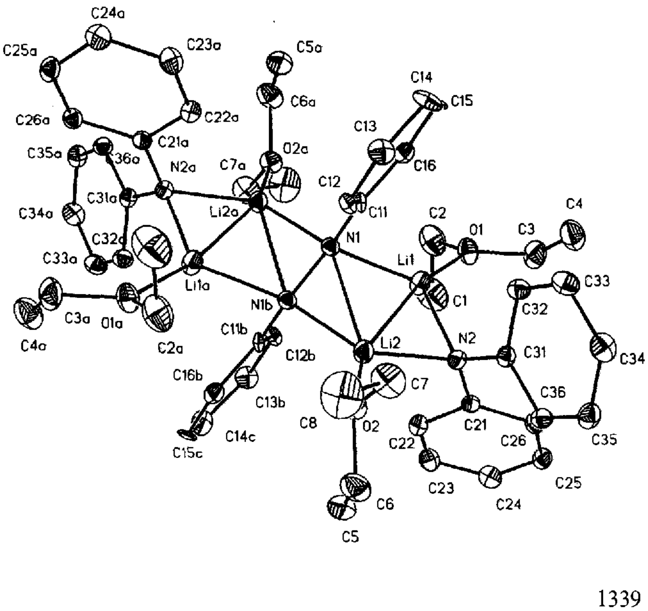


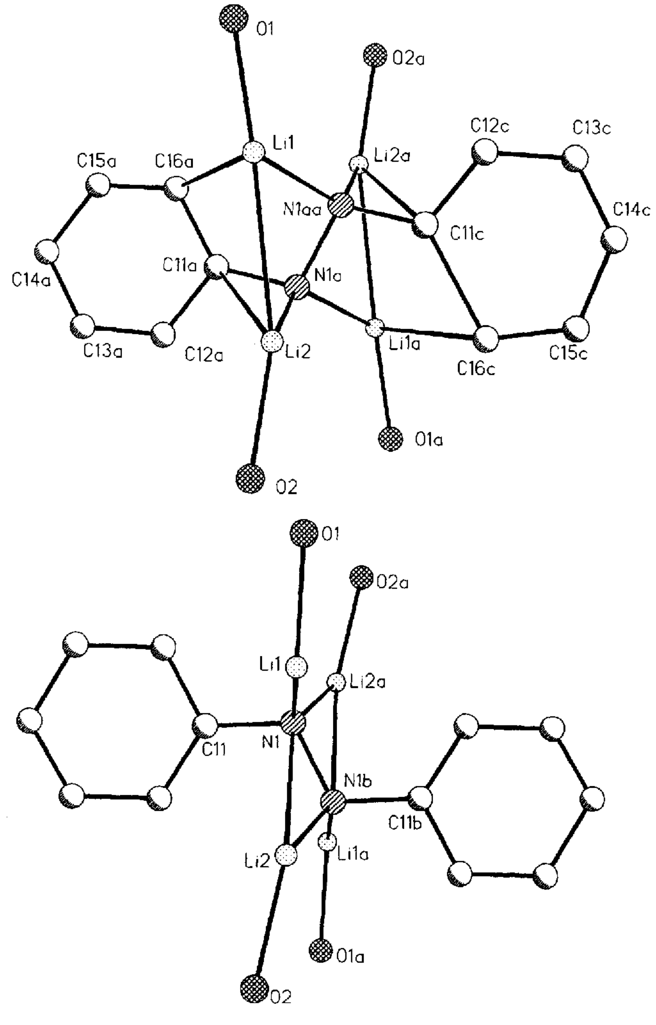
Figure 8. Molecular structure of $\mathrm{[Ph_2NLi \cdot Ph(Li)N{-}N(Li)Ph \cdot LiNPh_2 \cdot LiNPh_2]\ 4\ OEt_2}$ (**6a**) in the crystal. Thermal ellipsoids are drawn with 25% probability. Selected bond lengths and atom distances [Å]: N1−N1b 145(1), Li1−O1 1.930(6), Li1−N1 2.003(8), Li1−N2 2.026(6), Li2−N2 2.063(6), Li2−O2 1.964(6), N1−C11 1.398(8), Li2···N1 2.693(9), Li2−N1b 1.998(8), Li···Li2 2.781(8), Li2···N1 2.693(9), Li1···C11 2.440(9), Li2···C11b 2.62(1). Bond angles [°]: Li1−N2−Li2 85.7(2), C21−N2−C31 118.0(3), N1−Li1−N2 113.9(3), N1−Li1−O1 124.2(4), N2−Li1−O1 121.9(3), N2−Li2−N1 89.4(3), N2−Li2−N1b 114.4(3), N1−Li2−N1b 68.2(3), Li1−N1−Li2a 131.6(3), C11−N1−N1b 114.7(12), C11b−N1b−Li1a 117.3(6)



the atom Li2 is pentacoordinated. Neglecting the Li1···Li2 atom interaction, we have to consider four atoms to be close to Li2, namely O2 [1.964(6) Å], N1 [2.693(6) Å], N1B [2.095(8) Å], and N2 [2.063(8) Å]. Two more atoms, C11A and C31 [2.618(6), 2.674(6) Å] also add to the steric shielding of atom Li2, as well as two hydrogen atoms (H5b 2.63, H12a, 2.43 Å).

The Li2···N1 distance is similar to the Li1···N2 distance. Both are shorter than the Li1···Li2 distance, being a consequence of the smaller effective radius of N which is much smaller than that of Li. Consequently, the effective primary coordination at atom Li2 is three. The disorder at the central disphenylhydrazide unit leads to two different interactions with the Li atoms as shown in Figure 9. Figure 9 (top) reveals the double side-on coordination. Figure 9 (bottom) shows only a single interaction between the hydrazide unit and the Li atoms.

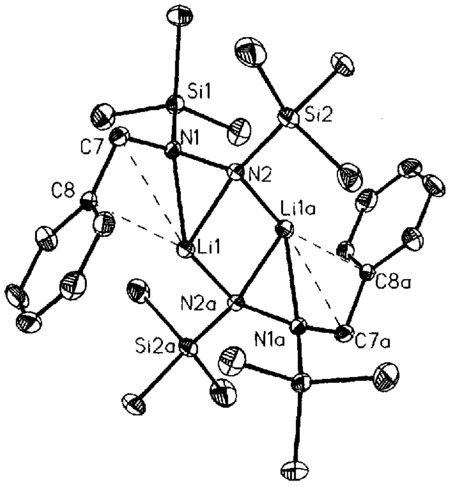
Figure 9. The two orientations of the disordered Ph(Li)N–N(Li)Ph group in compound **6a**



In compound **6a** two $Et_2O \cdot LiNPh_2$ molecules are added to the $Li_2N_2Ph_2 \cdot 2\ OEt_2$ unit. Thus, the coordination of all Li atoms is raised by one unit by an additional LiN contact. The generated additional LiN moieties are asymmetric with respect to the other Li1–N bond length, resulting in a Li2–N1 atom distance of 2.693(6) Å. In spite of these structural features we note almost equal N–C bond lengths to the phenyl rings. These are 1.398(8) Å for the central PhN–NPh unit and 1.404(4) Å for the Ph_2N group. These bond lengths are not significantly different in spite of the fact that the N atom of the Ph_2N part would be compatible with a distorted tetrahedral environment. However, the N–Li distance of Li1 to N2 which is 2.026(6) Å differs from the Li2–N2 distance of 2.063(8) Å. This is reflected by the bond angles Li1–N1–N2 [85.7(2)°] and C21–N2–C31 [118.0(3)°]. However, these data refer to only one orientation of the Ph–N–N–Ph unit. Figure 9 depicts the orientation of the two units to one another, and the refined site occupation factors reveal that each of the two orientations are of equal weight.

The lithium benzylhydrazide $(PhCH_2)(SiMe_3)N{-}NLi(SiMe_3)$ (**7**) crystallizes in the monoclinic system, space group $P2_1/c$ with $Z=4$. The four molecules are present as two centrosymmetric dimeric molecules $\mathbf{7}_2$. One dimeric molecule is depicted in Figure 10. As expected, the monomeric molecules are associated by Li–N bonds. This generates a four-membered Li_2N_2 ring. The crystallographic center of inversion lies in the ring center. In addition, there are two three-membered LiN_2 rings showing the side-on coordination of Li to the hydrazide unit which is so typical of lithium hydrazides.

Figure 10. Molecular structure of $(PhCH_2)(SiMe_3)N{-}NLi(SiMe_3)$ ($\mathbf{7}_2$) in the crystal. Thermal ellipsoids represent a 25% probability. Selected bond lengths and atom distances [Å]: N1–Li 2.069(5), N1–N2 1.493(3), N1–C7 1.73(4), N1–Si1 1.737(2), N2–Si2 1.711(2), N2–Li1 1.922(5), Li1–N2a 2.001(5), Li1···C8 2.527(5), Li1···C7 2.758(9). Bond angles [°]: Si1–N1–N2 119.8(2), Si1–N1–C7 117.7(2), Si1–N1–Li1 131.8(2), Li1–N1–N2 62.3(2), Si2–N2–N1 122.6(2), Si2–N2–Li1a 111.3(2), Li1–N2–Li1a 71.0(3), N1–N2–Li1a 113.7(2), N2–Li1–N2a 109.0(2), N2–Li1–N1 43.5(1), N2–Li1–C8 88.1(2), N1–C7–C8 112.9(2)



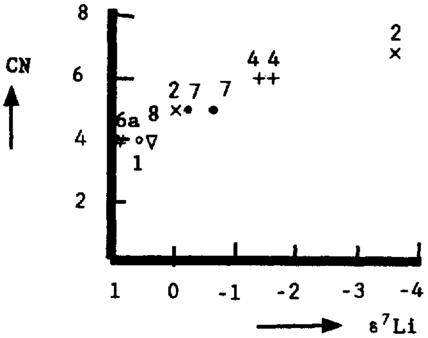
The N1–N2 bond length is 1.493(3) Å, and the Li1 atom is 2.089(5) and 1.922(5) Å apart from these atoms. Also, the Li1–N2A distance fits into this pattern with 2.001(5) Å. Thus, the Li atom is tricoordinated. In addition, there are fairly short distances to C7 and particularly C8 [2.758(9) and 2.527(5) Å, respectively].

The bond angles subtending at atom N1 – ignoring the Li1 atom – add to 360° suggesting sp^2 hybridization for N1. However, there is no way to derive the hybridization for atom N2 from bond angles. If we take the bond angles to atoms Si2, N1, and Li1 into account, the sum is 389.7°. If we include atom Li1a, then the sum of bond angles is 648.6°. This is close for a tetrahedral arrangement which is of course highly distorted. Both symmetry-related N atoms have four nearest neighbors, while the coordination number at the Li atoms is only three (to N atom). However, if we expand the coordination sphere to $(r_{Li} + r_x + 0.7)$ Å, then the Li atoms are pentacoordinated. In addition, there are two H atoms comparatively close to the Li atoms (2.58 and 2.75 Å).

NMR Spectra

As remarked previously, δ^7Li is indicative of the coordinative environment of the Li atoms. High-field ^7Li-NMR signals are compatible with high (formal) coordination numbers. In Figure 11 the coordination number of Li as determined in the solid state is plotted against the shielding values δ^7Li. The NMR data for **1** in C_6D_6 solution are compatible with its solid-state structure. There is a single ^7Li resonance and a single ^{27}Si resonance. Four ^{13}C signals for the phenyl group indicate free rotation about its C–N bond while two resonances for the methyl groups at rather high field suggest hindered rotation about the Si–N bond. This is supported by the ^1H resonance for the Me protons which are represented by three signals in the range of $\delta^1H = 0.21$ to 0.23 (intensity ratio 6:1). However, there was no change in the ^{13}C-NMR spectra recorded at a 65°C.

Figure 11. Coordination number (CN) of Li plotted against δ^7Li



When $[Ph(Li)N{-}N(SiMe_3)_2]_4$ (**2_4**) was prepared from the parent hydrazine and BuLi hexane the solution was yellow and displayed a single ^7Li resonance at $\delta = 0.3$. Within 3 days the solution turned green, and green crystals separated which showed a ^7Li-NMR signal at $\delta = -4$ typical of an η^6-aryl–Li interaction. These data indicate that in the first instance a lithium hydrazide is formed lacking aryl–Li interaction which is establishd within a few days. When the green crystals are dissolved in ether the ^7Li signal appears again at $\delta = 0.3$. On heating the yellow hexane solution of **2_4** immediately after its formation a green solution with $\delta^7Li = -4$ resulted. Therefore, the tetrameric **2** is the thermodynamic product.

Table 1. ^7Li-, ^{13}C-, and ^{27}Si-NMR data of compounds **1**, **2**, and **4–7** recorded in C_6D_6 solution

	1	**2**	**4**	**5**	**6**	**7**
δ^7Li	0.51	0.11	2.21	–	0.97	0.02
	–	–3.65	(1.60, 1.40	–	–	–0.652
$\delta^{27}Si$	5.28	8.68	–	–		4.99, 4.197, 5.67
$\delta^{13}C(Me)$	–2.70	1.01	0.47	–	0.43	–0.32
	–1.06		2.58	1.03	1.02	0.53
						1.44
	4	4	8 Sign.	6 Sign.	12	8 ar

In the solid state compound **4** is trimeric, and each of the three Li atoms are in a different environment. This is reflected by the ^7Li-NMR spectrum of **4_3** which shows two signals, one of them being assigned to a particularly deshielded atom. We attribute the signal at $\delta = 1.40$ to atom Li3 because it coordinates to both N atoms of the hydrazide unit, while we assume that the signal at $\delta = 2.21$ belongs to atom Li1 as a result of the lower coordination. However, this is a somewhat arbitrary assignment. There are two ^{13}C resonance signals for the Me_3Si groups. These arise most likely from a methyl group at atom Si1 which is in closer contact to the phenyl rings than the other two. Since it is unlikely that **4_3** remains static in solution, atoms Si1 and Si5 may become more readily chemically equivalent in contrast to atom Si3 which is different. Moreover, the six phenyl groups in compound **4_3** are represented in solution by eight ^{13}C resonances. This suggests free rotation about the respective N–C bonds while the nonequivalence of the phenyl groups can be interpreted to result from the puckered Li_3N_3 ring structure.

The dimeric sodium hydrazide $Na(Ph)N{-}N(Ph)SiMe_3 \cdot NH_3$ (**5_2**) shows a single ^{13}C resonance for the $SiMe_3$ group and 6 signals for the phenyl groups in accordance with its solid-state structure, which is obviously retained in solution.

The mixed hydrazide-amide **6a** reveals only a single ^7Li resonance, and the chemical shift values indicate absence of any Li–η^6-Ph interaction as proven by the molecular structure of **6a** in the solid state. A total of twelve ^{13}C-resonances were observed: this suggests either two sets of phenyl groups in an unsymmetrical environment or three sets in a chemically different environment for rotating phenyl groups leading to four signals each. The latter situation is more likely in terms of the molecular structure of **6a** in the solid state. This renders the phenyl groups C21 to C26 and C31 to C36 chemically different while the C atoms in the two disordered phenyl groups would be pairwise equivalent. Thus, the structure of **6a** seems to be retained in solution.

In solution compound **7** shows two ^7Li resonances in a 2:1 ratio. This suggests a higher symmetry of the dimer **7_2** with a mirror plane or a C_2 axis passing through one Li atom. There are, however, three ^{27}Si resonances as well as two ^1H signals for the methyl groups and two ^{13}C resonances for the methylene group of the benzyl substituent as well as eight signals for the phenyl groups. These data are best explained by a dimer-monomer equilibrium in solution.

Discussion

The transformation of several phenylhydrazines and phenyl(trimethylsilyl)hydrazines into their corresponding alkali metals salts by reaction with butyllithium, sodium amide, or caesium metal in the presence of a suitable solvent proceeded without major problems in spite of the well-known fact that silyl migration can occur[4]. In the present study only the lithiation of *N,N'*-diphenylhydrazine gave an unexpected result because the product obtained from ether solution turned out to be $Li(Ph)N-N(Ph)Li \cdot 2\,LiNPh_2 \cdot 4\,OEt_2$. This not only implies phenyl group migration but also reduction of the hydrazine $H(Ph)N-N(Ph)H$ to the amine $HNPh_2$ as depicted in eq. (1).

$$2\,PhHN-NHPh + 2\,LiR \rightarrow 2\,LiNPh_2 + 2\,RH + N_2 + H_2 \qquad (1)$$

The mechanisms of the redox-rearrangement process that leads to the Ph_2N^- unit is, at the present time, not yet understood in spite of preliminary silylation experiments[7]. Obviously, dilithiation weakens the N–N bond, and it may be expected that this tendency will increase by substituting the Li atoms by the heavier alkali metal atoms, and we shall investigate this point in the future.

Although the structural motifs **B** and **C** can be readily recognized in the molecular structures of the lithium hydrazides described in this work there seem to be exceptions to the rule, because compound $[Et_2OLi(Ph)N-N(SiMe_3)Ph]_2$ is closer in its structure to a lithium amide[2] as demonstrated by the considerably different Li···N atom distances to N1 and N2.

A comparison of ether-solvated lithium phenylhydrazides with those of the unsolvated compounds clearly reveals that the ether molecules *prevent* or retard the interaction of the Li atoms with the phenyl rings. The most notable interaction of this sort is observed for the *tetrameric* molecule $(Me_3Si)_2N-N(Ph)Li$ where association of the monomeric units occurs by asymmetric η^6-coordination of Li with phenyl rings. In all other cases only some of the phenyl carbon atoms come close enough to the Li atoms to be regarded as a Li···C interaction.

In addition to the "intramolecular" Li–N interactions (which we consider rather arbitrarily to range from 1.95 to 2.3 Å) there are also "secondary intramolecular" interactions in the associated lithium phenylhydrazides (Li···N > 2.35 Å). Particularly, the Li···C atom distances belong to the latter type because the shortest interaction were found in **2** with (Li···C)=2.310 Å, while most of the Li···C distances cover the range from 2.5 to 2.8 Å. In addition, there are also several fairly short Li···H interactions with H atoms from the methyl groups of the Me_3Si groups.

There are of course close analogies between the structures of lithium amides and lithium hydrazides. A good example is the dimeric **7** which can be compared with trimeric $LiN(CH_2Ph)_2$[8]. The latter shows also LiN and LiC interactions. However, these are restricted to the *ipso*- and one *meta*-C atom per phenyl group while the C atom of the CH_2 group and *ipso*-C atom is involved in **7**.

The number of structurally characterized caesium amides is still rare and the caesium compound **3** is the first caesium hydrazide so far reported. There are, however, a few organocaesium compounds related to **3**, e.g. the diethyltriamino derivative $[Me_2N-CH_2-CH_2-NMe-CH_2-CH_2-NMe_2]CsCPh_3$[9] and the caesium carbazolide complex $(PTED)_2Cscarbaz$ $(PTED=Me_2N-CH_2-NMe-CH_2-CH_2-CH_2-NMe_2)$[10], and the recently reported Cs salt of the 1,1,4,4-tetraphenylbutadiene-2,3-diyl anion[11]. It should be noted that the Cs–N interactions in the caesium carbazolide are similar to those in **3**. However, η^6-phenyl Cs-π interactions occur only in the butadiene-2,3-diyl anion which is characterized by 15-fold coordinated Cs centers. These metal–phenyl π interactions result primarily from electrostatic forces[12]. In **3**, the "coordination" number for Cs is 16. On average the Cs···C distance is 3.64 Å in **3** (corresponding to the $Cs-C_6$ centroid of 3.25 Å), and this corresponds well with the 3.24 Å for the $Cs-C_6$ centroid in the Cs–butadiene-2,3-diyl compound[11].

Conclusion

The results presented here clearly indicate that the alkali metal atoms prefer to be coordinated by ether or ammonia. Thus, a metal–aryl π interaction is prohibited or retarded. Three-membered N_2Li interactions are observed for compounds **1**, **5**, and **6a**, but these are absent in compounds **2**, **3**, and **4**. Compounds **2** and **3** have a $(Me_3Si)_2N$ group in common. This can be rationalized for **2** and **3** by $M\cdots\eta^6-\pi-C_6H_5$ interactions, inducing steric shielding of the metal center. Compound **4** features not only partial η-bonding to the phenyl group but also steric shielding by hydrogen atoms.

On the other hand three-membered MN_2 moieties are detected in compounds **1**, **5**, and **6**. In all these compounds either OEt_2 or NH_3 are present as a donor molecule. Here this structural feature is realized only by the presence of a donor molecule, making the metal centers tetracoordinate. If no donor molecule is present, η^n-interaction of the metal centers compensates for metal-electron pair donor interactions such as ammonia or ethers. However, in the case of the caesium hydrazide **3** the THF molecules are not coordinated to the caesium centers but occupy positions in channels formed in the three-dimensional structure.

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Experimental

All experiments were conducted in anhydrous solvents and under nitrogen by using the Schlenk techniques. The hydrazines used were commercially available. The hydrazides were prepared by metalation of the respective hydrazines with butyllithium followed by silylation with Me_3SiCl.

NMR: Jeol FX 270 (^7Li, ^{29}Si) and Jeol 400 (^1H, ^{13}C), TMS and a 1 M LiCl solution as standards. – IR spectra were not conclusive and will not be described here. – Data of the crystal structure determinations were collected with a Siemens P4 automated four-circle diffractometer by using Mo-K_α radiation and a graphite monochromator. The programs XS, SHELXTL-Plus[13] and SHELX93[14] were used for data collection, structure solution, and refinement.

Dimeric N-Lithio-N-phenyl-N'-(trimethylsilyl)hydrazine-Diethyl Ether (**1_2**): To a solution of *N*-phenyl-*N'*-(trimethylsilyl)hydrazine (1.87 g, 10.4 mmol) in 20 ml of hexane *n*-butyllithium (6 ml, 1.5 M solution) in hexane was added with continuous stirring. Gas evolution started immediately, and the solution turned yellow. After some time a white precipitate formed which was dissolved by stirring overnight after diethyl ether had been added. Yellow crystals of dimeric **1** precipitated from this solution after several hours. This precipitate contained a fair amount of single crystals. Yield: 2.2 g of **1_2** (81%), m.p. 279–281°C. – NMR (C_6D_6): $\delta^1H=0.24-0.31$ (m, SiMe, 9H), 2.27 (broad, NH, 1H), 6.52–7.33 (m, C_6H_5, 5H). – $\delta^7Li=0.51$. – $\delta^{13}C=-2.70$, -1.06 ($SiMe_3$), 15.55 (CH_3CH_2), 65.87 (CH_2O), 112.67, 119.10, 121.32, 129.13 (C_6H_5). – $\delta^{29}Si$ = 5.28. – $C_9H_{15}LiN_2Si \cdot C_4H_{10}O$ (260.4): calcd. C 59.57, H 9.68, N 10.76; found C 58.07, H 10.20, N 11.20.

Tetrameric N-Lithio-N-phenyl-N',N'-bis(trimethylsilyl)hydrazine (**2_4**): To a stirred solution of *N*-phenyl-*N,N'*-bis(trimethylsilyl)hydrazine (0.82 g, 3.25 mmol) in 50 ml of benzene a solution of LiBu in hexane (2.1 ml, 1.56 M) was slowly added. The metalation started immediately with gas evolution. A yellow solution resulted which turned green after several days. Single crystals separated after 4 d at ambient temp. Yield: 0.71 g of **2_4** (83%), dec. 104°C. – NMR (C_6D_6): $\delta^1H=0.10$, 0.14 ($SiMe_3$, 18H in the ratio 4:5), 6.64–7.17 (C_6H_5, 5H). – $\delta^7Li=0.11$, -3.65. – $\delta^{13}C=1.01$ ($SiMe_3$), 112.56, 118.60, 128.53, 129.11 (Ph). – $\delta^{27}Si=8.68$. – δ^7Li at 85°C: -0.227, $h_{1/2}=41.4$ Hz. – $C_{12}H_{12}LiN_2Si$ (258.4): calcd. C 55.77, H 8.94, N 10.84; found C 53.77, H 9.28, N 9.92.

Caesium N-Phenyl-N',N'-bis(trimethylsilyl)hydrazide (**3**): Caesium metal (0.90 g, 6.8 mmol) was dispersed in 70 ml of benzene. To the stirred suspension a solution of $PhNH-N(SiMe_3)_2$ (1.71 g, 6.8 mmol) in 10 ml of THF was added. The mixture was then kept at reflux until the alkali metal had dissolved. An orange-colored solution formed from which orange crystals, m.p. 62–64°C, separated on cooling to 5°C. The yield was not determined. In vacuo the crystals became rapidly turbid due to loss of THF, but their shape remained unchanged. – NMR (C_6D_6): $\delta^1H=0.09$, 0.11, 0.16, 0.20 (18H), 1.42, 3.56 (THF); 7.10–7.19 (Ph, 5H). – $\delta^{13}C$ = 2.02 ($SiMe_3$), 25.78, 67.77 (THF). – $\delta^{29}Si=7.46$. – $C_{12}H_{23}CsN_2Si_2 \cdot OC_4H_8$ (456.5): calcd. C 42.09, H 6.84, N 6.14; found: C 40.98, H 6.59, N 5.97; calcd. for $C_{12}H_{23}CsN_2Si_2 \cdot 0.50\ C_4H_8O$ (420.46): C 39.99, H 6.47, N 6.66.

Trimeric N-Lithio-N',N'-diphenyl-N-(trimethylsilyl)hydrazine (**4_3**): A hexane solution of LiBu (3.1 ml, 1.56 M, 4.84 mmol) was added to a stirred solution of $(Me_3Si)HN-NPh_2$ (1.24 g, 4.84 mmol) in 20 ml of hexane. An orange-colored solution formed, and gas evolution proceeded rapidly. Orange-colored crystals separated within 14 h. Yield: 1.09 g of **4_3** (85.9%), m.p. 169–179°C. – NMR (C_6D_6): $\delta^1H=-0.09$, 0.00, 0.10, 0.18 (Me, 9H), 6.97–7.18 (Ph, 10H). – δ^7Li (C_6D_6/Et_2O): δ = 1.66, 1.40. – $\delta^{13}C=0.47$, 2.58 (Me), 119.61, 120.16, 121.47, 121.91, 128.99, 139.29, 150.51, 152.29 (Ph). No change in the NMR spectra up to 65°C. – $C_{15}H_{19}LiN_2Si$ (262.4): calcd. C 68.67, H 7.30, N 10.68; found: C 65.9 H 6.95 N 10.45.

Dimeric Sodium N,N'-Diphenyl-N-(trimethylsilyl)hydrazide–Monoammine (**5_2**): A suspension of sodium amide (110 mg, 2.82 mmol) in benzene (40 ml) was added to *N,N'*-diphenyl-*N*-(trimethylsilyl)hydrazine (0.72 g, 2.8 mmol). The mixture was then heated at reflux until all $NaNH_2$ had dissolved. Small amounts of ammonia were carried away in a slow stream of N_2 gas. The solution turned yellow. On cooling yellow-colored crystals separated. Yield: 0.63 g of **5_2** (76%), m.p. 74–76°C. The crystals turned quickly deep violet on exposure to traces of oxygen. – NMR (C_6D_6): $\delta^1H=0.22$ (Me 9H), 5.03 (NH_3, 3H), 6.55–7.14 (Ph, 10H). – $\delta^{13}C=1.03$ (Me), 112.42, 115.72, 119.89, 129.80,. 130.09, 150.3 (Ph). – $C_{15}H_{19}N_2NaSi \cdot NH_3$ (295.4); calcd. C 60.98, H 7.51 N 14.22; found: C 61.19 H 7.38 N 14.01.

N,N'-Dilithium N,N'-Diphenylhydrazide-Bis(lithium diphenylamide)-Tetrakis(diethyl ether) (**6a**): A solution of *N,N*-diphenylhydrazine (0.32 g, 2.33 ml) in 30 ml of hexane was heated at reflux. Then 3 ml of a 1.56 M solution of LiBu (4.66 mmol) in hexane was slowly added. Gas evolution set in immediately resulting in an orange-colored solution and formation of a precipitate. Small portions of diethyl ether were added to dissolve the solid material. Orange-colored crystals separated from this solution on standing overnight. Yield: 1.7 g of **6a** (86%), dec. 79°C. – NMR (C_6D_6): $\delta^1H=0.89$ (CH_3, 12H), 3.05 (OCH_2, 8H), 6.68, 7.32 (Ph, 15H). – δ^7Li: 0.97 ($h_{1/2}=14$ Hz). – $\delta^{13}C=15.8$ (CH_3), 66.11 (CH_2), 122.61, 123.54, 129.49, 144.13 (NPh_2), 118.38, 120.88, 121.34, 127.19, 129.82, 129.74, 131.34, 153.43, (NPh groups). – $C_{52}H_7Li_4N_4O_4$ (842.9): calcd. C 74.10, H 8.37, N 6.65; found: C 73.92 H 8.21 N 6.45.

Dimeric Lithium N-Benzyl-N,N'-bis(trimethylsilyl)hydrazide (**7_3**): Prepared in analogy to compound **6a** from *N*-benzyl-*N,N'*-(trimethylsilyl)hydrazine (1.10 g, 4.13 mmol), dissolved in 30 ml of hexane, and LiBu (2.65 m, 1.56 M). – Yellow crystals. Yield: 0.9 g of **7_3** (79%); m.p. 103–106°C. – NMR (C_6D_6): $\delta^1H=0.02$, 0.19 (Me, 18H), 2.91, 3.99 (CH_2, 2H), 7.15–7.35 (Ph, 5H). – $\delta^7Li=0.02$, -0.652 (3:2). – $\delta^{13}C$ = 0.32, 0.53, 1.44 (Me), 55.5, 60.17 (CH_2), 127.08, 127.63, 128.46, 128.63, 129.08, 129.17, 130.05, 138.64. – $C_{13}H_{25}LiN_2Si_2$ (272.5): calcd. C 57.3, H 9.25, N 10.28; found: C 56.60 H 9.09 N 9.96.

N-Lithium N,N'-Diphenyl-N'-(trimethylsilyl)hydrazide (**8**): A solution of $H(Ph)N-N(Ph)SiMe_3$ (0.91 g, 3.55 mmol) in 50 ml of hexane was heated at reflux, and LiBu (2.28 ml of a 1.56 M solution in hexane, 3.55 mmol) was added with stirring. Gas evolution commenced immediately, and an intensely yellow solution formed from which a microcrystalline precipitate separated. Attempts to obtain single crystals were unsuccessful so far. Yield: 0.43 g of **8** (71%), dec. 83°C. The molecular mass could not be determined due to the poor solubility in benzene. – NMR (C_6D_6): $\delta^1H=0.10$, 0.15, 0.21, 0.23 ($SiMe_3$, 9H), 6.50–7.27 (C_6H_5, 10H). – $\delta^7Li=0.69$. – $\delta^{13}C=0.43$, 1.02 (Me), 112.11, 115.27, 116.58, 119.27, 119.59, 123.29, 129.77, 129.55, 130.64, 131.09, 149.66 (Ph). – $C_{15}H_{19}LiN_2Si$ (262.4): calcd. C 68.67, H 7.30, N 10.68; found C 68.65, H 7.30, N 10.45.

Crystal Structure Determinations[15]: Selected single crystals were covered with perfluoroether oil and transferred under Ar to a glass capillary. After optical alignment on the diffractometer, 20–30 reflections of a rotation photo taken at 203 K were automatically centered, and the unit cell was determined from these setting angles. Data collection was performed at 203 K. Lorentz and polarization correction, but no absorption correction was applied except for the caesium compound **3** (min/max transmission 0.430/0.607). Direct methods were used to solve the structures. In the case of **3** the Patterson method led to the model structure. – Nonhydrogen atoms were refined anisotropically; most of the hydrogen atoms were found in difference Fourier maps. However, their positions were calculated and included in the final refinement as a riding

Table 2. Summary of data related to crystallography, data collection, and refinement

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Chem. formula	$C_{13}H_{25}LiN_2OSi$	$C_{12}H_{23}LiN_2Si_2$	$C_{12}H_{23}CsN_2Si_2$ $0.17\ OC_4H_8$	$C_{15}H_{19}LiN_2Si$	$C_{15}H_{22}N_3NaSi$	$C_{26}H_{35}Li_2N_2O_2$	$C_{13}H_{25}LiN_2Si_2$
Form. mass	260.38	258.44	389.08	262.35	295.44	421.44	272.47
Cryst. size [mm]	0.4×0.4×0.6	0.3×0.45×0.6	0.2×0.35×0.4	0.2×0.45×0.6	0.5×0.5×0.5	0.3×0.3×0.4	0.4×0.4×0.4
Cryst. system	Triclinic	Orthorhombic	Rhombohedral	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group (#)[a]	*P*-1 (2)	*Pbcn* (60)	*R*-3 (148)	*P*2(1)/*c* (14)	*P*2(1)/*c* (14)	*C*2/*c* (15)	*P*2(1)/*c* (14)
a [Å]	10.618(2)	27.496(5)	25.422(6)	9.208(2)	10.062(3)	23.926(9)	9.755(2)
b [Å]	12.915(3)	8.905(2)	25.422(6)	24.720(5)	13.410(5)	13.008(4)	19.690(3)
c [Å]	13.068(6)	26.707(5)	15.178(4)	20.158(4)	12.433(6)	18.023(7)	9.752(2)
α [°]	86.16(3)	90.00	90.00	90.00	90.00	90.00	90.00
β [°]	85.84(5)	90.00	90.00	96.65(2)	92.30(2)	116.26(3)	116.05(2)
γ [°]	66.00(3)	90.00	120.00	90.00	90.00	90.00	90.00
V [$Å^3$]	1631.4(9)	6539.3(23)	8495.0(36)	4557.5(16)	1676.3(11)	5030.4(31)	1682.8(6)
Z	4	16	18	12	4	8	4
ρ(calc) [Mg/m^3]	1.060	1.050	1.369	1.147	1.171	1.113	1.075
μ [mm^{-1}]	0.135	0.199	2.076	0.141	0.160	0.068	0.196
F(000)	568	2240	3498	1680	632	1816	592
Index range	$-1 \le h \le 6$ $-4 \le k \le 15$ $-15 \le l \le 15$	$0 \le h \le 32$ $0 \le k \le 10$ $0 \le l \le 31$	$0 \le h \le 28$ $-30 \le k \le 1$ $-18 \le l \le 18$	$-10 \le h \le 1$ $-28 \le k \le 0$ $-23 \le l \le 23$	$-1 \le h 11$ $0 \le k \le 15$ $-14 \le l \le 14$	$-7 \le h \le 27$ $0 \le k \le 15$ $-21 \le l \le 19$	$-11 \le h \le 10$ $-22 \le k \le 22$ $0 \le l \le 11$
2 θ [°]	49.00	49.00	50.00	48.00	49.00	49.00	49.70
Temp, [K]	213	193	193	213	198	193	198
Refl. collected	4283	5379	6921	8576	3293	5113	3630
Refl. unique	3486	5375	3327	7125	2776	4147	2636
Refl. observed (4σ)	2226	2893	2134	3867	2166	2382	1937
R (int.)	0.0979	0.0451	0.0903	0.0781	0.0390	0.0528	0.0368
No. variables	341	319	165	533	184	339	238
Weighting scheme[b] *x*/*y*	0.0587/1.3382	0.0692/7.7958	0.0432/11.5666	0.0332/2.7947	0.0453/0.8427	0.0969/4.5986	0.0666/0.5540
GOOF	1.041	1.015	1.061	1.051	1.044	1.037	1.033
Final *R* (4σ)	0.0584	0.0613	0.0505	0.0653	0.0421	0.0696	0.0462
Final *wR*2	0.1355	0.1408	0.1115	0.1185	0.1024	0.1705	0.1111
Larg. res. peak [$e/Å^3$]	0.198	0.321	0.850	0.228	0.221	0.498	0.400

[a] Space group number (#). – [b] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2 F_c^2)/3$.

model with fixed isotropic $U_i = 1.2\ U_i(C)$ (coupled to the respective C atom). The disorder found for the PhNNPh part in compound **4** was resolved and led to a 1:1 distribution of the two orientations. The THF molecules residing in the channels of the caesium compound **3** are disordered, and a refined SOF of 0.17 resulted. Results see Table 2.

☆ Dedicated to Professor *Rudolph Gompper* on the occasion of his 70th birthday.

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