Synthesis and Structures of Sodium Phenylhydrazides☆

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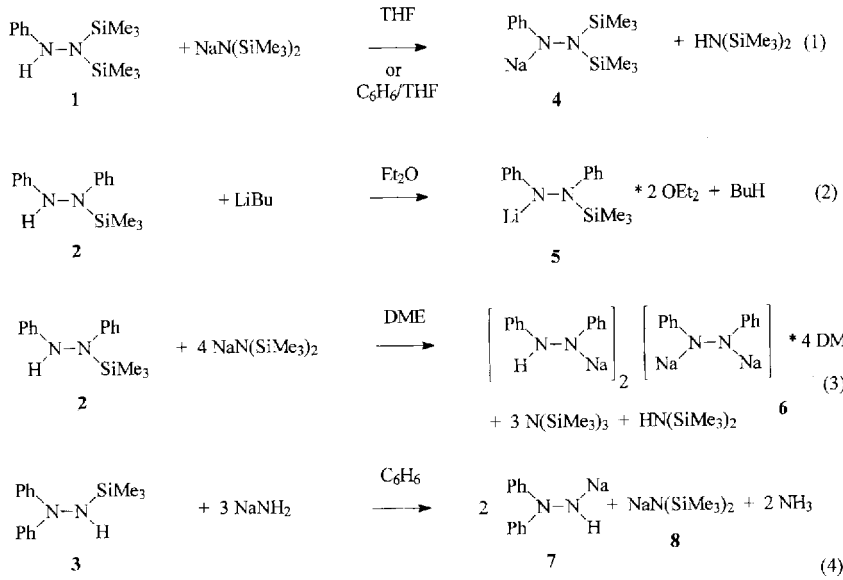
Monomeric Li(Ph)N−N(Ph)SiMe$_3$ · 2 OEt$_2$ was obtained by deprotonating the respective hydrazine with *n*BuLi in the presence of diethyl ether. Reaction of NaN(SiMe$_3$)$_2$ with PhHN−N(SiMe$_3$)$_2$ in a benzene/tetrahydrofuran mixture provided monomeric Na(Ph)N−N(SiMe$_3$)$_2$ · 3 THF, or Na(Ph)N−N(SiMe$_3$)$_2$ · THF using a small amount of THF. Its THF can be replaced by diethyl ether or *tert*-butyl methyl ether to give 1:1 solvates. These associate, forming chains in the solid state via η^n coordination (n = 2, 3) of their phenyl groups to the sodium centers of adjacent molecules. In contrast, not only deprotonation but also desilylation occurs on reaction of NaN(SiMe$_3$)$_2$ with H(Ph)N−N(Ph)SiMe$_3$ or of NaNH$_2$ with (Me$_3$Si)HN−NPh$_2$. The latter reaction results in the formation of hexameric (NaHN−NPh$_2$)$_6$, which adopts a face-sharing double-cubane structure.

The structural chemistry of metal amides is well developed[1], particularly that of compounds of the type MNR$_2$, while systems such as LiNHR[2] and Li$_2$NR[3] have been less well investigated. Depending on the steric requirements of the organyl group as well as on additional ligands, various states of aggregation are achieved via "laddering" and "stacking"[1]. These structural motifs are also present in lithium organylhydrazides, in addition to the "butterfly" arrangement of the Li$_2$N$_2$ unit[4]. Moreover, as far as phenylhydrazides are concerned, η^n interactions between alkali metal centers and the phenyl group, ranging from η^2 to η^6, also determine the structures of the lithium phenylhydrazides, resulting in the most exceptional structure being found for Li$_4$N$_4$Ph$_4$[4c]. Here, two of the Li centers are each sandwiched between two phenyl groups. To date, much of the structural chemistry of alkali metal hydrazides has been focused on lithium hydrazides. Information on the heavier alkali metal hydrazides is still scarce[4f]. In the present report we concentrate on sodium hydrazides in order to learn more about the influence of the larger ionic radius of Na$^+$ as compared to Li$^+$ on the structure of alkali metal hydrazides.

Preparation

Three phenylhydrazines, **1**−**3**, were studied with respect to possible deprotonation: **1** by NaN(SiMe$_3$)$_2$, **2** by *n*BuLi and NaN(SiMe$_3$)$_2$, and **3** by NaNH$_2$.

While the deprotonation of **1** by NaN(SiMe$_3$)$_2$ according to eq. (1) proceeded smoothly to give the sodium hydrazide **4**, as did the deprotonation of **2** by *n*BuLi (eq. 2) to give lithium hydrazide **5**, the reaction of **2** with NaN(SiMe$_3$)$_2$ in dimethoxyethane not only occurred with deprotonation but



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also with desilylation, giving access to the sodium hydrazide **6** of an unexpected composition (see the idealized eq. 3). Desilylation is even more specific in the case of **3** with $NaNH_2$ as the reagent. The reaction not only furnishes the sodium hydrazide **7** but also $NaN(SiMe_3)_2$, as represented by eq. (4). To prove eq. (4), a second reaction using this molar ratio was performed. The ammonia evolved was estimated by titration and the formation of $NaN(SiMe_3)_2$ was verified by ^{29}Si-NMR. Thus, the desilylation was confirmed as proceeding according to eq. (4).

When reaction (1) is performed in THF as the solvent, the hydrazide **4** crystallizes as **4** · 3 THF. However, when a minimum amount of THF is used in benzene solution, the product is the yellow, mono-solvated hydrazide **4** · THF. Its coordinated THF can be readily replaced by diethyl ether or diveron (*tert*-butyl methyl ether), furnishing the solvates **4** · OEt_2 and **4** · MeO*t*Bu, respectively.

Most of these sodium hydrazides are sparingly soluble or even insoluble in both aliphatic and aromatic hydrocarbons, thus, for example, preventing detailed study of their NMR spectra in C_6D_6, as well as the determination of their molecular weights by cryoscopy. They show, however, a better though still limited solubility – except **4** · 3 THF and **4** · THF – in tetrahydrofuran. Since the dissolution in THF was found to be an exothermal process, the state of aggregation and solvation is most probably changed upon dissolution and hence NMR data would not be representative of the structures of the hydrazides in the crystal. For this reason we will not discuss here the relatively few NMR data at hand. Details are, however, presented in the Experimental Section.

Molecular Structures

The Lithium Hydrazide $Ph(Me_3Si)N-N(Ph)Li(OEt_2)_2$ (5)

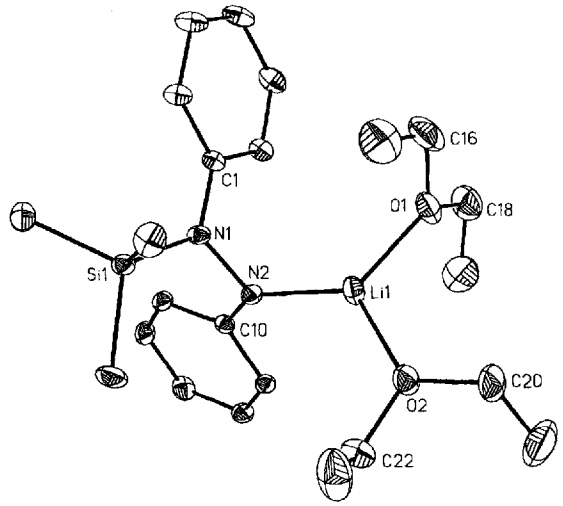
Compound **5** crystallizes from ethereal solutions in colorless needles belonging to the triclinic system, space group $P\bar{1}$. There are two independent molecules in the unit cell, the structural parameters of which are not significantly different. Therefore, we depict only one of these in Figure 1.

First of all we note a tricoordinated lithium center, which is surrounded by two oxygen atoms and a nitrogen atom in a distorted trigonal-planar fashion, as evidenced by the sum of bond angles (359.9°) and a comparatively compressed O–Li–O bond angle of 109.7(3)°. The two Li–O atom distances are similar, differing only by 0.01 Å. Interestingly, the Li–O atom distances are larger than the Li–N distance, on average by 0.015 Å.

The two C_2O planes of the ether molecules are differently oriented with respect to the O_2N plane around the Li center. One of these, C16–O1–C18, is almost perpendicular to this plane (88.2°), while the other, C20–O2–C22, is almost coplanar (1.5°). The O atom of the latter plane exhibits the shorter Li–O atom distance.

While the N–N bond length is 1.455(4) Å, we note two comparatively short N–C bonds which differ by 0.035 Å. The shorter bond is found at the Li-bearing nitrogen atom N2. Both phenyl groups tend to be coplanar with the planes

Figure 1. The molecular structure of the lithium hydrazide **5** in ORTEP representation; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 20% probability level[a]



[a] Selected bond lengths [Å] and angles [°]: Li1–N2 1.901(6), Li1–O1 1.921(6), Li1–O2 1.912(6), N1–N2 1.457(4), N1–Si1 1.743(3), N1–C10 1.399(4), N2–C1 1.364(4); N2–Li1–O2 123.8(3), N2–Li1–O1 126.1(3), Li1–N2–N1 110.8(3), Li1–N2–C1 134.1(3), N1–N2–C1 112.8(2), N2–N1–Si1 116.1(2), N2–N1–C10 117.0(2), Si1–N1–C10 126.8(2).

around the respective nitrogen atoms, the twist angles for the phenyl group being 5.4° for N2 and 14.1° for N1. Both nitrogen atoms can be considered as being essentially sp^2 hybridized, since the sum of the bond angles is 359.9° at N1 and 357.7° at N2, respectively. Moreover, it is found that the planes around the nitrogen atoms are orthogonal to one another, as evidenced by the torsion angle C1–N1–N2–C10 of 89.6°.

As far as we are aware, compound **5** is the first structurally characterized monomeric alkali metal hydrazide.

The Series of Solvated Sodium Hydrazide $(Me_3Si)_2N-N(Ph)Na$ (4)

Sodium hydrazide **4** was obtained in the form of single crystals of various ether solvates. Among these, the compound **4** · 3 THF proved to have the most simple molecular structure because, as Figure 2 shows, it is present in the crystal in the form of unassociated molecular units.

4 · 3 THF crystallizes in the monoclinic system, space group $P2_1/m$ with two molecules in the unit cell. The molecule itself is positioned on a crystallographic mirror plane that incorporates the sodium atom, the two nitrogen atoms, the carbon atoms of the phenyl group, as well as an oxygen atom of one of the coordinated THF molecules. The sodium atom is tetracoordinated by three oxygen atoms and one nitrogen atom. However, distortion from an ideal tetrahedral array is significant, as is evident from the wide N2–Na1–O2 bond angle of 145.8(4)° associated with the somewhat longer Na–O atom distance (see Table 1). The bond angle between the equivalent O atoms and the Na atom is much closer to the tetrahedral bond angle [114.6(4)°] than the O1–Na1–O2 bond angle, which is as acute as 91.2(3)°. It should be noted that the Na–N and

Figure 2. ORTEP plot of a molecule of the sodium hydrazide **4** · 3 THF; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn at the 25% probability level

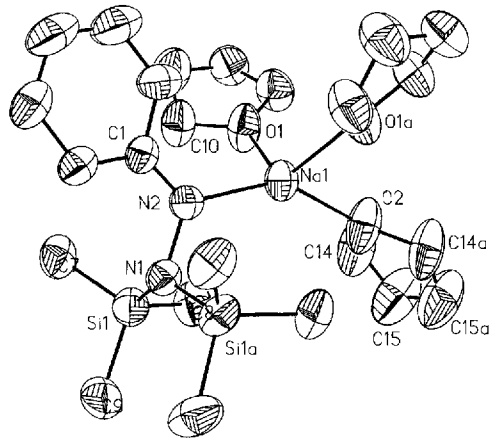
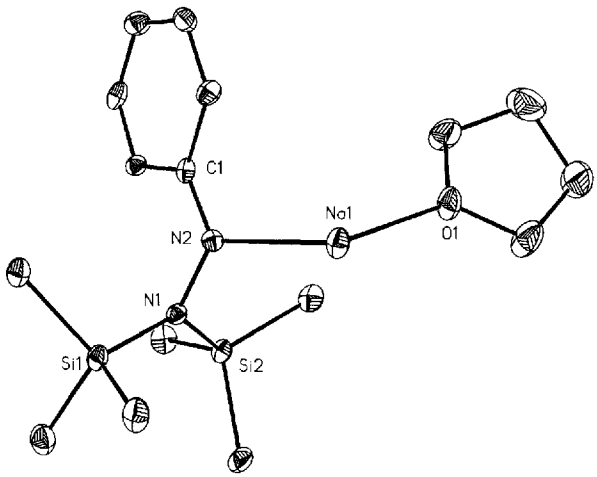


Figure 3. ORTEP plot of a molecule of the sodium hydrazide **4** · THF; hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn on a 25% probability limit



Na–O distances do not differ significantly and that the sum of bond angles Σ at each of the oxygen atoms is very close to 360° (358.9 and 358.6°).

Table 1. Distances between atoms of the solvates of compound **4**

	4 · 3 THF	**4** · THF	**4** · OEt_2	**4** · MeO*t*Bu	
Na1–N2	2.315(9)	2.299(5)	2.309(3)	2.328(5)	2.322(6)
Na1–O1	2.319(6)	2.268(5)	2.278(3)	2.318(8)	2.288(7)
Na1–O2	2.326(10)	–	–	–	–
N1–N2	1.508(10)	1.466(6)	1.502(4)	1.488(7)	1.490(7)
N2–C1	1.335(11)	1.346(7)	1.356(4)	1.346(8)	1.358(7)
N1–Si1	1.722(4)	1.710(5)	1.728(3)	1.736(5)	1.727(5)
N1–Si2	–	1.735(5)	1.726(3)	1.721(5)	1.709(5)
Na1···C	–	2.859(7)[4]	3.034(4)	2.985(7)	2.979(8)
	–	2.701(6)[5]	2.574(4)	2.727(8)	2.857(7)
	–	2.789(6)[6]	–	–	–

Both N-atoms of **4** · 3 THF are tricoordinated, with a planar geometry at the atom N2 (Σ = 359.9°) and a flat trigonal-pyramidal geometry at N1 (Σ = 349.3°). Nevertheless, the two halves of the hydrazine are close to perpendicular, as demonstrated by the 88.9° interplanar angle between the planes C1N2N1 and Si1N1Si1a. The very short N2–C1 bond [1.34(1) Å] is in accord with the coplanarity of the phenyl group and the NaN_2 plane. Finally, the N–N bond in **4** · 3 THF is fairly long, indicating a substantial negative charge on atom N2.

The compound **4** · THF crystallizes in the orthorhombic system, space group $Pca2_1$. There are 4 molecules in the unit cell. The molecular structure of **4** · THF in the asymmetric unit is depicted in Figure 3.

It shows the same general features as **4** · 3 THF, except that the sodium atom seems to be bis-coordinated. Both atom distances Na1–N2 and Na1–O1 are shorter than in **4** · 3 THF, and the Na–N distance is longer than the Na–O distance, in accord with the larger effective radius of the N atom as compared to the O-atom. The sum of bond angles at atom O1 is 360°, and the C–O–C bond angle measures 106.5°. Both nitrogen atoms have an almost planar geometry (Σ at N1: 359.1° and at N2: 357.2°), and once again the interplanar angle C1N2N1/Si1N1Si2 is close to orthogonality (99.1°). The N–N bond length is 1.466(6) Å and is, therefore, significantly shorter than in **4** · 3 THF.

We again note a short N–C bond [1.346(7) Å] to the phenyl group, in accordance with only a slight torsion of the phenyl group out of the C1N2N1 plane (6.4°). However, the two Si–N bond lengths differ significantly, by 0.025 Å. This seems to be a consequence of the N–N–Si bond angles, because the more open angle is associated with the longer Si–N bond. The reason for this asymmetry becomes apparent when we look at the interactions between the **4** · THF molecules in the crystal.

Clearly, the sodium center in the molecular unit of **4** · THF is coordinatively unsaturated. Indeed, in the solid state, this molecule associates with its neighbours in such a manner that infinite chains are built up, as depicted in Figure 4. The association is accomplished by an η^3-interaction of the phenyl ring of a neighbouring molecule, involving particularly its *meta* and *para* carbon atoms. In addition, there are two close contacts with two hydrogen atoms of a methyl group attached to Si1. Taking these contacts into account, we arrive at a hepta-coordination for the Na atom. These chains of associated **4** · THF molecules are oriented along the *b* axis of the unit cell.

Figure 4. Association of **4** · THF molecules in the crystal, forming chains via intermolecular Na···C contacts and agostic H···Na contacts

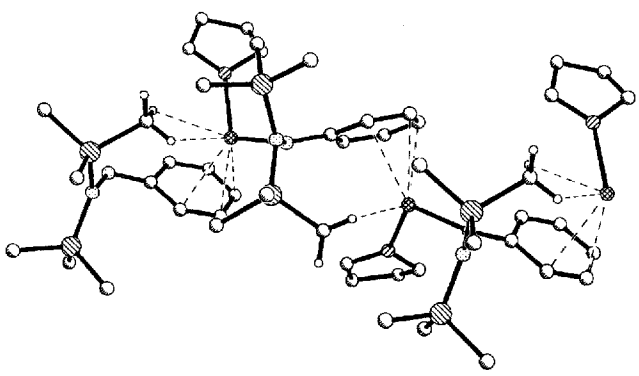
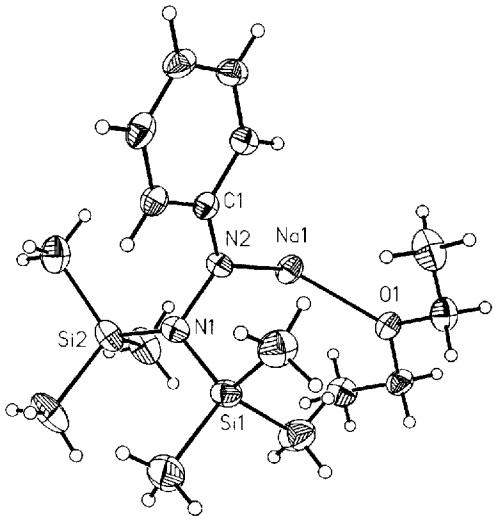


Figure 5. ORTEP plot of a molecule of the sodium hydrazide **4** · OEt_2; thermal ellipsoids are drawn on a 25% probability level



Compound **4** · OEt_2 displays a molecular structure essentially very similar to that of **4** · THF, as can be seen by comparing Figure 3 with Figure 5.

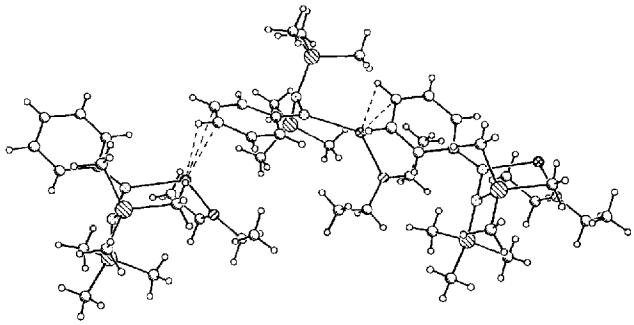
The sodium phenylhydrazide **4** · OEt_2 crystallizes in orange-colored needles of the monoclinic system, space group $P2_1/n$, with one molecule in the asymmetric unit. Both Na−O and Na−N distances are longer by 0.01 Å compared to those in **4** · THF, maintaining a difference of 0.03 Å. However, the N1−N2 as well the N2−C1 bond lengths are longer, while the two Si−N bonds are of equal lengths (1.727 Å average).

Atom N2 is the center of a distorted trigonal plane, as is evident from the sum of bond angles being 360°, but the bond angles deviate from 120°. Its phenyl group is twisted by only 0.6° with respect to the Na1N2N1 plane, allowing a strong π-interaction with the lone pair of electrons on the N2 atom. In accord with the structure of **4** · THF, we find that the Si_2N plane is practically perpendicular to the C1N2N1 plane (91.3°), but that atom N1 is slightly pyramidalized (Σ = 353.7°). In contrast, the oxygen atom is the center of a distorted trigonal plane (Σ = 358.9°) and shows a C−O−C bond angle of 111.8(3)°.

As was to be expected from the low coordination at the Na1 atom in the molecular unit of **4** · OEt_2, the molecules are associated in the solid state. Chains are formed, as shown in Figure 6, by η^2 interaction of the sodium atom with two carbon atoms of an adjacent phenyl ring. In addition, there is a comparatively close intermolecular contact with the hydrogen atom attached to C4 (Na1···H4: 2.674 Å). This distance is the same as for Na···C4, while the distance Na1−C3 is significantly longer [3.024(4) Å]. A stronger intermolecular interaction of Na1 with the phenyl ring is obviously prevented by the steric requirement of the ether molecule; its methyl groups are directed towards the sodium center, thereby increasing the steric shielding at this metal ion.

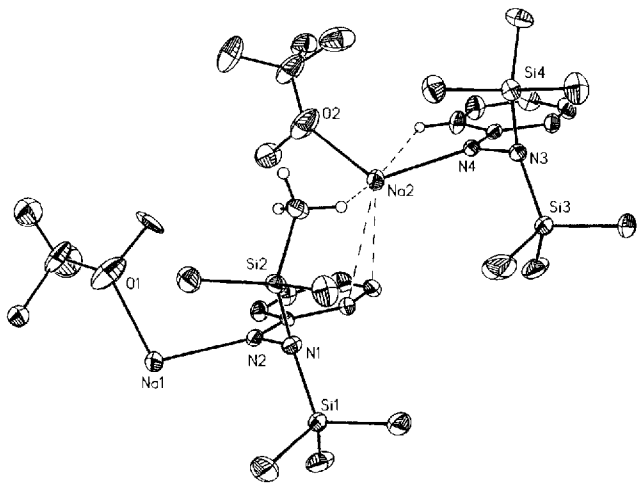
From this point of view it was of interest to learn how a more bulky ether would change the interaction between the

Figure 6. Part of the chain of **4** · OEt_2 molecules generated by intermolecular η^2 interaction of the phenyl group with the adjacent sodium center, including closest Na···H contacts



molecules of **4**, and **4** · MeO*t*Bu, which crystallizes in colorless prisms, seemed to be a good model compound. Crystals of **4** · MeO*t*Bu exhibit monoclinic symmetry, and the noncentrosymmetric space group $P2_1$ was determined with $Z = 4$. There are, therefore, two independent molecules in the asymmetric unit, which are shown in Figure 7. The structural parameters of these two molecules are the same within the limits of standard deviations, apart from small differences in the Si−N bond lengths (see Table 1). It can be noted, however, that the orientations of the ether molecules are different, thus allowing a distinction to be made between the two **4** · MeO*t*Bu molecules. In molecule (1), characterized by the sodium atom Na1, we note that the methyl group of MeO*t*Bu is oriented towards the phenyl group of the molecule. In molecule (2), however, it is the *tert*-butyl group that points in this direction.

Figure 7. ORTEP plot of the two independent molecules of **4** · MeO*t*Bu; thermal ellipsoids are drawn on a 25% probability level

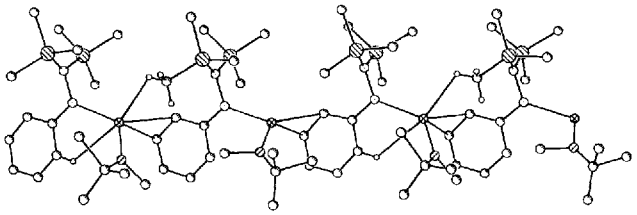


The phenyl group-bearing nitrogen atoms N2 and N4 reside in almost planar environments (Σ = 359.8 and 358.9°), while the nitrogen atoms associated with the Me_3Si group adopt a slightly pyramidal geometry (Σ = 354.8 and 353.6° for N1 and N3, respectively). The planes at the nitrogen atoms Na1N2C1/Si1N1Si2 are close to perpendicular (interplanar angles are 84.2 and 84.3°, respectively), and the phenyl groups are again only twisted slightly with respect

to the NaN_2 planes [0.5° for molecule (1) and 1.45° for molecule (2)].

In the lattice, the two independent molecules **4** · MeO*t*Bu form chains oriented parallel to the crystallographic *a* axis, and part of this chain is shown in Figure 8. It is apparent that the sodium ions are differently sterically shielded, because Na1 has only two fairly close intermolecular contacts to an *ortho*- and *meta*-carbon atom of a neighbouring phenyl group, raising its coordination number to 4, while the sodium center Na2 additionally has two short Na···H contacts, one to a hydrogen atom of a methyl group of molecule (1) and a second to an *ortho*-H-atom of the phenyl group. Thus, the coordination number for Na2 is 6.

Figure 8. Part of the chain generated by intermolecular C···Na contacts as well as Na···H interactions for compound **4** · MeO*t*Bu



The most noticeable difference in the chains made up from **4** · OEt_2 and **4** · MeO*t*Bu molecules is that the latter allows intermolecular contacts with *ortho*- and *meta*-carbon atoms, while the former involves *meta*- and *para*-carbon atoms. The latter of these, in particular, allows for the shortest Na···C interaction (2.674 Å).

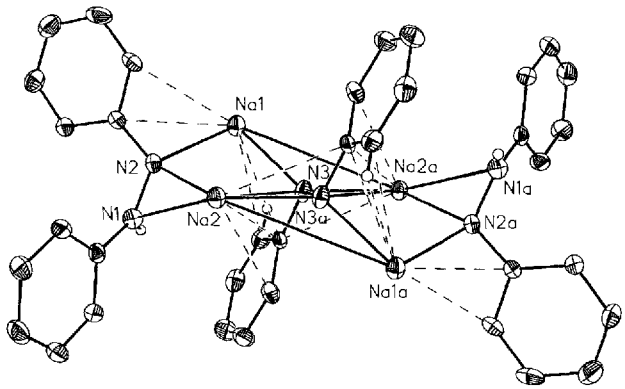
The Sodium Diphenylhydrazides 6 and 7

The red crystals of **6**, the composition of which was elucidated by X-ray structure analysis, belong to the monoclinic system, space group $P2_1/n$. There are two molecules $[NaHN_2Ph_2]_2[Na_2N_2Ph_2]$ · 4 DME in the unit cell. The molecule has a crystallographical center of symmetry at the midpoint of the central N–N bond, as shown in Figure 9. For the sake of clarity, hydrogen atoms as well as the DME molecules are omitted.

The molecule can be described as the adduct of a central disodium-*N*,*N*′-diphenylhydrazide with two molecules of sodium-*N*,*N*′-diphenylhydrazide. This results in an unusual arrangement with a central, almost planar PhN–NPh dianion. Its phenyl groups occupy *trans* positions, attached to nitrogen atoms that show a comparatively short N–N bond length of only 1.423(9) Å. This unit can be regarded as being asymmetrically bonded to two side-on coordinated sodium ions Na2/Na2a, with N3–Na2 and N3a–Na2 distances of 2.856(5) and 2.400(5) Å, respectively. The second unit, the NaPhN–NHPh moiety, exhibits a somewhat longer N–N bond [1.442(7) Å]. The phenyl groups of this unit are mutually twisted by 80.4° and this is also reflected in the C9–N1–N2–C15 torsion angle of 86.3°.

This suggests, on the basis of data collected for the previously described sodium hydrazides, that the atoms N1 and N2 are sp^2 hybridized and are present in a planar coordination sphere. Indeed, the sum of bond angles at atom N1 (neglecting the Na···N interaction) is 360°. However, the

Figure 9. ORTEP representation of the sodium hydrazide **6**; hydrogen atoms and the DME molecules are omitted for clarity; thermal ellipsoids are drawn at a 25% probability level[a]



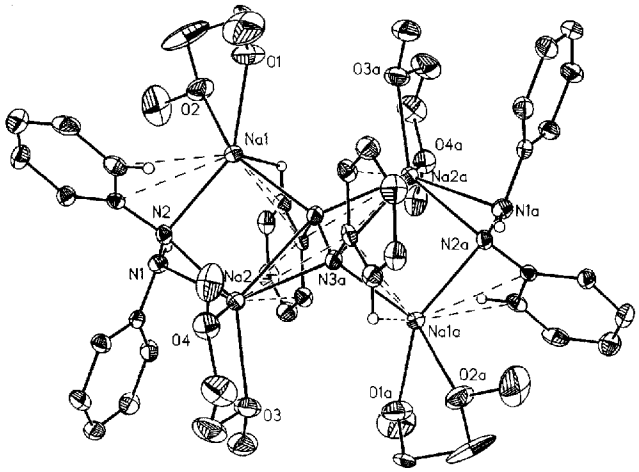
[a] Selected bond lengths [Å] and angles [°]: Na1–N2 2.421(5), Na1–N3 2.369(5), Na2–N1 2.927(5), Na2–N2 2.373(5), Na2–N3 2.856(5), Na2–N3a 2.400(5), N1–N2 1.442(7), N3–N3a 1.423(9), N1–C1 1.402(8), N2–C7 1.371(7), N3–C13 1.385(8), Na1···Na2 3.412(3), Na1···Na2a 4.158(3); C1–N1–N2 119.0(5), C7–N2–N1 112.4(4), C1–N1–Na2 87.9(3), N1–N2–Na2 97.2(3), N1–N2–Na1 118.6(3), Na2–N2–Na1 90.7(2), C7–N2–Na2 142.3(4), C7–N2–Na1 94.7(4), C13–N3–N3a 110.5(6), C13–N3–Na1 100.3(4), C13–N3–Na2 86.1(3), C13–N3–Na2a 106.8(4), Na1–N3–Na2a 121.4(2), Na3a–N3–Na2a 93.1(4), Na2–N3–Na2a 150.2(2), N2–Na1–N3 93.9(2).

nitrogen atom N2 has a pyramidal geometry. This is shown by the C15–N2–N1 bond angle of 112.4(4)° as compared to the C9–N1–N2 bond angle of 119.0(5)°, as well as the sum of bond angles at this nitrogen (325.7°), neglecting the N2–Na2 interaction. On the other hand, the bond angle Na1–N2–N1 is 118.6(3)° and the Na1–N2 distance of 2.421(5) Å is amongst the shorter Na–N contacts in molecule **6**.

These two parts of **6** are joined together, resulting in additional Na–N interactions. The Na2 atom of the $Na_2N_2Ph_2$ unit binds asymmetrically, side-on to the N1–N2 unit, while the Na1 atom of the NaPhN–NHPh substructure is in contact with only the nitrogen atom N3 of the $Na_2N_2Ph_2$ moiety. Thus, Na2 has contacts with four nitrogen atoms, in contrast to atom Na1, which has only two nitrogen atoms in its vicinity. The coordination sphere of Na2 is completed by two oxygen atoms of the DME solvent molecule [Na2–O3 2.365(5) Å, Na2–O4 2.324(5) Å], as well as by three Na···C contacts to the phenyl groups of the central PhNNPh unit, raising its coordination number to 9. Atom Na1 on the other hand, is coordinated by two nitrogen and two oxygen atoms, in addition to four carbon atoms, resulting in an overall coordination number of 8. Figure 10 depicts all these interactions to oxygen and carbon atoms by additional dotted lines.

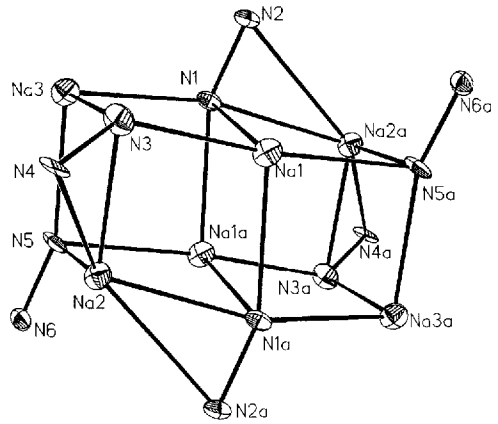
In contrast to the sodium-*N*,*N*′-diphenylhydrazide **6**, the "isomeric" sodium-*N*′,*N*′-diphenylhydrazide **7** crystallizes free of donor solvent molecules in yellow prisms from benzene solution. The triclinic crystals, space group $P\bar{1}$, have a single centrosymmetric hexameric molecule $(NaHN–NPh_2)_6$ in their unit cell. In addition, there are 3 molecules of benzene in the lattice. Hence, the composition is $(NaHN–NPh_2)_6 \cdot 3\ C_6H_6$.

Figure 10. ORTEP plot of the sodium hydrazide **6** including the DME molecules and selected H atoms; dotted lines indicate the Na···C interactions; only the H atom at nitrogen atom N1 is shown



Due to some disorder of these solvent molecules and the fact that only tiny prisms of comparatively low diffractive power were obtained, the quality of the X-ray structure determination (R = 0.16) allows only the description of the topology of this sodium hydrazide, which is depicted in Figures 11 and 12.

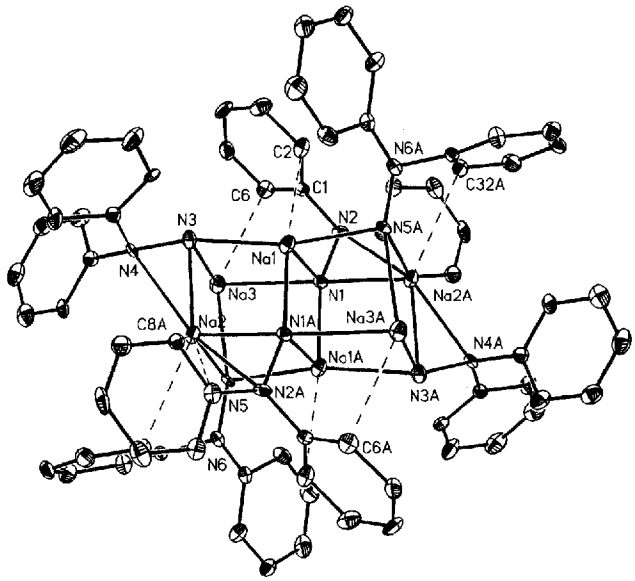
Figure 11. The core structure of $(Ph_2N-NHNa)_6$[a]



[a] Selected bond lengths [Å] and angles [°]: Na1–N3 2.44(1), Na1–N1a 2.50(1), Na1–N1 2.602(9), Na2–N3 2.39(1), Na2–N4 2.452(9), Na2–N5 2.40(1), Na2–N1a 2.50(1), Na2–N2a 2.71(1), Na3–N1 2.57(1), Na3–N3 2.32(1), Na3–N5 2.53(1), N1–N2 1.44(1), N3–N4 1.48(1), N5–N6 1.45(1); Na2–N1a–Na3 108.7(6), Na2–N1a–Na1 97.5(5), Na3–N1–Na1 79.7(3), Na3–N3–N4 121.1(7), Na2–N3–N4 74.4(5), Na2–N3–Na3 81.2(5), Na3–N3–Na1 88.2(3), Na2–N3–Na1 78.7(3), N3–N4–Na2 70.1(5), N6–N5–Na2 106.0(6), N6–N5–Na3 161.3(7), Na2–N5–Na3 77.0(3).

The molecular structure is built up from three pairs of $NaHN-NPh_2$ units. Their Na and N atoms associate in such a manner that a face-shared double-cubane structure with alternating N and Na atoms results. Two nitrogen atoms on opposite corners of the double cubane (N5, N5a) bear exohedral Ph_2N groups. Two additional pairs of Ph_2N groups are in contact with the sodium atoms Na2 and Na2a, which have a total of five nitrogen atoms as neighbours. In contrast, atoms Na1 and Na1a are tetracoordinated by four nitrogen atoms, while atoms Na3 and Na3a

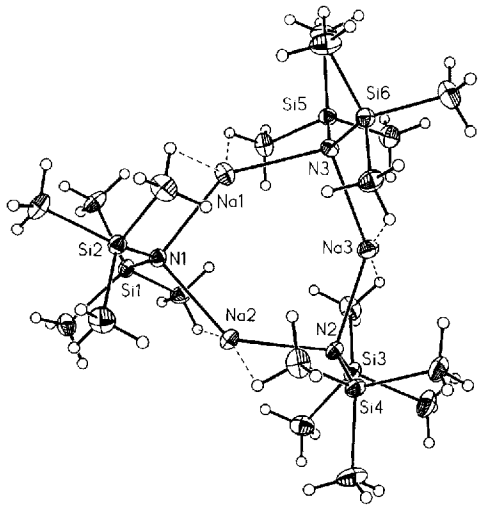
Figure 12. The molecular structure of **7** including the phenyl groups to demonstrate the intramolecular interaction of the sodium centers with the phenyl carbon atoms[a]



[a] Selected bond lengths [Å] and angles [°]: N–C 1.41–1.46(1); C7–N2–C1 117.8(3), C7–N2–N1 120.3(8), C1–N2–N1 115.2(9).

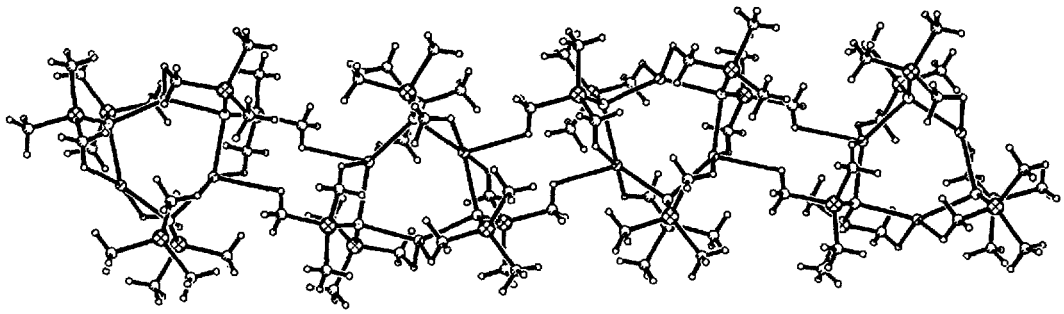
have only three nitrogen atoms as coordination partners. Even if one takes intramolecular Na···C contacts into account, atoms Na3 and Na3a are seemingly coordinatively unsaturated. This, however, is remedied by intermolecular Na3a···C contacts with the terminal Ph_2N groups of adjacent molecules, as shown in Figure 12.

Figure 13. ORTEP representation of the molecular structure of the trimeric unit of $NaN(SiMe_3)_2$; thermal ellipsoids are drawn at a 25% probability limit[a]



[a] Selected bond lengths [Å] and angles [°]: Na1–N1 2.376(8), Na1–N3 2.394(7), Na2–N2 2.358(8), Na2–N1 2.382(8), Na3–N2 2.363(8), Na3–N3 2.394(8), N–Si 1.680(8)–1.706(8); Na1–N1–Na2 100.0(3), Na2–N2–Na3 102.2(3), Na3–N3–Na1 97.7(3), N1–Na1–N3 141.8(3), N1–Na2–N2 137.6(3), N2–Na3–N3 139.8(3), Si1–N1–Si2 124.6(4), Si3–N2–Si4 126.2(4), Si5–N3–Si6 126.0(4).

Figure 14. Association of the trimeric units of $NaN(SiMe_3)_2$ in the crystal via intermolecular Na···H interaction (Na···H distances ranging from 2.613 to 2.616 Å)



The Sodium Bis(trimethylsilyl)amide $[NaN(SiMe_3)_2]_3$

This amide is formed as a by-product in reactions according to eq. (4), and crystals of good quality were obtained as colorless prisms from hexane solution. Since the dimensions of the unit cell differed from those reported in the literature (monoclinic)[5] its structure was solved by X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$ with $Z = 2$ (two trimeric units). As depicted in Figure 13, the molecular unit is built up from three monomers joined by Na–N bonds to form a slightly puckered Na_3N_3 six-membered ring system. Deviation from planarity is not pronounced, the torsion angles vary only from 5–7°.

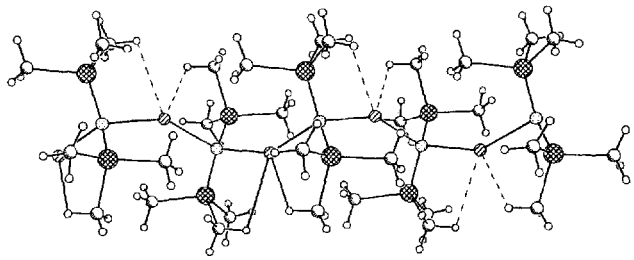
Na–N bond lengths span a range from 2.358(8) to 2.394(8) Å, while the N–Si bond lengths [1.680(8)–1.706(8) Å] can be considered as being of equal lengths. The differences in the Na–N bond lengths are associated with insignificantly different Na–N–Na and N–Na–N bond angles. Thus, the molecule deviates considerably from the point group D_{3h} expected for a symmetrical six-membered planar N_3Na_3 ring system. In contrast, the Si–N–Si bond angles span only a narrow range from 124.6(4) to 126.2(4)°.

Each Na atom is not only coordinated to two nitrogen atoms, but there are also two comparatively short intramolecular Na···H distances (2.384–2.616 Å) as well as two intermolecular Na···H interactions per molecule, bringing the coordination spheres around the sodium centers to 4 and 5, respectively. This is depicted in Figure 14.

The structure of $[NaN(SiMe_3)_2]_3$ corresponds with the structure found for the Li analogue $LiN(SiMe_3)_2$, which is also trimeric in the solid state[6]. Its structural parameters are comparable to those of $[NaN(SiMe_3)_2]_\infty$[5] as far as SiN bond lengths and SiNSi bond angles are concerned. For comparison, the chain of $NaN(SiMe_3)_2$ is shown in Figure 15[7].

However, the Na–N atoms distances are, on average longer (2.378 vs. 2.355 Å in the chain structure) and vary over a larger range (2.363–2.394 Å). On the other hand, the N–Na–N bond angles are more acute in the trimer (137.6, 139.8, 141.8°) as compared to the chain form (150.2°), while the Na–N–Na bond angles are comparable (97.7–102.2° vs. 102.0°). We note that in $[NaN(SiMe_3)_2]_3$, each sodium atom has two hydrogen atoms in its vicinity with Na···H distances ranging from 2.384–2.616 Å. The longer ones are associated with the two intermolecular Na···H distances of 2.613 Å (to Na3) and 2.616 Å (to Na2).

Figure 15. Stick-and-ball model of the previously determined structure of $NaN(SiMe_3)_2$[5]; this form of $NaN(SiMe_3)_2$ was obtained from a mesitylene solution



Discussion

The structures of the sodium hydrazides described in this study present new, and in part surprising examples of how the monomeric units associate to oligomeric molecules. In line with principles established for lithium amides is the observation that oligomerization can be inhibited by suitable donor molecules that add to the alkali metal centers preventing the formation of additional M–N interactions. The lithium hydrazide **5** is an excellent example, demonstrating that only two ether molecules are sufficient to stabilize it as a monomeric molecular entity without the help of additional Li···$\eta^n(C_6H_5)$ contacts. To date, only a few examples have been reported where diethyl ether stabilizes a monomeric lithium amide, e.g. the borylamides $(Et_2O)_2LiN(Ph)BMes_2$[8] or $(Et_2O)_2LiN(Mes)BMes_2$[9]. Compound **5** is comparable to these, as far as the bulkiness of substituents is concerned. Compared with $(Et_2O)_2LiN(Ph)BMe_2$ [Li–O: 1.932(5), 1.934(5) Å, Li–N 1.943(3) Å], the ether molecules in **5** are more strongly bonded, as is evident from the shorter Li–O distances. This is also true for the Li–N bond, which is significantly shorter by 0.04 Å.

If there is only one diethyl ether molecule per Li atom present in the hydrazide, then association to dimers or higher oligomers is observed. Thus, $(Et_2O)LiNH(Smes)$ (Smes = 2,4,6-tri-*tert*-butylphenyl)[10] is dimeric, featuring a four-membered Li_2N_2 ring system. This also holds for $[(Et_2O)LiN(CH_2Ph)_2]_2$[11] or $[(Et_2O)LiN(Ph)CH_2tBu]_2$[12],

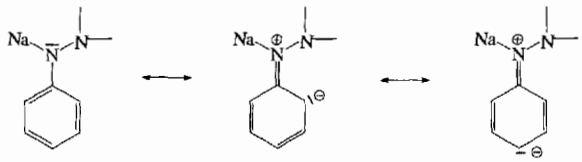
the hydrazide $[(Et_2O)LiPhN-NHSiMe_3]_2$[4f], or Ph(Li)N–NLi(Ph) · 2 OEt_2[4f]. In the first of these lithium hydrazides, the Li–O distance [1.977(6) Å] is longer than in **5**, and this is also true for the more complex lithium phenylhydrazide [1.930(6) Å]. This latter distance is, however, closer to that in **5**, probably due to the fact that tricoordinated Li centers are present in these two compounds, while the Li atom in $[(Et_2O)LiPhN-NHSiMe_3]_2$ is tetracoordinated.

Tetrahydrofuran is a stronger base than diethyl ether and better suited for stabilizing monomeric lithium amides. Typical examples are $(THF)_2LiN(SiMePh_2)_2$ or $(THF)_2LiN(SiPh_3)_2$[13] and $(THF)_2LiN(C_6F_5)SitBu_2F$[14].

To date, no monomeric lithium hydrazide solvated by THF has been reported, nor a sodium hydrazide. Thus, compound **4** · 3 THF is the first example of its kind. Removal of two solvent molecules causes association of the **4** · THF molecules into a chain structure as a result of η^3 coordination to the phenyl group of adjacent molecules. In spite of this increase in coordination, both the Na–O and Na–N bonds are shorter in **4** · THF than in **4** · 3 THF. However, when the THF molecule is replaced by a diethyl ether molecule, as in **4** · OEt_2, we note a small increase of both of these bond lengths, indicating that diethyl ether is more weakly bonded to Na than THF. This is, of course, a well-known phenomenon[1,5]. In the solid state, the molecules of **4** · OEt_2 are associated, forming chains via η^2 coordination of the phenyl group to the sodium center. The bulkier MeO*t*Bu ether in **4** · MeO*t*Bu leads to a noticeable lengthening of the Na–O distances, which approach those observed in **4** · 3 THF. The Na–N distances are even longer, and are in fact the longest in this series. Association of the molecules to chains in the solid state again occurs via η^2 coordination of adjacent phenyl groups, in this case involving an *ortho* and a *meta* position.

The most striking feature of the series of solvates of the sodium phenylhydrazide is that the nitrogen atom of the $(Me_3Si)_2N$ group is *not* involved in coordination to the sodium center. Such behaviour has also been observed for solvent-free $[Li(Ph)N-N(SiMe_3)_2]_4$[4f], but not for $[Li(Me_3Si)N-N(SiMe_3)_2]_2$[4a,4c] or $[(Et_2O)Li(Ph)N-NHSiMe_3]_2$[4f]. The preference of the Cs ion to coordinate in an η^6-manner to the phenyl group, as for instance in $[Cs(Ph)N-N(SiMe_3)_2]_\infty$, not using the donor ability of the $(Me_3Si)_2N$ group, is consistent with this structural behaviour[4f]. The reason for this striking feature is certainly not an insufficient basicity of the nitrogen atom of the $(Me_2Si)_2N$ group, as is clear from the formation of oligomeric $MN(SiMe_3)_2$ compounds (vide infra).

The N–N bond lengths of the solvates of **4** vary to some extent, but lie in the range observed for other metal organylhydrazides[4]. The nitrogen atoms can be considered as being sp^2-hybridized with small deviations of the $(Me_3Si)_2N$ group nitrogen atom toward a trigonal-pyramidal geometry. The lone pairs of electrons at the nitrogen atoms approach orthogonality, thus minimizing their electronic interaction. Electronic repulsion between the nitrogen atoms is obviously reduced by strong interaction of the phenyl group with the lone pair at its nitrogen atom, as demonstrated by short N–C bonds (1.331 to 1.336 Å) and a coplanar orientation with the NNNa plane. Thus, the forms **B** and **C** contribute significantly to the ground state of the molecules.



A **B** **C**

Comparison of the structures of **5**, **4** · 3 THF, **4** · D (D = THF, OEt_2, MeO*t*Bu) and $[(H_3N)Na(Ph)N-N(Ph)SiMe_3]_2$[4f] with those of **6** and **7** reveals the role of the bulky Me_3Si groups: they prevent oligomerization to clusters. Compound **6** represents the first example of side-on coordination of a hydrazide N_2 unit to a sodium center. However, butterfly-bonding of an N_2 unit to two metal atoms and an additional coordination of each of these two nitrogen atoms to another metal center is not uncommon in clustered lithium hydrazides, as examplified by $[Li(Me_3Si)N-NLi(SiMe_3)]_4$ and $[(Me_3Si)_2N-NLi(SiMe_3)]_2$[4]. However, the butterfly substructure in **6** is quite flat and its Na_4N_6 skeleton represents a new feature akin to the aforementioned lithium trimethylsilylhydrazide. Astonishingly, the N–N bond length of the central N–N bond in compound **6** is quite short [1.423(9) Å]. This is worthy of mention, because in the two known lithium hydrazide clusters[4e,f] the comparable N–N bonds are quite long [e.g. 1.570(3) or 1.556(2) Å]. At present we cannot give a reasonable explanation for this difference.

The sodium diphenylhydrazide $(7)_6$ also represents an interesting structure. The central Na_6N_6 core, however, has an analogy in the mixed metal amide $[Ph(tBu)C=N]_6Li_4Na_2$[16], which also possesses two face-sharing heterocubane units that can be considered as resulting from successive stacking of M_2N_2 four-membered rings. This example demonstrates the close relationships that exist between the structures of alkali metal hydrazides and amides or imides. However, due to additional functions in the hydrazides, their reactivity and structural chemistry can be expected to be even more varied.

Finally, we add a remark concerning the bonding of the ether molecules. We note that irrespective of the type of ether ligand (diethyl ether, tetrahydrofuran, monoglyme), the oxygen atom resides in a distorted trigonal-planar environment. This could be taken as evidence for sp^2 hybridization of the oxygen atoms. However, the C–O–C bond angles are close to those observed in the free ligands [e.g. for THF: ∡C–O–C = 111(2)°[17]; $O(C_2H_5)_2$: ∡C–O–C = 110(3)°[18]]. It is therefore unlikely that rehybridization at the oxygen atom occurs on coordination to the Li or Na centers in the alkali metal hydrazides[2]. In fact, the observed geometry can be readily explained by in terms of ion-dipole interactions between the alkali metal ions and the ether molecules.

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Experimental Section

All reactions were performed under an argon or nitrogen atmosphere using Schlenk techniques. Solvents were dried by conventional methods ($LiAlH_4$, sodium/diphenylketyl, P_4O_{10}) and stored under argon. $PhNH-NH_2$, $Ph_2N-NH_2 \cdot HCl$, *n*BuLi, C_6D_6, $CDCl_3$ were used as purchased. The compounds $NaN(SiMe_3)_2$[19], $PhNH-NHSiMe_3$[20], $Ph(H)N-NPh(SiMe_3)$, and $Ph_2N-NHSiMe_3$[21] were prepared according to literature methods.

Elemental analyses of the compounds were difficult due to their lability: they hydrolyse quickly and can even catch fire on exposure to air. Moreover, they lose coordinated solvent quite readily.

Lithium N,N'-Diphenyl-N'-trimethylsilylhydrazide–Diethyl Ether (1/2) (**5**): A solution of *n*BuLi in hexane (6.4 ml, 10.5 mmol) was slowly dropped into a stirred solution of $Ph(H)N-NPh(SiMe_3)$ (2.69 g, 10.5 mmol) in benzene (100 ml) and tetrahydrofuran (0.5 ml). The mixture was refluxed until butane evolution had ceased. A yellow, microcrystalline precipitate formed within 5 d (2.13 g). Crystallization from diethyl ether at −20°C yielded colorless needles of m.p. 55–56°C (dec.), which were suitable for an X-ray structure investigation. – ^1H NMR (C_6D_6): δ = 0.32 (s, 9H, $SiMe_3$), 0.96 (t, 12H, OCH_2Me), 3.11 (q, 8H, OCH_2), 6.44–6.78 (m, 4H, Ph), 6.92–7.28 (m, 6H, Ph). – ^{13}C NMR (C_6D_6): δ = 1.16 ($SiMe_3$), 14.73 (OCH_2Me), 65.40 (OCH_2), 113.37 (Ph), 115.24 (Ph), 117.78 (Ph), 129.48 (*m*-CH), 151.95 (*i*-CH), 162.32 (*i*-CH); ^7Li NMR: δ = 0.63. – $C_{15}H_{19}N_2SiLi \cdot 2\ Et_2O$ ($C_{23}H_{39}N_2O_2SiLi$) (410.60): calcd. C 67.28, H 9.57, N 6.82; found C 66.15, H 9.36, N 7.14.

Sodium N-Phenyl-N',N'-bis(trimethylsilyl)hydrazide–Tetrahydrofuran (1/3) (**4a**): *N*-Phenyl-*N'*,*N'*-bis(trimethylsilyl)hydrazide (2.589 g, 10.2 mmol) was dissolved in a mixture of hexane (30 ml) and tetrahydrofuran (3 ml). The solution was stirred and a suspension of $NaN(SiMe_3)_2$ (1.869 g, 10.2 mmol) in hexane (20 ml) was added. The resulting mixture was heated to reflux for 40 h. The insoluble material, which *proved* to be **4a**, was then filtered off from the orange-colored solution, which was kept at 6°C. Single crystals of m.p. 182°C (dec.) separated from this solution. The bulk of **4a** could not be recrystallized from hexane, benzene, or toluene in order to obtain it in a crystalline state, free of THF. – $C_{12}H_{23}N_2Si_2Na \cdot 3$ THF ($C_{24}H_{47}N_2O_3Si_2Na$) (490.81): calcd. C 58.73, H 9.65, N 5.71; found C 55.90, H 9.65, N 6.14.

Sodium N-Phenyl-N',N'-bis(trimethylsilyl)hydrazide–Tetrahydrofuran (**4b**): $PhHN-N(SiMe_3)_2$ (2.01 g, 8 mmol) was dissolved in a mixture of hexane (20 ml) and tetrahydrofuran (2 ml). A solution of $NaN(SiMe_3)_2$ (1.41 g, 8 mmol) in benzene (20 ml) was added with stirring over a period of 1 h. After heating the mixture to reflux for 3 h, the solid material that had formed was filtered off, leaving a brown filtrate. At 6°C, the product separated as a colorless, microcrystalline material, which also contained a few single crystals suitable for an X-ray structure determination.

Sodium N-Phenyl-N',N'-bis(trimethylsilyl)hydrazide–Diethyl Ether (**4c**): A solution of $NaN(SiMe_3)_2$ (1.86 g, 10.0 mmol) in benzene (20 ml) was slowly dropped into a stirred solution of $PhHN-N(SiMe_3)_2$ (2.53 g, 10.0 mmol) in benzene (20 ml) and tetrahydrofuran (0.3 ml). The mixture turned brown on refluxing for 2 h. It was then passed through a G3-frit and the filtrate was stored at 6°C. A yellow, microcrystalline precipitate formed within 4 d (1.95 g). Crystallization from diethyl ether at −20°C yielded orange-colored needles of m.p. 147°C (dec.), which were suitable for an X-ray structure investigation. – $C_{12}H_{23}N_2Si_2Na \cdot OC_4H_{10}$ (348.62): calcd. C 55.13, H 9.54, N 8.04; found C 50.32, H 8.51, N 8.53.

Sodium N-Phenyl-N',N'-bis(trimethylsilyl)hydrazide–tert-Butyl Methyl Ether (**4d**): As described for compound **4c**, a yellow, microcrystalline sodium salt was isolated and was crystallized from a minimum amount of hot diveron. Storage of the orange-colored solution at −20°C produced colorless crystals of m.p. 79°C (dec.). Yield 2.02 g (67%). – ^1H NMR (C_6D_6): δ = 0.13 (s, 18H, $SiMe_3$), 1.04 (s, 9H, CMe_3), 3.00 (s, 3H, MeO), 5.91 [t, $^3J(H,H)$ = 6.9 Hz, 1H, *p*-CH], 6.41 [d, $^3J(H,H)$ = 6.9 Hz, 2H, *o*-CH], 6.95 (m, 2H, *m*-CH). – ^{29}Si NMR: δ = −2.46. – $C_{12}H_{23}N_2Si_2Na \cdot OC_5H_{12}$ (362.64): calcd. C 56.31, H 9.73, N 7.72; found C 56.17, H 8.57, N 8.01.

Bis(sodium N,N'-diphenylhydrazide)–Disodium N,N'-Diphenylhydrazide–Dimethoxyethane (1/1/4) (**6**): A solution of $NaN(SiMe_3)_2$ (1.91 g, 10.4 mmol) in DME (10 ml) was added to a stirred solution of $PhHN-N(Ph)SiMe_3$ (2.66 g, 10.4 mmol) in 30 ml of DME. The solution turned intensely red after refluxing for 12 h. Red crystals separated within a few hours on cooling the solution to −20°C. Analysis by ^{29}Si-NMR gave evidence for the formation of $HN(SiMe_3)_2$ (δ = 2.53) and $N(SiMe_3)_3$ (δ = 0.88). The crystals were filtered off and recrystallized from DME. Red single crystals separated at −20°C (m.p. >237°C, dec.). The yield was not determined. – ^1H NMR (C_6D_6): δ = 3.05 (s, 24H, MeO), 3.20 (s, 16H, OCH_2), 4.82 (s, 2H, NH), 6.38–7.23 (m, 30H, Ph). – $C_{52}H_{72}N_6O_8Na_4$ (1001.14): calcd. C 62.39, H 7.25, N 8.39; found C 59.29, H 6.42, N 8.33.

Sodium N',N'-Diphenylhydrazide (**7**): A suspension of $NaNH_2$ (410 mg, 10.4 mmol) in 20 ml of benzene was added over a period of 30 min to a solution of $Ph_2N-NHSiMe_3$ (2.67 g, 10.4 mmol) in benzene (40 ml). This mixture was refluxed until NH_3 evolution had ceased. Analysis of the solution by ^{29}Si NMR gave evidence for the formation of $NaN(SiMe_3)_2$ (δ = −14.69). A trace amount of undissolved material was filtered off from the deep-red mixture, which was subsequently stored at 6°C. After several days, yellow crystals had formed, which were isolated. They were identified as **7** by X-ray structure analysis.

A second reaction was performed using the same molar ratio according to eq. (4). A suspension of $NaNH_2$ (620 mg, 15.9 mmol) in 20 ml of benzene was added slowly to a stirred solution of $Ph_2N-NHSiMe_3$ (2.58 g, 10.1 mmol) in benzene (40 ml). This mixture was refluxed until NH_3 evolution (titration: 5.3 mmol) had ceased. Analysis of the solution by ^{29}Si NMR gave evidence for the formation of $NaN(SiMe_3)_2$ (δ = −14.69). Storage of the deep-red mixture at 6°C resulted in the deposition of a yellow, microcrystalline precipitate. Yield 0.92 g (45%). – ^{13}C NMR (C_6D_6): δ = 115.21, 118.25 (*o*-CH), 121.47 (*p*-CH), 129.46, 130.6 (*m*-CH).

X-ray Structure Analysis (Table 2): All crystals had to be handled carefully under an atomosphere of argon, preferably in a glove box or in a closed Schlenk system. Once the selected crystal was covered with oxygen-free perfluoroether oil, it was easily mounted in a glass capillary and transferred to the goniometer head of a Siemens P4 diffractometer (Mo-K_α radiation, λ = 0.71063 Å, graphite monochromator) equipped with a CCD detector, and cooled in the cold stream of the Siemens LT2 device. Determination of the unit cell parameters was performed with the data of reflections collected from a total of 60 frames, taking 15 frames each with ω rotation of 0.3° for four different settings. The axes calculated for the unit cell were checked by recording the reflections in the 100, 010 and 001 planes. The final unit cell param-

Table 2. Data related to the X-ray structure determinations

Compound	4a	4b	4c	4d	5	6	7	8
Chem. formula	$C_{24}H_{47}N_2NaO_3Si$	$C_{16}H_{31}N_2NaOSi_2$	$C_{16}H_{33}N_2NaOSi_2$	$C_{17}H_{35}N_2NaOSi_2$	$C_{23}H_{39}LiN_2O_2Si$	$C_{26}H_{36}N_3Na_2O_4$	$C_{51}H_{45}N_6Na_3$	$C_{18}H_{54}N_3Na_3Si_6$
Form wght.	490.80	346.60	348.61	362.64	410.59	500.56	810.90	550.15
Cryst size [mm]	0.15x0.2x0.2	0.1x0.2x0.3	0.3x0.3x0.4	0.2x0.2x0.3	0.25x0.3x0.6	0.05x0.05x0.17	0.07x0.1x0.15	0.1x0.2x0.2
Cryst system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P2(1)/m	Pca2(1)	P2(1)/n	P2(1)	P-1	P2(1)/n	P-1	P-1
a, [Å]	10.428(25)	11.473(7)	9.10330(10)	13.1036(2)	9.732(3)	11.1143(3)	9.4866(8)	8.7486(2)
b, [Å]	14.705(22)	8.825(4)	20.71000(10)	12.3341(2)	16.476(3)	20.0712(4)	13.4815(12)	12.5014(4)
c, [Å]	10.816(15)	19.824(9)	11.7700(2)	14.5071(3)	16.970(5)	13.0454(3)	17.9986(12)	16.8295(5)
a, [°]	90.00	90.00	90.00	90.00	101.885(1)	90.00	102.370(1)	102.280(1)
b, [°]	114.28(12)	90.00	102.76	109.764(1)	95.544(8)	104.8260(1	99.544(2)	94.399(2)
g, [°]	90.00	90.00	90.00	90.00	100.829(1)	90.00	93.444(1)	105.550(1)
V, [Å^3]	1511.8(48)	2007.1(17)	2164.19(5)	2206.54(7)	2589.2(12)	2813.25(11)	2206.4(3)	1715.12(8)
Z	2	4	4	4	4	4	2	2
ρ(calc), [Mg/m^3]	1.078	1.147	1.070	1.092	1.053	1.182	1.221	1.065
μ [mm^{-1}]	0.156	0.201	0.187	0.186	0.109	0.106	0.098	0.292
F(000)	536	752	760	792	896	1068	852	600
Index range	-13≤h≤13 -18≤k≤18 -8 ≤l≤8	-14≤h≤13 -10≤k≤11 -23≤l≤22	-11≤h≤10 -26≤k≤26 -14≤l≤14	-15≤h≤15 -15≤k≤15 -18≤l≤19	-11≤h≤11 -21≤k≤14 -20≤l≤20	-13≤h≤14 -25≤k≤25 -16≤l≤16	-12≤h≤12 -16≤k≤16 -24≤l≤14	-9 ≤h≤11 -15≤k≤15 -21≤l≤21
2 θ [°]	54.56	54.40	58.32	58.48	58.04	58.12	57.56	58.42
Temp, [K]	193	183(2)	193	183(2)	168	173	173(2)	173(2)
Refl. collected	7857	9977	11811	12871	14358	15360	12245	9860
Refl. unique	2482	3854	4130	8405	7798	4930	6769	5326
Refl. observed (4σ)	1051	2012	2120	5398	5894	2046	3129	2546
R (int.)	0.0798	0.1165	0.1237	0.0552	0.0591	0.1767	0.1619	0.0901
No. variables	164	205	208	435	566	340	541	289
Weighting scheme[1] x/y	0.2080/0.8646	0.0000/3.5143	0.0860/2.0640	0.0818/4.9006	0.0332/3.1271	0.0000/5.5508	0.0000/17.7419	0.1041/10.5889
GOOF	1.131	1.171	1.209	1.107	1.213	1.259	1.336	1.129
Final R (4σ)	0.1074	0.0584	0.0753	0.0764	0.0678	0.0982	0.1686	0.0868
Final wR2	0.2948	0.1069	0.1864	0.1827	0.1422	0.1490	0.2900	0.2195
Larg. res. peak [e/Å^3]	0.318	0.250	0.260	1.106	0.276	0.282	0.421	0.809

[1] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$

eters were calculated from the whole set of observed reflections. Data collection was performed in a standard manner with an exposure time of 10 s per frame and a 0.3° difference in φ-orientation. However, for the weakly diffracting compounds **6** and **7** the exposure time was 20 and 30 s, respectively, per frame. Data reduction was performed with the program SAINT[22] and the structure was solved by direct methods or by the sharpened Patterson method as implemented in the SHELXTL system[23]. Either this program or the SHELX93 program[24] was used for the final refinement. All nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically in calculated positions as a riding model. The correct absolute configuration of compound **4** · THF was checked by its Flack parameter. Further details of the crystal structure determinations are deposited at the Cambridge Crystallographic Data Centre and may be obtained by quoting the depository numbers CCDC-100366, the names of the authors, and the journal citation.

☆ Dedicated to Professor Dr. *Walter Siebert* on the occasion of his 60th birthday.

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