Bent phenyl groups in lithiosilanes—crystal structures and interpretation of this unanticipated feature†

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Based on the crystal structures of PMDTA coordinated lithiosilanes, the bend of aromatic substituents in anionic group fourteen and neutral group fifteen compounds (third row and higher) is explained by means of quantum chemical calculations, which indicate the deformation to be a result of Pauli-repulsion of the electrons in the occupied frontier orbitals.

Coordination and synthetic chemistry is often based on molecules with a lone-pair as the reactive site. Amongst the most familiar representatives are group 15 compounds with coordination number three and the iso-electronic anionic group 14 systems.[1] Due to eased crystallisation or facile synthetic access, many of these building blocks bear aromatic substituents at the central element.[2] As part of our studies on phenyl substituted lithiosilanes,[3] we observed a systematic and so far unrecognized bending of the phenyl group (torsional angle Si–C_i–C_o–C_m $<<$ 180°).[4] Structural research also showed that all higher homologous elements of silicon (R_2PhEl^-, El = Si, Ge, Sn, Pb) and group 15 systems (R_2PhEl, El = P, As, Sb, Bi) are affected by this deformation—yet, neither carbon nor nitrogen show this bend.

What differs carbon systems (benzyllithiums) from the higher homologues (*e.g.* phenyl substituted silyllithiums)? The planar geometry dominating in benzyllithiums (El = C)[5] is changed to a significant pyramidalization in all higher homologues. Thus, the lone pair in silyllithiums has a considerably high s-character, whereas it is supposed to be in a p-orbital in benzyllithiums. Based on experimental and theoretical investigations, we herein present the explanation for the bent phenyl groups. As the deformation is particularly pronounced in lithiosilanes, we circumscribe in the following discussion on these compounds.

To accomplish a detailed study of the bent arenes, we synthesized a series of phenyl substituted lithiosilanes. Sufficient crystal quality was of crucial necessity for the following discussion to exclude deformation due to disorder or bad crystal quality. To minimize sterical influences of the ligand at lithium, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylene-triamine (PMDTA) was chosen as it is the smallest commonly used triamine to saturate all coordination sites at lithium. The bis(diethylamino)-substituted lithiosilane **1** (Fig. 1) was selected to examine the influence of a highly electronegative substituent at silicon on the bent structure of the arene. Though the deformation is more pronounced in **1**, the solely organyl substituted compounds **2** and **3** (Fig. 2) exhibit the bent arenes likewise.

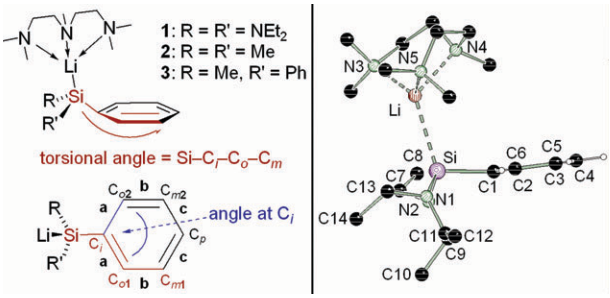

Fig. 1 Scheme of the bent phenyl substituents in lithiosilanes and the deformation within the ring (left). Molecular structure of $(Et_2N)_2PhSiLi \cdot PMDTA$ (**1**, right) in the crystal (some hydrogens omitted for clarity). Selected bond lengths [Å] and angles [°] of **1**: C(1)–Si 1.9364(13), Li–Si 2.684(2), C(7)–N(1)–C(9) 113.93(11), C(7)–N(1)–Si 120.75(9), C(9)–N(1)–Si 125.29(8), C(11)–N(2)–C(13) 113.14(11), C(11)–N(2)–Si 124.00(9), C(13)–N(2)–Si 116.85(9).

The lithiosilanes **1** and **2** crystallized in the monoclinic crystal system (space group: **1** $P2_1/c$; **2** $C2/c$), **3** in the orthorhombic crystal system (space group: *F*dd2).[6] The central structural motif is a tetrahedral four-coordinate lithium with Si–Li contacts between 2.628(4) Å (**2**) and 2.684(2) Å (**1**). The sum of the C–Si–R (R = NEt_2, Me or Ph) angles have values of 311.7° (**1**), 305.0° (**2**) and 302.0° (**3**) and thus are in the range of other lithiated silanes.[7] All systems show a significantly longer Si–C_i distance compared to the average bond lengths of

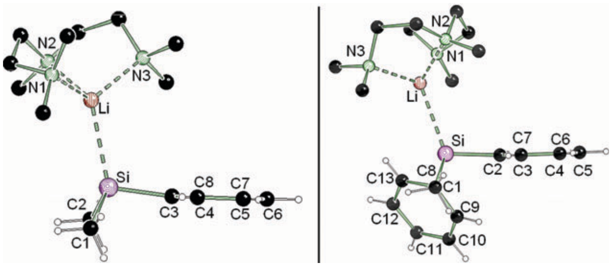

Fig. 2 Molecular structures of $Me_2PhSiLi \cdot PMDTA$ (**2**, left) and $Ph_2MeSiLi \cdot PMDTA$ (**3**, right) in the crystal (some hydrogens omitted for clarity). Selected bond lengths [Å] and angles [°] of **2**: C(1)–Si 1.927(3), C(2)–Si 1.930(3), C(3)–Si 1.918(3), Li–Si 2.628(4), C(3)–Si–Li 109.40(13), C(3)–Si–C(1) 101.35(12), C(3)–Si–C(2) 101.55(12), C(1)–Si–C(2) 102.10(13); **3**: C(1)–Si 1.943(3), C(2)–Si 1.938(3), C(8)–Si 1.946(3), Li–Si 2.663(5), C(2)–Si–C(1) 100.29(14), C(2)–Si–C(8) 100.71(12), C(1)–Si–C(8) 100.96(14), C(2)–Si–Li 111.61(15), C(1)–Si–Li 124.03(15), C(8)–Si–Li 115.85(13).

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† Electronic supplementary information (ESI) available: Crystallographic data for CCDC 666392 (**1**), 666394 (**2**) and 666393 (**3**) and experimental and computational data. For ESI and crystallographic data in CIF or other electronic format see. See DOI: 10.1039/b802211a

Table 1 Bond lengths a, b and c, angles at C_i and torsional angles Si–C_i–C_o–C_m of the three lithiosilanes **1**, **2** and **3** (negative values: Si–C_i–C_{o1}–C_{m1}; positive values: Si–C_i–C_{o2}–C_{m2}; see Fig. 1)

Lithiosilane	a/Å	b/Å	c/Å	Angle at C_i/°	Torsional angle (Si–C_i–C_o–C_m)/°
1	1.403 (2)	1.397 (2)	1.380 (2)	115.69 (0.11)	±170.5(0.10)
2	1.404 (4)	1.381 (4)	1.373 (5)	114.61 (0.25)	−172.9(0.25)/+172.0(0.23)
3	1.403 (4)	1.374 (5)	1.394 (5)	115.19 (0.26)	−175.9(0.28)/+176.3(0.27)
	1.395 (4)	1.393 (4)	1.377 (5)	116.08 (0.29)	−178.6(0.26)/+179.4(0.25)

a Si–C single bond [about 1.89 Å;[3d] **1**: 1.9364(13); **2**: 1.918(3); **3**: 1.938(3) and 1.946(3)]. Both nitrogen atoms of **1** show an almost planar environment (N1: 360.0°; N2: 354.0°), comparable to other amino-functionalized lithiosilanes.[3a,d]

The values for the angles at C_i of 115.69(0.11)° (**1**), 114.61(0.25)° (**2**) and 115.19(0.26)°/116.08(0.29)° (**3**), respectively, differ significantly from the ideal angle of a non-deformed aromatic substituent (120°). This phenomenon was discussed based on theoretical results by Domenicano *et al.* and can be explained by Bent's rule.[8] Furthermore, due to the σ-donating capability of silicon, the aromatic bond lengths decrease with increasing distance to the silicon ($a > b > c$, Table 1).

The torsional angles Si–C_i–C_o–C_m of **1**, **2** and **3** systematically fall under the expected angle of 180° (see Table 1). In particular, the two phenyl groups of **3** attract attention, as one of the two aromatic substituents is clearly more bent than the second (average: 176.1° *vs.* 179.0°). Furthermore, the deformed aromatic substituents are bent, without exception, *towards* the lithium. Structural research in the Cambridge Structural Database[9] indicated that all known solid-state structures of phenyl substituted lithiosilanes show this bend.[3a,d,10] Moreover, not only the torsional angles El–C_i–C_o–C_m of the silicon compounds, but of all higher homologues (R_2PhElLi, El = Ge, Sn and Pb)[11] and even those of neutral group 15 compounds with a central lone pair (R_2PhEl, El = P, As, Sb, Bi)[12] are affected and are significantly smaller than 180°. Intuitively, based on simple steric concepts, it is expected that the substituents try to avoid each other by changing the angles at silicon or "propeller type" arrangement but *without* the bending of the phenyl ring at C_i.

What are the reasons for this unanticipated structural deformation of the aromatic substituents? Based on the experimental data, two model compounds were constructed and examined by means of quantum chemical calculations [B3LYP/6-31+G(d)].[13] Both model systems, $Ph(Me_2N)_2SiLi\cdot$PMDTA (**A**, model system for **1**) as well as $PhMe_2SiLi\cdot$PMDTA (**B**, model system for **2**) show a significant bend of their phenyl substituent (**A**: −171.1/171.4; **B**: ±175.0°). Also, all other deformations (bond lengths, angle at C_i) are in accordance with the crystal data. Moreover, further calculations on the anionic model system $(Me_2N)_2PhSi^-$ (**C**) indicate, that even the silyl anion has a bent phenyl substituent (torsional angle: ±170.6°). Therefore, neither the lithium nor its ligand can be responsible for the deformation. As a result, the deformed aromatic substituents of the solid state structures are confirmed by gas phase calculations and thus can not be explained by disorder, bad crystal quality or libration.

Subsequent natural bond orbital (NBO) analysis of the calculated systems revealed that the "lone pair" (HOMO) on each silicon has a considerably high s-character, especially with the electronegative nitrogen of the amino substituents (**A**: s 53.19%, p 46.79%; **B**: s 48.08%, p 51.92%; **C**: s 59.92%, p 40.08).

Fig. 3 shows exemplarily two of the calculated frontier orbitals of the model compound **A** (the general shape is identical to the frontier orbitals of **B** and **C**). The high lying HOMO of all lithiosilanes is predominantly located at silicon, with the main part directed to the lithium. The highest occupied orbital located at the arene (HOMO–3 for **A** and **C**; HOMO–1 for **B**) is clearly deformed compared to an undisturbed aromatic group possessing a symmetrical distribution. The deformation is a result of Pauli-repulsion between the electrons located in the occupied frontier orbitals—resulting, for example, in elongated Si–C_i bonds of all three compounds in the experiment. Thus, the Pauli-repulsion is minimized by the bending and an unsymmetrical distribution of the frontier orbitals located at the arene: the part of the orbitals on the same side as the "s-orbital" is decreased, the part below the ring is increased (see Fig. 4).[15]

The repulsion is most pronounced if the occupied frontier orbital at silicon possesses an almost parallel orientation to the occupied orbital at the arene. Sterical effects can prevent this crucial, spatial orientation of the occupied frontier orbitals resulting in less pronounced bent arenes. Hence, only one phenyl substituent is significantly bent in bulky systems like **3**. Increasing the s-character of the "lone-pair" by nitrogen substituents at silicon results in a more bent phenyl ring. Therefore, the bend is most pronounced in the bis(diethylamino)-substituted lithiosilane **1**.

Based on these explanations, it is understandable that all corresponding heavier homologues of group 14 and 15 show this deformation likewise if their "lone pair" (with considerable high s-character) and the occupied frontier orbital located at the arene possess the adequate orientation.

In conclusion, we describe herein a special feature of silylanions based on the crystal structures of PMDTA coordinated lithiosilanes. Due to Pauli-repulsion of the electrons in the high lying "s-orbital" at the central element and the highest occupied orbital at the arene, the torsional angles of all phenyl groups are significantly smaller than 180°. All higher homologous, anionic species of silicon (R_2PhEl^-, El = Ge, Sn, Pb) and group 15 systems with coordination number three (R_2ElPh, El = P, As, Sb, Bi) show the same deformation. Forming a directed bond out of the lone-pair, such as in substitution reactions of anionic group 14 species or the coordination of phosphanes or its higher homologues, results in a decrease of the Pauli-repulsion. This can contribute to the driving force of these reactions and thus support the understanding of these processes.

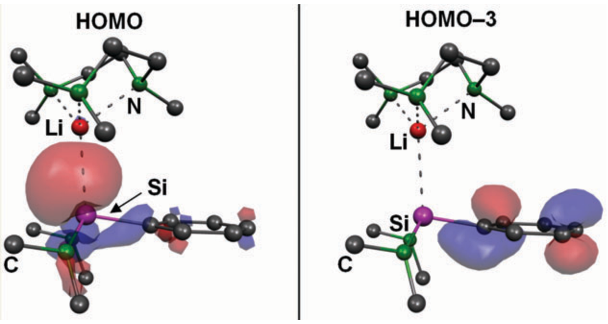

Fig. 3 Energy optimized structure [B3LYP/6-31 + G(d)] of the model compound $Ph(Me_2N)_2SiLi \cdot PMDTA$ (**A**); visualization of the HOMO (left), HOMO–3 (right).[14]

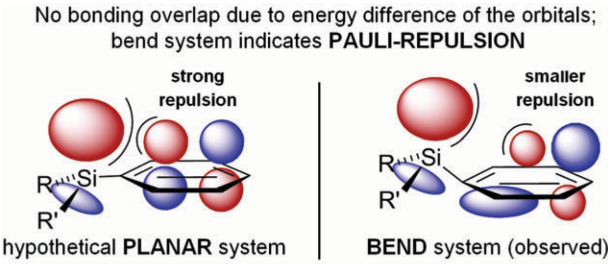

Fig. 4 Schemata of some frontier orbitals of hypothetical planar (left) and observed bend (right) phenyl substituents; combination of the HOMO and the highest occupied orbital located at the arene.

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