The Most Stable SiH_3Li Structure is Inverted

Paul von Ragué Schleyer* and Timothy Clark

Institut für Organische Chemie der Friedrich-Alexander-Universität, Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany

Because of more favourable electrostatic interactions in the ion pair, $SiH_3^-Li^+$, the inverted C_{3v} geometry of silyl-lithium (**2**) is calculated to be 2.4 kcal/mol (MP4/SDTQ/6–31G**//6–31G* + ZPE) more stable than the 'tetrahedral' (C_{3v}) isomer (**3**); the 13.5 kcal/mol barrier separating (**2**) and (**3**) involves movement of Li^+ from one side of the SiH_3^- moiety to the other. (1 cal = 4.184 J.)

Bicyclo[1.1.1]propellane (**1**) is a striking example of a molecule with inverted tetraco-ordinate carbon atoms, which have been the subject of much recent interest.[1,2] While the nature of the bonding in such species is intriguing,[2] the inverted geometries are achieved only at the cost of a great deal of deformation strain. Silyl-lithium[3] is, however, likely to be the simplest molecule that prefers an inverted C_{3v} geometry (**2**) over the conventional van't Hoff C_{3v} structure (**3**).

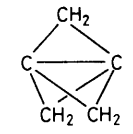
As we have shown previously, a large number of simple methane[4] and silane[5] derivatives, containing an alkali metal and at least one halogen substituent (carbenoids and their relatives), adopt inverted structures *naturally*; these are preferred energetically over the 'tetrahedral' alternatives. The 'inside-out' isomer of CCl_3Li (**4**), although no longer indicated to be the global energy minimum,[6] illustrates the point. The relatively low energy of this geometry is due largely to electrostatic Li^+–Cl^- interactions in the $CCl_3^-Li^+$ ion pair. The negative charge resides on the chlorine atoms since these are more electronegative than carbon. Similarly, the negative charge in SiH_3^-, despite its conventional formal assignment to silicon, is localized on the three hydrogens. Hence, we reasoned that structure (**2**) for silyl-lithium should be favourable electrostatically. An *ab initio* examination of the SiH_3Li potential energy surface confirming this prediction is the subject of this report.

After preliminary investigations at lower theoretical levels, the final geometries shown in (**2**), (**3**), and (**5**)—(**9**) were obtained by full optimization with the 6–31G* polarization

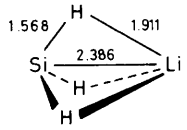
Table 1. Total (hartrees), zero point, and final relative energies (kcal/mol) of SiH_3Li species (6–31G* geometries). 1 Hartree = 2625.544 kJ.

Species		6–31G*[a]	ZPE[b]	MP4SDTQ/ 6–31G**	Dipole moment	Relative energy[c]
(**2**),	C_{3v}	298.07356[0]	15.2	298.22567	6.5	0.0
(**3**),	C_{3v}	298.07968[0]	15.6	298.22243	7.4	2.4
(**5**),	C_{3v}	298.02688[1]	14.4	298.18210	6.0	24.5
(**6**),	C_{2v}	298.00413[2]	14.7	298.157795	5.3	40.0
(**7**),	C_s	298.03612[2]	13.9	—	10.7	(26.1)
(**8**),	C_s	298.06446	—	—	—	(9.6)
(**9**),	C_1	298.05807[1]	14.6	298.20573	6.0	13.5
(**10**),	C_s	298.05695[2]	14.0	298.20339	6.2	14.9

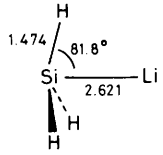
[a] The number of imaginary frequencies is given in square brackets. [b] Zero point energies in kcal/mol, unscaled. [c] Final relative energies in kcal/mol obtained from the MP4/6–31G** data corrected for the ZPE differences scaled by 0.9. Values in parentheses are at 6–31G*.



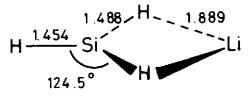
(**1**), C_{3v}



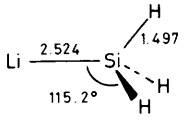
(**2**), C_{3v} [0]



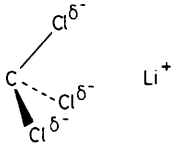
(**5**), C_{3v} [1]



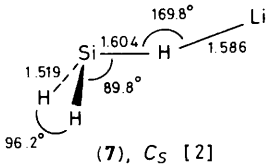
(**6**), C_{2v} [2]



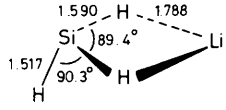
(**3**), C_{3v} [0]



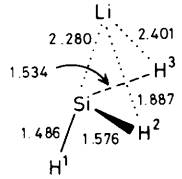
(**4**)



(**7**), C_S [2]



(**8**), C_S
(SiH_2Li held planar)



(**9**), C_1 [1]

∠ H^1SiH^2 = 98.7°

∠ H^1SiH^3 = 101.4°

∠ H^2SiH^3 = 90.2°

basis set,† which was also employed for the frequency analyses to characterise each stationary point by the number of negative eigenvalues (shown in square brackets) of the force constant (Hessian) matrix.[4b] On this basis, both (**2**) and (**3**) are indicated to be minima. Consequently, transition structures ('states') separating these two isomers were sought. The simplest process, inversion of the silyl anion moiety in C_{3v} symmetry, did yield a geometry with a single negative eigenvalue (**5**), but this proved to be relatively high in energy (Table 1). Likewise, (**6**), which is of interest with regard to the planar tetraco-ordination problem,[7] is also unfavourable and is not a true transition structure, since it possesses two negative eigenvalues.

Since the pyramidal inversion barrier of the silyl anion is quite high, 26 kcal/mol,[8]‡ pathways in which the silyl anion moiety remains more or less rigid and the lithium counter-ion wanders over the surface are more favourable for the interconversion of (**2**) and (**3**). In C_s symmetry, this amounts to a rotation of Li^+ around the SiH_3^- unit; the cation can pass by a single hydrogen (**7**) or between two hydrogens (**8**); (**7**) corresponds to a stationary point with two negative eigenvalues. Although considerably lower in energy, (**8**) could only be calculated by imposing local C_{2v} symmetry onto the $Si(H)_2Li$ moiety. In C_s symmetry, a second stationary point (**10**) [related to (**9**), but not shown] has Li^+ on one of the SiH_2 triangular faces, but this also had two negative eigenvalues. The true transition structure (**9**) has C_1 symmetry, and was finally located by means of Baker's EF optimization procedure.[9]

The final energies of all these SiH_3Li species (Table 1) were calculated with the 6–31G* geometries at the MP4SDTQ/6–31G** level, with a correction for zero point energy. Although not favoured at SCF levels, the inverted SiH_3Li structure (**2**) is 2.4 kcal/mol more stable than (**3**). The best interconversion pathway involves transition structure (**9**) which lies 13.5 kcal/mol higher in energy than (**2**). This barrier should be high enough to permit observation of both isomers, (**2**) and (**3**), in matrix isolation.

In effect, the higher co-ordination of lithium in (**2**) is responsible for its greater stability relative to (**3**). As is shown by model MNDO calculations, donor solvents will solvate (**3**) better than (**2**).[10] Hence, the stability order should be reversed in solution. The hydrogens in SiH_3Li are essential for the inverted structure. Consequently, lithiated alkylsilanes, like $LiSiMe_3$, favour 'tetrahedral' geometries.[11]

Two isomers are also exhibited by silylsodium,[12] but the geometry corresponding to (**3**) is 1 kcal/mol more stable than that related to (**2**). In three co-ordinate molecules, the inverted AlH_2Li (C_{2v}) structure is favoured over the regular

† The Gaussian 82 series of programs and the standard theoretical levels [see ref. 4(b)] were employed.

‡ 1 cal = 4.184 J.

$LiAlH_2$ (C_{2v}) geometry. We will report these results[13] later along with a more general survey of inverted structures.

Finally, a comment on the nature of Si–Li bonding, which is of current interest.[14] Natural population analysis (NPA) using natural localized molecular orbitals (NLMO)[15] indicates the lithium charges to be +0.73 in (**3**) and higher in (**2**), +0.90, and in (**9**), +0.93. The charges on hydrogen (−0.36) and on silicon (+0.18) in (**2**) confirm the electrostatic bonding model. The small NLMO/NPA bond index of 0.27 (which measures the number of shared electrons) also indicates the degree of Li–Si covalent bonding in (**3**) to be small. The covalent contributions to the bonding in (**2**) are much smaller (NLMO/NPA bond indexes: Li–H, 0.02; Si–Li, 0.04). Like the C–Li bond,[15] the Si–Li bond is essentially ionic, even in the regular structures like (**3**). Minor covalent contribution may help explain the Si–Li n.m.r. couplings,[13] but 'covalent' descriptions are misleading.

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