Structures and Energies of the Lithiated Silanes

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Preliminary *ab initio* calculations for the entire series of lithiated silanes $SiH_{4-n}Li_n$ are reported. Tetrahedral and planar structures of these species are fully optimized and the resulting tetrahedral–planar energy differences are estimated and compared with those of the lithiated methanes. Basis set effects on the calculated structures of lithiated silanes are discussed. In addition performance of the semiempirical MNDO method in the case of the silicon–lithium systems considered is assessed.

The geometries of organolithium compounds have been the subject of much theoretical interest.[1] In fact, theoretical predictions are considered to be one of the best sources of information in this case.[1] Among the organolithium systems studied theoretically are also lithiated methanes, $CH_{4-n}Li_n$ (n = 1—4), which were all examined by computational methods.[2–7] Especially, methyl-lithium, CH_3Li, has been explored extensively by these methods in recent years.[3] Experimentally, the entire series of lithiated methanes was synthesized[8] and investigated initially in the gas phase[9] (solid-state studies of CH_3Li and CH_2Li_2 should also be noted).[10]

By contrast, not all members of the series of lithiated silanes, $SiH_{4-n}Li_n$ (n = 1—4), are known. Actually, only the first, SiH_3Li,[11] and last, $SiLi_4$,[12] members of this series have been synthesized to our knowledge, and no structural determination by experimental methods is available. On the other hand, the only lithiated silane for which prior *ab initio* calculations have been reported is silyl-lithium.[7] In fact, few silicon–lithium systems were examined by *ab initio* methods, including (apart from SiH_3Li) SiLi,[13] SiHLi,[14,15] $SiLi_2$,[16,17] and Si_2Li_4[16] species. A triplet ground state of both SiHLi (predicted to be bent[14,15]) and $SiLi_2$[16,17] (for which two lowest triplets, bent and linear, are competitive in energy[17]) as well as the unusual unsymetrically bridged planar (C_{2h}) arrangement, corresponding to the lowest energy singlet of Si_2Li_4,[16] appear to be the most interesting features revealed by the calculations.

The purpose of this paper is to provide *ab initio* predictions, initially without inclusion of electron correlation effects and for the lowest singlet states, of the geometries and energies of the entire series of lithiated silanes, assuming tetrahedral† and planar conformations. The structures considered here are analogous to those assumed previously for the series of lithiated methanes.[2] For completeness, relevant *ab initio* calculations on the tetrahedral and planar conformations of the parent silane are also reported (with two lumomers taken into account for its planar form). The structures examined are displayed in the Figure.

In order further to investigate the performance of the semiempirical MNDO method[18] with regard to the prediction of geometries and energetics of lithium compounds (extensive use of the MNDO approach for organolithiums should be noted[1]) results obtained by this method for the silicon–lithium systems considered are also presented and compared with the *ab initio* findings.

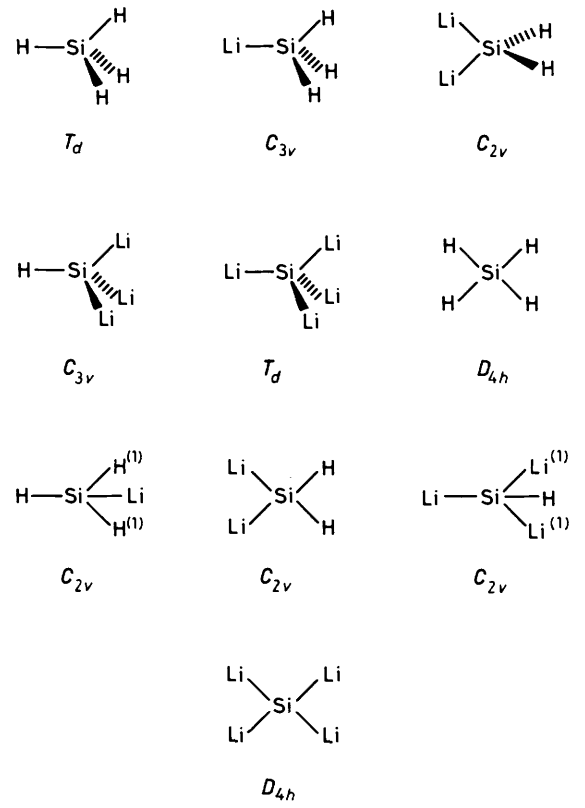

Figure. Structures of the $SiH_{4-n}Li_n$ (n = 0—4) species

Computations

Molecular geometries were fully optimized at the restricted Hartree–Fock level within assumed symmetry constraints (Figure). The split-valence 3-21G[19] and 3-21G*[20] basis sets (the latter augmented by a set of six Gaussian d orbitals on Si) were used for geometry optimization. For comparison purposes, minimal STO-3G basis[21] was also employed. All *ab initio* calculations were carried out using the GAUSSIAN 82 program.[22]

MNDO Results were obtained with the MOPAC system[23a] and employing the parametrization for lithium by Thiel and Clark.[23b]

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† Following the convention in ref. 2, we also employ 'tetrahedral' for the case when the four substituents are not the same.

Results and Discussion

In Table 1, geometrical parameters of the tetrahedral and planar structures of the lithiated silanes (and silane itself), $SiH_{4-n}Li_n$ (n = 0—4), as optimized by *ab initio* and MNDO methods are summarized. Also listed in Table 1 are the total energies corresponding to the *ab initio* optimized structures. Results of the Mulliken-type population analysis, as carried out with the 3-21G* basis for both types of structures considered, appear in Table 2; for planar $SiLi_4$, the 3-21G populations referring to its 3-21G optimized geometry are additionally included.

Tetrahedral Structures.—We begin our discussion with the basis set effects on the calculated tetrahedral forms of $SiH_{4-n}Li_n$ (n = 0—4). The Si–Li distances obtained for these forms with the minimal basis are consistently shorter than the corresponding 3-21G results, by 0.093—0.170 Å; the STO-3G bond angles predicted in the tetrahedral case differ from the 3-21G values by 1.6—10.5°, where the most notable difference of 10.5° is that for the LiSiLi angle in SiH_2Li_2. Unlike Si–H distances in the tetrahedral species in Table 1, which shorten on going from 3-21G to 3-21G* (by 0.012—0.024 Å), Si–Li distances of these species lengthen slightly. The latter effect, not exceeding 0.012 Å, is reduced gradually with increasing lithium substitution, and for $SiLi_4(T_d)$, the 3-21G* and 3-21G bond lengths are essentially the same (Table 1). The similar (slight) Si–X bond length increase, on going from 3-21G to 3-21G*, was pointed out recently[7] in the case where the electropositive elements were inserted in the H_3SiX systems. The change in calculated bond angles of the tetrahedral lithiated silanes, caused by adding the d functions to Si, is indicated here to be marginal (*i.e.* not exceeding 0.5°).

It can be deduced from Table 1 that *ab initio* optimized Si–H bond lengths of the tetrahedral forms increase in the order $SiH_4 < SiH_3Li < SiH_2Li_2 < SiHLi_3$, whereas the corresponding Si–Li bond lengths decrease in the order $SiH_3Li > SiH_2Li_2 > SiHLi_3 > SiLi_4$. Our *ab initio* LiSiH(HSiLi) bond angles for $SiH_3Li(C_{3v})$ and $SiHLi_3(C_{3v})$ (being 115.1 and 106.4°, respectively, at the 3-21G* level) do not deviate far from the true tetrahedral value (109.5°).

As expected by electronegativity arguments (atomic electronegativities[24] decrease in the order H > Si > Li), the 3-21G* Mulliken atomic charge on the silicon in tetrahedral SiH_4 is positive (+0.50). Substitution of the first lithium for hydrogen in $SiH_4(T_d)$ results in a nearly neutral silicon in $SiH_3Li(C_{3v})$ (Table 2). Further lithium substituents cause the silicon atom of the tetrahedral forms to acquire more and more negative charge, up to −0.84 in $SiLi_4(T_d)$. Dipole moments obtained here for tetrahedral SiH_3Li, SiH_2Li_2, and $SiHLi_3$ (respective 3-21G* values 7.4, 5.8, and 4.5 D) as well as the corresponding atomic charges (see Table 2) indicate ionic character.

MNDO calculations performed for the tetrahedral lithiated silanes agree with the *ab initio* results in that Si–Li distances are predicted to decrease with increasing lithium substitution (Table 1). The good agreement between the MNDO and *ab initio* 3-21G (3-21G*) findings regarding bond angles of tetrahedral SiH_3Li, SiH_2Li_2, and $SiHLi_3$ is also worth mentioning. On the other hand, the MNDO approach appears to underestimate seriously the Si–Li distance of tetrahedral species, relative to the *ab initio* 3-21G(3-21G*) results.

Planar Structures.—As in the tetrahedral case, Si–Li distances predicted for the planar lithiated silanes (Table 1) using minimal basis are consistently shorter than the corresponding 3-21G values, by 0.168—0.372 Å (with the largest difference of 0.372 Å observed for planar SiH_3Li). The most notable basis set effect on the calculated Si–Li bond lengths of the planar forms, resulting from addition of d functions to the 3-21G basis, is that for $SiLi_4(D_{4h})$ (an increase of 0.233 Å); this effect originates, however, mostly from the concomitant change of electronic configuration (see later). Upon going from STO-3G to 3-21G, the bond angles of planar SiH_3Li, SiH_2Li_2, and $SiHLi_3$ change by 3.2—10.2°, where the most remarkable result, 10.2°, concerns the LiSiLi angle in SiH_2Li_2. The corresponding changes caused by inclusion of d functions are much smaller, not exceeding 3.3°.

A short review of our *ab initio* calculated planar forms of the $SiH_{4-n}Li_n$ (n = 0—4) species starts with that of the parent silane. Our initial SCF geometry optimization of $SiH_4(D_{4h})$, using GAUSSIAN 82 and the three basis sets considered, resulted in a structure having the electronic configuration with an $a_{2u}(\pi)$ HOMO and a $b_{1g}(\sigma)$ LUMO, *i.e.* corresponding to lumomer 1.[25b] Geometry reoptimization of planar SiH_4 with the HOMO and LUMO switched, *i.e.* for lumomer 2[25b] possessing a b_{1g} HOMO and an a_{2u} LUMO, led to the more stable structure, the result obtained by STO-3G, 3-21G, and 3-21G* (actually, we were not able to complete the STO-3G optimization for lumomer 2, and values taken from ref. 25*b* are used in that case). The true ground-state configuration of (singlet) planar SiH_4, with b_{1g} HOMO, was indicated previously by Schleyer *et al.*[25] Those authors, however, failed to optimize that higher energy D_{4h} geometry of SiH_4, *i.e.* corresponding to lumomer 1.[25b] In Table 1, *ab initio* optimized geometries and total energies for both forementioned lumomers of $SiH_4(D_{4h})$ are collected.

The planar D_{4h} form of tetralithiosilane, $SiLi_4$, is also an interesting case. Its geometry optimization using the 3-21G (and STO-3G) basis resulted in a structure possessing an $a_{2u}(\pi)$ HOMO and an $a_{1g}(\sigma)$ LUMO, with a (3-21G) HOMO − LUMO separation of 3.9 eV. Inspection of Tables 1 and 2 reveals that the 3-21G optimized structure of $SiLi_4(D_{4h})$ seems to have 'normal' Si–Li bond in the sense that the appropriate Si–Li distance (2.405 Å) and Si–Li overlap population (0.705) are comparable with those calculated at the *ab initio* 3-21G (3-21G*) levels for the other planar species considered. Interestingly, the 3-21G* geometry optimization of $SiLi_4(D_{4h})$ led to a structure with the HOMO and LUMO switched, *i.e.* $a_{1g}(\sigma)$ HOMO and $a_{2u}(\pi)$ LUMO, where the HOMO − LUMO splitting was computed to be 2.7 eV. For the 3-21G* optimized structure of planar $SiLi_4$, with an $a_{1g}(\sigma)$ HOMO, the Si–Li bond suffers strong weakening, recognized by its notable lengthening (to 2.638 Å) and extremely low Si–Li overlap population (0.17). This is mainly due to the significant Si–Li antibonding character of the a_{1g} HOMO, as obtained from the 3-21G* calculation. For both kinds of D_{4h} structures of $SiLi_4$ predicted here, some Li–Li bonding effect is also shown (Table 2).

For the planar form of SiH_3Li, *ab initio* calculations predict an acute H(1)SiLi angle (55° at 3-21G*) for an attractive H(1)–Li interaction (Table 2), a result similar to that obtained previously[2] for the analogous structure of CH_3Li. Passing now to planar SiH_2Li_2 one finds that its (*ab initio*) calculated LiSiLi angle is reduced markedly compared with that in tetrahedral SiH_2Li_2 (*cf.* the 3-21G* values of 81.5 and 127.2°, respectively). This can be attributed (at least in part) to a much more favourable Li–Li interaction in the former structure (Table 2).* For planar $SiHLi_3$, the calculated LiSiLi(1) angle is close to 90° at the *ab initio* 3-21G(3-21G*) levels (the 3-21G* result is 87.1°). The slight distortion of Li(1) atoms towards Li, as predicted by *ab initio* calculations for this structure, agrees with some Li–Li(1) bonding effect indicated in that case (Table 2). We note

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* Additional *ab initio* calculations for planar SiH_2Li_2, assuming a (D_{2h}) *trans* conformation, has led to the conclusion that this form is about 50 kcal mol^{-1} (3-21G) less stable than the *cis* (C_{2v}) structure shown in the Figure.

Table 1. Optimized structures and total energies of the $SiH_{4-n}Li_n$ species (n = 0—4)[a]

			Ab initio			
Species	Symmetry	Parameter	STO-3G	3-21G	3-21G*	MNDO
SiH_4	T_d	r(Si–H)	1.421	1.487	1.475	1.376
			−287.917 281	−289.686 982	−289.784 260	
SiH_4	D_{4h}[b]	r(Si–H)	1.466	1.554	1.520	1.397
			−287.674 72	−289.519 358	−289.633 459	
SiH_4	D_{4h}[c]	r(Si–H)	1.442	1.518	1.515	
			−287.382 954	−289.338 277	−289.396 285	
SiH_3Li	C_{3v}	r(Si–H)	1.425	1.512	1.496	1.401
		r(Si–Li)	2.437	2.530	2.543	2.153
		∠ LiSiH	113.7	115.3	115.1	114.8
			−294.667 168	−296.509 924	−296.590 961	
SiH_3Li	C_{2v}	r(Si–H)	1.410	1.460	1.454	1.375
		r[Si–H(1)]	1.455	1.499	1.483	1.459
		r(Si–Li)	1.968	2.340	2.296	2.185
		∠ H(1)SiLi	58.1	54.9	55.5	55.6
			−294.552 142	−296.436 932	−296.514 709	
SiH_2Li_2	C_{2v} (tetrahedral)	r(Si–H)	1.430	1.529	1.508	1.419
		r(Si–Li)	2.392	2.525	2.537	2.068
		∠ HSiH	102.8	100.7	100.8	105.3
		∠ LiSiLi	117.1	127.6	127.2	127.1
			−301.426 180	−303.323 647	−303.392 018	
SiH_2Li_2	C_{2v} (planar)	r(Si–H)	1.437	1.512	1.496	1.437
		r(Si–Li)	2.145	2.331	2.334	2.038
		∠ HSiH	103.2	107.3	107.8	113.5
		∠ LiSiLi	74.6	84.8	81.5	103.8
			−301.360 219	−303.290 578	−303.357 176	
$SiHLi_3$	C_{3v}	r(Si–H)	1.437	1.537	1.513	1.420
		r(Si–Li)	2.311	2.472	2.478	2.024
		∠ HSiLi	109.5	106.1	106.4	104.8
			−308.209 015	−310.148 138	−310.205 537	
$SiHLi_3$	C_{2v}	r(Si–H)	1.445	1.530	1.508	1.449
		r(Si–Li)	2.103	2.272	2.266	2.018
		r[Si–Li(1)]	2.247	2.441	2.447	2.022
		∠ Li(1)SiH	96.6	90.6	92.9	80.4
			−308.168 248	−310.132 085	−310.188 613	
$SiLi_4$	T_d	r(Si–Li)	2.252	2.422	2.420	2.011
			−315.018 632	−316.988 182	−317.035 550	
$SiLi_4$	D_{4h}	r(Si–Li)	2.221[d]	2.405[d]	2.638[e]	2.042[d]
			−314.993 081[d]	−316.980 181[d]	−316.980 592[e]	

[a] Bond lengths in Å, bond angles in degrees, total energies in hartrees. [b] HOMO is of b_{1g} symmetry and LUMO is of a_{2u} symmetry; the STO-3G values are taken from ref. 25*b*. [c] HOMO is of a_{2u} symmetry and LUMO is of b_{1g} symmetry. [d] HOMO is of a_{2u} symmetry and LUMO is of a_{1g} symmetry. [e] HOMO is of a_{1g} symmetry and LUMO is of a_{2u} symmetry.

here that the distortion shown in the Figure for planar $SiHLi_3$ corresponds rather to the MNDO prediction (*cf.* Table 1).

Further inspection of Table 1 reveals that the *ab initio* optimized Si–Li distances of the planar lithiated silanes are always shorter than those of the corresponding tetrahedral species obtained at the same theoretical level (except for the 3-21G* optimized D_{4h} form of $SiLi_4$, a case already discussed).

Relative to the *ab initio* findings with the 3-21G and 3-21G* basis sets, the MNDO method appears to underestimate seriously Si–Li distances of the planar lithiated silanes, and to yield wider LiSiLi bond angles (in the case of planar SiH_2Li_2 and $SiHLi_3$).

Tetrahedral – Planar Energy Differences.—Perusing the total energies in Table 1, one finds that the tetrahedral forms of all lithiated silanes are preferred energetically over the corresponding planar structures; the same result has been obtained at the MNDO level. Lithium substituents, however, lower drastically the appropriate tetrahedral – planar energy differences compared with that for the parent silane. These tetrahedral – planar energy differences, predicted in the present work at both *ab initio* and MNDO levels, are listed in Table 3. For comparison, the corresponding *ab initio* results, obtained previously[2,6] for the lithiated methanes (assuming analogous structures), are also shown in Table 3.

As can be seen from Table 3, our *ab initio* calculated energy barriers are especially low for $SiHLi_3$ and $SiLi_4$, 10 and 5 kcal mol^{-1}, respectively, at the 3-21G level. A sharp increase in the $SiLi_4$ energy difference, observed on going from 3-21G to 3-21G* (to 34.5 kcal mol^{-1}), is caused mostly by the concomitant change of electronic configuration of planar $SiLi_4$ (see earlier). Comparing *ab initio* results for the silicon and carbon species in Table 3 shows that in general the tetrahedral – planar energy differences of the lithiated silanes are larger than the corresponding values for the lithiated methanes. This is not unexpected since lithium substituents were indicated to stabilize preferentially the rather planar tetraco-ordinate carbon[2,25] although, on the other hand, a system with planar tetraco-ordinate silicon was suggested[25] to be easier to realize than that involving planar tetraco-ordinate carbon (*cf. ab initio* results for SiH_4 and CH_4 in Table 3).

Using the split-valence (3-21G) basis set instead of the minimal one leads to a stabilization of the planar forms of the lithiated silanes with respect to their tetrahedral structures; a similar effect was discussed earlier[25b] in the case of XH_4 systems. Consequently, the appropriate tetrahedral – planar

Table 2. 3-21G* Mulliken population analyses[a]

	SiH_4	SiH_3Li	SiH_2Li_2	$SiHLi_3$	$SiLi_4$
Tetrahedral case	(T_d)	(C_{3v})	(C_{2v})	(C_{3v})	(T_d)
Atomic charges					
Si	0.503	−0.001	−0.353	−0.615	−0.844
H	−0.126	−0.143	−0.130	−0.101	
Li		0.431	0.306	0.239	0.211
Total overlap populations					
Si–H	0.777	0.742	0.706	0.682	
Si–Li		0.679	0.699	0.706	0.698
H–H	−0.027	−0.028	−0.032		
Li–H		−0.024	−0.012	−0.011	
Li–Li			−0.231	−0.122	−0.040
Dipole moment (D)	0.0	7.45	5.78	4.54	0.0
Planar case	(D_{4h})	(C_{2v})	(C_{2v})	(C_{2v})	(D_{4h})
Atomic charges					
Si	0.686[b]	−0.105	−0.406	−0.546	−0.591;[c] −0.564[d]
H[H(1)]	−0.171[b]	−0.046 (−0.114)	−0.111	−0.113	
Li[Li(1)]		0.379	0.314	0.165 (0.247)	0.148;[c] 0.141[d]
Total overlap populations					
Si–H[Si–H(1)]	0.695[b]	0.797 (0.632)	0.690	0.649	
Si–Li[Si–Li(1)]		0.513	0.664	0.838 (0.636)	0.166;[c] 0.705[d]
H–H	−0.150[b]	−0.048[e]	−0.011		
Li–H		0.127[f]	0.024	0.043[g]	
Li–Li			0.209	0.139[h]	0.241;[c] 0.145[d]
Dipole moment (D)	0.0	5.19	6.88	3.54	0.0

[a] Corresponding to the 3-21G* optimized structures. For the numbering scheme employed in the case of the planar (C_{2v}) geometries of SiH_3Li and $SiHLi_3$ see Figure. [b] Obtained for the structure with HOMO of b_{1g} symmetry and LUMO of a_{2u} symmetry. [c] Corresponding to the 3-21G* optimized structure in which case the electronic configuration with HOMO of a_{1g} symmetry and LUMO of a_{2u} symmetry is obtained. [d] 3-21G result referring to the 3-21G optimized structure in which case the electronic configuration with HOMO of a_{2u} symmetry and LUMO of a_{1g} symmetry is obtained. [e] Corresponding to the H(1)–H(1) population; the calculated (3-21G*) H–H(1) overlap population is −0.020. [f] This value refers to the H(1)–Li overlap population. [g] This value refers to the Li(1)–H overlap population. [h] Corresponding to the Li–Li(1) population; the calculated (3-21G*) Li(1)–Li(1) overlap population is −0.121.

Table 3. Tetrahedral – planar energy barriers[a] for the lithiated silanes and lithiated methanes (in kcal mol^{-1})

	Ab initio[b]					*Ab initio*[c]	
Species	STO-3G	3-21G	3-21G*	MNDO[b]	Species	STO-3G	3-21G
$SiH_4(T_d\ vs.\ D_{4h})$[d]	152.2	105.2	94.7	50.0	$CH_4(T_d\ vs.\ D_{4h})$	240	170.2
$SiH_3Li(C_{3v}\ vs.\ C_{2v})$	72.2	45.8	47.9	35.0	$CH_3Li(C_{3v}\ vs.\ C_{2v})$	52	37.3
$SiH_2Li_2(C_{2v}\ vs.\ C_{2v})$	41.4	20.8	21.9	7.3	$CH_2Li_2(C_{2v}\ vs.\ C_{2v})$	17	7.5
$SiHLi_3(C_{3v}\ vs.\ C_{2v})$	25.6	10.1	10.6	5.5	$CHLi_3(C_{3v}\ vs.\ C_{2v})$	10	5.1
$SiLi_4(T_d\ vs.\ D_{4h})$	16.0[e]	5.0[e]	34.5[f]	8.8[e]	$CLi_4(T_d\ vs.\ D_{4h})$	22	14.4

[a] Differences in total energies (*ab initio*) or heats of formation (MNDO) between planar and tetrahedral (singlet) structures. Symmetries of the tetrahedral and planar species, as given in parentheses, refer either to the structures indicated in the Figure (lithiated silanes) or to the analogous arrangements assumed for the lithiated methanes.[2] [b] This work. [c] Refs. 2 and 6. [d] Relative to the planar form with b_{1g} HOMO and a_{2u} LUMO; the following barriers (in kcal mol^{-1}) are obtained if the D_{4h} form having a_{2u} HOMO and b_{1g} LUMO is considered: 335.4 (STO-3G), 218.9 (3-21G), and 243.5 (3-21G*). [e] Relative to the D_{4h} structure having a_{2u} HOMO and a_{1g} LUMO. [f] Relative to the D_{4h} structure having a_{1g} HOMO and a_{2u} LUMO.

energy differences decrease substantially on going from STO-3G to 3-21G (Table 3). By contrast, upon addition of *d* functions to the 3-21G basis, the energy differences for the Si–Li systems slightly increase (with the exception of $SiLi_4$).

Our MNDO tetrahedral – planar energy barriers for the lithiated silanes are generally lower than the corresponding *ab initio* predictions with three basis sets considered. In fact, these MNDO results are very similar to the ones of the analogous C-Li species as computed[6] at the *ab initio* 3-21G level (see Table 3).

Finally, let us mention the limitations of the present work.

(1) Only limited number of structures of the lithiated silanes have been examined. In particular, more *'exotic'* geometries have not been attempted (for organolithium compounds, *e.g.*, appearance of such unusual geometries has been confirmed theoretically many times).[1] Consequently, we do not claim that the tetrahedral structures of lithiated silanes are the global minima.

(2) A search for the low-lying triplet states was not made, especially for planar $SiLi_4$, in which case the HOMO – LUMO separation is relatively small.

(3) The stability of the species considered with respect to dissociation reactions has not been explored.

(4) Electron-correlation effects were omitted.

Note added in proof

We have performed a stability test[26] of our RHF 3-21G* wavefunction for SiLi$_4$(D_{4h}) and an instability of the type real RHF $\longrightarrow$ real UHF[26] has been detected in this case. Subsequent UHF 3-21G* optimization of this structure leads to an Si–Li bond distance of 2.399 Å with a corresponding total energy of − 317.028155 a.u.; this, in turn, would give the 3-21G* SiLi$_4$ tetrahedral − planar energy difference of 4.6 kcal mol^{-1}, a result close to the 3-21G prediction (*cf.* Table 3). The UHF 3-21G* calculation also restores the correct energy level ordering and the bonding properties of planar SiLi$_4$ (*cf.* the RHF 3-21G results for this structure in the text and in Table 2).

After the submission of this paper, a contribution by Schleyer and Clark[27] was brought to our attention, indicating that the non-classical inverted (C_{3v}) structure of SiH$_3$Li is more stable than its tetrahedral arrangement studied here (by 2.4 kcal mol^{-1} at the MP4/6-31G**//6-31G* level, with the ZPE correction included); both forms proved to be minima[27] on the potential energy surface.

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