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# WHEN MIGHT SILYLENES BEHAVE MORE LIKE CARBENES?

## SiHLi, A TRIPLET SILYLENE

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**Abstract**—Qualitative arguments and preliminary theoretical studies by Harrison suggest that lithiosilylene (SiHLi) may have a triplet electronic ground state. This possibility has been confirmed in the present detailed *ab initio* quantum mechanical study. Using double-zeta and double-zeta plus polarization basis sets, the different low-lying electronic states of SiHLi have been investigated using self-consistent-field and configuration interaction methods. The triplet ground state potential surface is very flat, with two nearly degenerate minima at $\theta$(HSiLi) values of 137° and 48°, respectively. The lowest singlet state lies $\sim 7$ kcal higher in energy and is predicted to have an equilibrium bond angle of $\sim 93°$, much like the parent silylene $SiH_2$. Vibrational frequencies are predicted for all stationary points.

## INTRODUCTION

The energetic separation between the lowest singlet and triplet electronic states of a carbene is perhaps the most critical parameter required for the prediction of the reactivity of these fascinating species.[1] While the parent methylene ($CH_2$) has a triplet ground state, and $\Delta E$(S–T) $\sim 9$ kcal,[2] nearly all other carbenes have smaller singlet–triplet separations, and in fact many carbenes have singlet electronic ground states.[3]

With the increasingly important role of carbenes in the development of contemporary organic chemistry, it is not surprising that considerable interest has arisen in the valence-isoelectronic silylenes : $SiR_2$. The principal difference between silylenes and carbenes is the fact that all known silylenes have singlet ground states.[4–6] For the parent $SiH_2$ the only available experimental value of the singlet–triplet splitting is $\Delta E(\text{S–T}) \leqslant 14$ kcal, from the laser photodetachment experiments of Lineberger *et al.*[7] The most reliable theoretical value for $SiH_2$ is 18.6 kcal,[8] which should be reliable to within $\pm 3$ kcal. Due to the difficulty of observing singlet–triplet electronic transitions directly, very few silylene $\Delta E$(S–T) values are known. One exception appears to be $SiF_2$ for which the spectroscopic value 75.2 kcal has been reported.[9] The best theoretical prediction of the singlet–triplet separation for $SiF_2$ is 73.5 kcal,[10] in close agreement with experiment.

The purpose of this paper is to inquire whether it might not be possible to design a triplet silylene. It should be noted that the silylidenes $:\mathrm{Si{=}C{=}O}$ and $:\mathrm{Si}{=}\overset{+}{\mathrm{N}}{=}\overset{-}{\mathrm{N}}$ have been shown to have triplet ground states,[11] but these are rather different electronically from the silylene family  $:\mathrm{Si}\begin{matrix}\diagup \mathrm{R}\\ \diagdown \mathrm{R}\end{matrix}$. A triplet silylene would of course be expected to react rather differently than the known singlet silylenes.[4–6]

*Why might lithiosilylene have a triplet ground state?*

It is well established[3,12–16] that electronegative substituents will lower the singlet–triplet gap of carbenes by stabilizing the singlet state, eventually reversing the order of these states and giving rise to a singlet ground state in species like HCF or HCCl. Electropositive substituents are expected to produce the opposite effect.

A recent study[10] of the substituted silylenes SiHF and $SiF_2$ suggests that electronegative substituents produce the same effect in silylenes, i.e. stabilizing the singlet state with respect to the triplet state. In this regard Harrison *et al.*[15] note unpublished work on SiHLi which supports the idea that this simple molecule has a triplet ground state, due to the effect of the electropositive Li substituent. It is our intention here to study in more detail the SiHLi molecule.

In light of a compendium of theoretical data on the multiplicity of substituted carbenes, Harrison *et al.*[15] proposed an electronegativity related theory which rationalizes all the data known for carbenes and silylenes. In the limit of two very electronegative substituents it is of course seen that $CH_2$ behaves like $C^{2+}(1s^2 2s^2)$ which has a singlet ground state. Conversely, two extremely electropositive substituents will make $CR_2$ look like $C^{2-}(1s^2 2s^2 2p^4)$ which has a triplet ground state. The same argument may be applied to the silylenes $SiR_2$. Intermediate cases require a somewhat modified argument.

Harrison suggests that going from a triplet to a singlet ground state essentially involves going from a $\sigma p$ configuration to a $\sigma^2$ one. The reasonable way to understand such a situation is that the $\sigma$ orbital be sufficiently lower in energy than the p orbital to compensate for the increase in electronic repulsion in $\sigma^2$. An electronegative ligand will increase the s character of the $\sigma$ orbital and consequently lower its energy, therefore stabilizing the singlet state with respect to the triplet in carbenes as well as in silylenes. The same argument holds for the comparison between carbenes and silylenes. Silicon is indeed less

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electronegative than carbon, which implies that for similar substituents a silylene will preferentially favor the singlet state with respect to the situation prevailing in the analogous carbene. This difference in electronegativity is sufficient to make the ground state of $SiH_2$ singlet whilst the ground state of $CH_2$ is triplet. It is expected that Li will be sufficiently electropositive to give SiHLi a triplet ground state.[15]

### *Theoretical approach*

Relatively standard double-zeta (DZ) and double-zeta plus polarization (DZ + P) basis sets were used in this research. These are the Si(11s 7p 1d/6s 4p 1d),[17] Li(9s 4p/4s 2p)[18] and H(4s 1p/2s 1p)[19] sets developed by Dunning, Hay and Huzinaga. Polarization function orbital exponents were $\alpha_d(\mathrm{Si}) = 0.5$ and $\alpha_p(\mathrm{H}) = 0.75$. No d functions were added to Li, the feeling being that p functions serve to a significant degree as polarization functions.

The lowest triplet electron configuration was found at all bent geometrical configurations to be

$$1a'^2\, 2a'^2\, 3a'^2\, 1a''^2\, 4a'^2\, 5a'^2\, 6a'^2\, 7a'^2\, 8a'\, 2a'' \quad {}^3A''. \qquad (1)$$

For linear geometries the ground state orbital occupancy is

$$1\sigma^2\, 2\sigma^2\, 1\pi^4\, 3\sigma^2\, 4\sigma^2\, 5\sigma^2\, 6\sigma^2\, 2\pi^2 \quad {}^3\Sigma^-. \qquad (2)$$

Similarly the lowest energy singlet state electron configuration was found to be

$$1a'^2\, 2a'^2\, 1a''^2\, 3a'^2\, 4a'^2\, 5a'^2\, 6a'^2\, 7a'^2\, 8a'^2 \quad {}^1A'. \qquad (3)$$

Interestingly, for much smaller bond angles (see below) there is a second closed-shell configuration

$$1a'^2\, 2a'^2\, 3a'^2\, 4a'^2\, 1a''^2\, 5a'^2\, 6a'^2\, 7a'^2\, 2a''^2 \quad {}^1A' \qquad (4)$$

which gives rise to a secondary minimum on the lowest singlet potential energy hypersurface.

Electron correlation effects were taken into account via configuration interaction, specifically using the "shape-driven" graphical unitary group approach.[20] All single and double excitations with respect to the SCF reference function were included in the CI treatment. The core electrons (Si 1s, 2s and 2p; Li 1s) were not involved in the CI, nor were their virtual counterparts (the six highest virtual orbitals). At the DZ + P CISD level of theory, this represents 1609 and 2077 configuration state functions for the $^1A'$ and $^3A''$ states, respectively. Although giving rise to rather small expansions in this particular case, this type of CI is known to give reasonable agreement with much more sophisticated methods.[21]

In order to characterize the stationary points obtained by gradient minimization techniques,[22] vibrational frequency analyses were performed via analytic determination of second derivatives of the SCF energy.[23] This was done at both the DZ SCF and DZ + P SCF levels of theory.

Table 1. Two predicted equilibrium geometries on the $^3A''$ ground state potential energy hypersurface for SiHLi

| | DZ | DZ+P |
|---|---|---|
| $^3A''$ (I) | | |
| $r_e$(Si—H) | 1.509 | 1.494 |
| $r_e$(Si—Li) | 2.403 | 2.420 |
| $\theta_e$(HSiLi) | 143.6° | 137.3° |
| $\nu_1$(Si—H) | 2157 | 2231 |
| $\nu_2$(bend) | 225 | 277 |
| $\nu_3$(Si—Li) | 490 | 481 |
| $^3A''$ (II) | | |
| $r_e$(Si—H) | 1.659 | 1.605 |
| $r_e$(Si—Li) | 2.504 | 2.449 |
| $\theta_e$(HSiLi) | 46.1° | 47.7° |
| $\nu_1$(Si—H) | 1440 | 1656 |
| $\nu_2$(bend) | 862 | 840 |
| $\nu_3$(Si—Li) | 357 | 397 |

Bond lengths are in Å and vibrational frequencies in $cm^{-1}$. DZ and DZ + P refer to the use of double-zeta and double-zeta plus polarization basis sets.

### *The triplet ground state potential energy hypersurface*

The triplet state corresponding to configuration (1) is found to be lower than the singlet state (3) for all values of the HSiLi angle $\theta$. This was first found to be true at the DZ SCF and subsequently at the DZ + P SCF level of theory. More interesting, however, is the fact that there are two well characterized minima on the triplet ground state surface. Their equilibrium geometries are given in Table 1, along with the three real vibrational frequencies predicted at the SCF(DZ) and SCF(DZ + P) levels of theory. As can be seen, the most important distinction between these two structures lies in their bond angle. $\theta$(HSiLi) is ~ 140° for the lower energy (at the SCF level) minimum (called I hereafter), which is a rather conventional value due to the effect of the electropositive substituent. The surprisingly small value of $\theta$(HSiLi) ~ 45° for the higher minimum (called II hereafter) is especially noteworthy. The different triplet state stationary point geometries are sketched in Fig. 1.

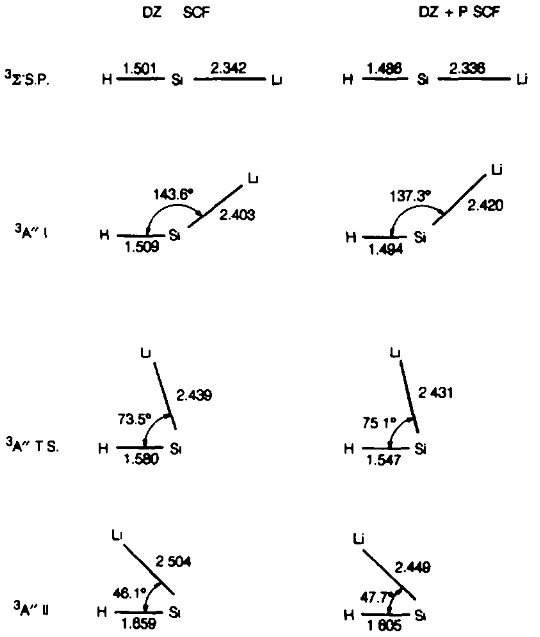


Fig. 1. Triplet state stationary point geometries for the SiHLi molecule. DZ and DZ + P refer to double-zeta and double-zeta plus polarization basis sets, while SCF refers to the use of self-consistent-field wave functions. Bond distances are in Å.

The DZ+P SCF Mulliken atomic charges for the two triplet minima are

$$\begin{array}{llll} H(-0.17) & Si(-0.20) & Li(+0.38) & \theta_e = 137.3^\circ \\ H(-0.32) & Si(-0.09) & Li(+0.40) & \theta_e = 47.7^\circ. \end{array}$$

Although these charges have no absolute validity, it seems that the qualitative picture $H^-Si^-Li^+$ is applicable in both cases. However for the ring-like ($\theta = 48^\circ$) structure, the amount of $Li^+H^-$ character is considerably greater, consistent with the much shorter Li–H distance.

It is interesting to observe here that the C—Li bond in the analogous carbene CHLi is also ionic, as shown by Harrison *et al.*[15] However, the carbene CHLi was predicted to be linear in contrast with our bent SiHLi molecule.

On the whole, $^3A''$(I) with bond angle 137.3°, seems to be a "normal" structure for a triplet silylene. Indeed, the Si—Li bond length of 2.420 Å (DZ + P) is very similar to the bond length for diatomic SiLi ($X^4\Sigma^-$) predicted by Mavridis and Harrison,[24] namely 2.432 Å. The agreement between vibrational frequencies is also acceptable: 481 $cm^{-1}$ for the Si—Li stretch in SiHLi, compared to 447 $cm^{-1}$ for diatomic SiLi ($X^4\Sigma^-$).[24] The Si—H bond length (1.494 Å) in SiHLi is also very similar to the 1.520 Å experimental bond length[25] for the $X^2\Pi$ state of diatomic SiH. The same conclusion holds for the Si—H stretching frequency, which is predicted to be 2231 $cm^{-1}$, close to the experimental diatomic SiH value of 2042 $cm^{-1}$ if one takes into account a standard correction[26] of ~10%.

The situation is quite different for the $^3A''$ structure with HSiLi bond angle 47.7°. There the Si—Li bond still seems "normal" but the Si—H bond suffers an extreme weakening, recognized by the longer bond length and smaller vibrational frequency. Specifically the Si—H distance for this small bond angle $^3A''$ minimum is 1.605 Å, more than 0.1 Å longer than for the more conventional SiHLi triplet structure with $\theta_e = 137.3^\circ$. Also, the Si—H stretching frequency is only 1656 $cm^{-1}$, down by ~500 $cm^{-1}$ from the analogous prediction for diatomic Si—H. Moreover, the bending frequency for the 47.7° structure is predicted to be 840 $cm^{-1}$, more than three times higher than that for the normal triplet silylene. This increase in bending frequency is a sign that minimum II on the $^3A''$ surface is perhaps better described as a 3-membered ring than an ordinary bent triatomic molecule. All these differences may be at least in part ascribed to $Li^+H^-$ character in the bonding associated with minimum II.

It was possible to locate a transition state between the $^3A''$ structures I and II, at a $\theta_e$ value of about 75°. This $^3A''$ transition state (hereafter labeled T.S.) is described in Fig. 1 and Table 2. It is an intermediate structure with respect to the predicted structural parameters. The unique imaginary vibrational frequency, which clearly corresponds to the bending motion in the normal coordinate analysis, is also intermediate between the bending frequencies of the two minima.

A fourth triplet stationary point (labeled S.P. hereafter) was located and corresponds to a linear HSiLi arrangement of the three atoms. For structure S.P., which is of $^3\Sigma^-$ symmetry, the doubly-degenerate bending frequency is imaginary, namely 150 i (DZ SCF) and 201 i (DZ + P SCF).

We consider it unlikely that the double minima feature of the $^3A''$ energy surface for SiHLi is an artifact of the methods used here. Not only does our finding seem to be independent of basis set effects but, moreover, the analytic CI gradients[27] calculated at the DZ + P SCF geometries were rather small. This suggests that both structures will remain at the CI level, not collapsing into a single SiHLi minimum.

Table 2. Two other stationary points on the triplet ground state potential energy hypersurface of SiHLi

| | DZ | DZ+P |
|---|---|---|
| T.S. $^3A''$ | | |
| $r_e$(Si—H) | 1.580 | 1.547 |
| $r_e$(Si—Li) | 2.439 | 2.431 |
| $\theta_e$(HSiLi) | 73.5° | 75.1° |
| $\nu_1$(Si—H) | 1811 | 1964 |
| $\nu_2$(bend) | 512 i | 508 i |
| $\nu_3$(Si—Li) | 430 | 429 |
| S.P. $^3\Sigma^-$ | | |
| $r_e$(Si—H) | 1.501 | 1.486 |
| $r_e$(Si—(Li) | 2.342 | 2.336 |
| $\theta_e$(HSiLi) | 180° | 180° |
| $\nu_1$(Si—H) | 2200 | 2279 |
| $\nu_2$(bend) | (2) 150i* | (2) 201i* |
| $\nu_3$(Si—Li) | 512 | 511 |

Bond lengths are in Å and vibrational frequencies in $cm^{-1}$.
* Doubly degenerate bending frequency.

Table 3. Theoretical predictions for the lower singlet electronic states of SiHLi

| | DZ | DZ+P |
|---|---|---|
| $\ldots 1a''^2\,7a'^2\,8a'^2\ {}^1A'$ (I) | | |
| $r_e$(Si—H) | 1.545 | 1.519 |
| $r_e$(Si—Li) | 2.651 | 2.644 |
| $\theta_e$(HSiLi) | 94.6° | 93.2° |
| $\nu_1$(Si—H) | 1983 | 2106 |
| $\nu_2$(bend) | 402 | 424 |
| $\nu_3$(Si—Li) | 396 | 394 |
| $\ldots 1a''^2\,7a'^2\,2a''^2\ {}^1A'$ (II) | | |
| $r_e$(Si—H) | 1.629 | 1.588 |
| $r_e$(Si—Li) | 3.082 | 2.570 |
| $\theta_e$(HSiLi) | 16.4° | 38.4° |
| $\nu_1$(Si—H) | 1977 | 1771 |
| $\nu_2$(bend) | 599 | 1080 |
| $\nu_3$(Si—Li) | 39 | 223 |
| $\ldots 1a''^2\,7a'^2\,8a'\,2a''\ {}^1A''$ (I)* | | |
| $r_e$(Si—H) | 1.502 | 1.486 |
| $r_e$(Si—Li) | 2.341 | 2.336 |
| $\theta_e$(HSiLi) | 180° | 180° |
| $\nu_1$(Si—H) | 2200 | 2281 |
| $\nu_2$(bend) | 175, 178† | 97, 102† |
| $\nu_3$(Si—Li) | 513 | 514 |
| $\ldots 1a''^2\,7a'^2\,8a'^2\,2a''\ {}^1A''$ (II) | | |
| $r_e$(Si—H) | 1.651 | 1.601 |
| $r_e$(Si—Li) | 2.621 | 2.555 |
| $\theta_e$(HSiLi) | 42.8 | 44.7 |
| $\nu_1$(Si—H) | 1462 | 1667 |
| $\nu_2$(bend) | 848 | 832 |
| $\nu_3$(Si—Li) | 323 | 338 |

Bond lengths are in Å and vibrational frequencies in $cm^{-1}$.
* In the DZ basis set, the equilibrium electron configuration is $\ldots 6\sigma^2\,2\pi^2\ {}^1\Delta$.
† Doubly degenerate ($\pi$) bending frequency.

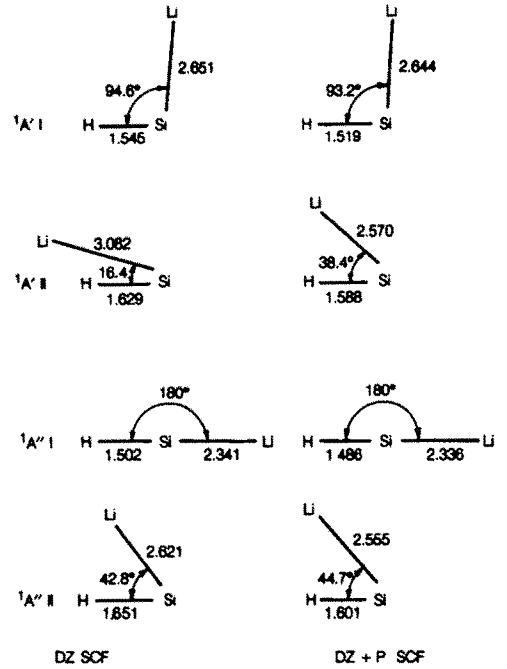


Fig. 2. Singlet state stationary point geometries for SiHLi.

## *Singlet electronic states of* SiHLi

The optimized geometry of the lowest-lying singlet state, corresponding to electron configuration 3, is given in Table 3. First we note the conventional value of ~95° for $\theta_e$ (HSiLi), similar to the values found for other closed shell silylenes.[10] Note also that the Si—Li distance, predicted to be 2.644 Å (DZ + P SCF), is more than 0.2 Å longer than that predicted for the triplet states of SiHLi. The Mulliken populations for the lowest singlet state Si(−0.01), H(−0.22), Li(+0.23) suggest that the silicon atom is nearly neutral, but that there is some $Li^+H^-$ character.

As noted earlier in the section labeled "Theoretical approach", there is a second closed-shell singlet minimum, with equilibrium bond angle 38.4° (DZ + P SCF), corresponding to electron configuration 4. The theoretical predictions for this small bond angle state are summarized in Table 3. The inability of the DZ basis to adequately describe the π-like 2a orbital is seen in the anomalous DZ ¹A′ (II) structure. This singlet state is

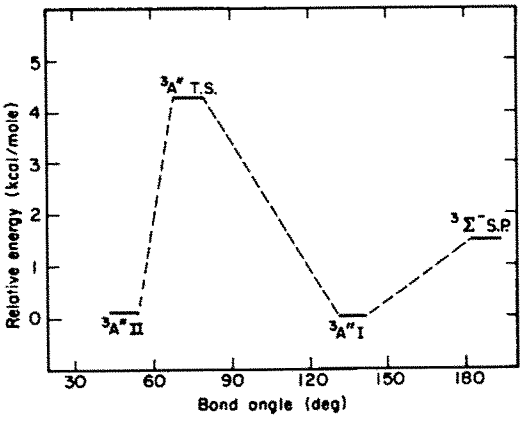


Fig. 3. Relative energies of the low-lying triplet stationary points of SiHLi.

Table 4. Total and relative energies for the different stationary point SiHLi structures considered

| | DZ + P SCF bond angle | DZ SCF | DZ CI | DZ + P SCF | DZ + P CI | Davidson corrected DZ + P CI |
|---|---|---|---|---|---|---|
| $^3\Sigma^-$ S.P. | 180° | −296.87299 (0.4) | −296.92263 (1.2) | −296.88441 (1.0) | −296.97098 (1.3) | −296.97607 (1.5) |
| $^3A''$ I | 137.3 | −296.87370 (0.0) | −296.92455 (0.0) | −296.88598 (0.0) | −296.97309 (0.0) | −296.97849 (0.0) |
| $^3A''$ T.S. | 75.1 | −296.86090 (8.0) | −296.91392 (6.7) | −296.87503 (6.9) | −296.96571 (4.6) | −296.97165 (4.3) |
| $^3A''$ II | 47.7 | −296.86607 (4.8) | −296.91866 (3.7) | −296.88023 (3.6) | −296.97222 (0.5) | −296.97824 (0.2) |
| $^1A'$ I | 93.2 | −296.84157 (20.2) | −296.90402 (12.9) | −296.85747 (17.9) | −296.95607 (10.7) | −296.96456 (8.7) |
| $^1A'$ II | 38.4° | −296.80013 (46.2) | −296.85992 (40.6) | −296.81380 (45.3) | −296.91632 (35.6) | −296.92783 (31.8) |
| $^1A''$ I | 180° | −296.83994 (21.2) | −296.88806 (22.9) | −296.85183 (21.4) | −296.93958 (21.0) | −296.94488 (21.1) |
| $^1A''$ II | 44.7° | −296.83167 (26.4) | −296.88568 (24.4) | −296.84592 (25.1) | −296.94028 (20.6) | −296.94699 (19.8) |

Total energies are given in hartrees and relative energies (in parentheses) in kcal/mol.

obviously "echoing" the $^3A''$ (II) state, and results from the single excitation $8a' \rightarrow 2a''$ relative to **1**. The lowest energy singlet state results, in contrast, from the monoexcitation $2a'' \rightarrow 8a'$ relative to **1**. This observation suggests that the orbital $2a''$ is responsible for the small bond angle values predicted here. The $2a''$ orbital of course correlates with the out-of-plane component of the 3p atomic orbital of silicon.

Two open-shell singlet states, of $^1A''$ symmetry, have also been considered, both arising from electron configuration **1**. Results for these two potential minima are summarized in Fig. 2 and Table 3. The two $^1A''$ minima are seen to be analogous to the $^3A''$ structures arising from the same electron configuration except that the wide-angle singlet is predicted to be linear.

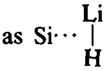
### *Energetic considerations*

Total and relative energies for the different SiHLi stationary points are given in Table 4. There the $^3A''$ minimum with $\theta_e \sim 140°$ is taken to be the zero of energy. As may be seen, the energies of the two $^3A''$ minima are extremely close at the highest levels of theory, as illustrated in Fig. 3. At the DZ+P CI level (with DZ+P SCF optimized geometries) the 137.3° minima is 0.5 kcal below the 47.7° minima. With the appendage of the Davidson correction[28] for unlinked clusters (quadruple excitations) this energy difference drops to only 0.2 kcal. Both the DZ+P CI and Davidson-corrected energy differences are smaller by an order of magnitude than the expected reliability of the level of theory. Thus we can only say that the two equilibrium structures of triplet SiHLi lie within a few kcal of each other. The fact that each of the two structures is a minimum is supported by the predicted barrier of 4.3 kcal. The barrier to linearity is only 1.5 kcal.

The fifth line of Table 4 gives perhaps the most important prediction of this study, namely the singlet–triplet separation $\Delta E$(S–T) of lithiosilylene. As previously shown for other carbenes[3] and silylenes,[10] the introduction of electron correlation into the wave functions lowers the energy of the singlet state relative to the triplet. The final prediction (Davidson corrected) is that singlet SiHLi lies 8.7 kcal above the triplet structure with $\theta_e$(HSiLi) = 137.3°. It follows that singlet SiHLi lies 8.5 kcal above the triplet ring state of lithiosilylene. If extensions to higher levels of theory follow the pattern now established for methylene,[29] one might expect the ultimate theoretical value of $\Delta E$(S–T) for SiHLi to be ~7 kcal. The similarity with the $CH_2$ singlet–triplet separation[2] of ~9 kcal is worth mentioning. Thus lithiosilylene might in some respects be expected to react in a manner similar to that known for the parent carbene $CH_2$. However, one should also note that while the triplet–singlet energetics of $CH_2$ and SiHLi are rather similar, the fact that SiHLi is a polar molecule is a difference which would be expected to affect its reactivity vis-à-vis $CH_2$.

At the highest levels of theory, the three other singlet state minima are predicted to lie at 19.8 kcal ($^1A''$ II, $\theta = 44.7°$), 21.1 kcal ($^1A''$ I, $\theta = 180°$) and 31.8 kcal ($^1A'$ II, $\theta = 38.4°$), respectively, relative to the $^3A''$ state with bond angle $\theta_e = 137.3°$. Thus there is no question that the "conventional" ($\theta = 93.2°$) singlet silylene is the lowest-lying of the singlet states. The results for the two open-shell singlet $^1A''$ minima show that this potential energy hypersurface is very flat, like the analogous $^3A''$ surface discussed in more detail above.

## CONCLUDING REMARKS

Lithiosilylene has been shown following the earlier prediction of Harrison *et al.*[15] to have a triplet ground state. The lowest singlet state lies about 7 kcal higher in energy. The most surprising feature of the SiHLi potential energy surfaces, both singlet and triplet, is the existence of equilibrium geometries with very small bond angles, $\theta$(H—Si—Li) ~ 50°. These ring-like structures might alternately be described as  $\mathrm{Si}\cdots\overset{\mathrm{Li}}{\underset{\mathrm{H}}{|}}$ complexes, since the Si—Li distances are 0.2–0.3 Å longer than for the more conventional silylene structures. This picture of the 3-membered rings is also supported by the predicted Li—H distances of 1.811 Å ($^3A''$) and 1.652 Å ($^1A'$), not too much longer than the 1.594 Å value observed[25] for diatomic LiH.

The small angle triplet minimum is not entirely without analogy for $CH_2$, the parent carbene. The existence of a low-energy $^3A_2$ state, arising from the electron configuration

$$1a_1^2\,2a_1^2\,3a_1^2\,1b_2\,1b_1$$

has been discussed by several authors.[30–32] Note that in $C_s$ symmetry (the symmetry of SiHLi) this $^3A_2$ state becomes a $^3A''$ state, in analogy with the small bond angle states of lithiosilylene.

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