

## Theory Predicts Triplet Ground-State Organic Silylenes

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Silylenes, SiR<sub>2</sub>, are highly important reactive intermediates in silicon chemistry and to date all known SiR<sub>2</sub> species possess a singlet ground state without any experimentally verified exception.<sup>1</sup> This is in contrast to the fact that the ground-state multiplicity of their carbon analogues CR<sub>2</sub> can be easily switched from triplet to singlet by modification of the substituents R.<sup>2</sup> As the chemistry of triplet silylenes is expected to be entirely different from that of singlet silylene (as found for carbenes<sup>2a</sup>), the preparation of a silylene which has a triplet ground state and the exploration of its chemistry is one of the most important challenges in contemporary silicon chemistry.<sup>1a</sup> For more than a decade now, a great deal of experimental as well as theoretical effort has been dedicated to this goal, but without success.<sup>1,3–13</sup> In this paper we use carefully calibrated approximate density functional theory (DFT) computations to predict specific silylenes

which have triplet ground states, hoping to stimulate experimental testing of these theoretical predictions.

The key ingredients needed for a ground-state triplet silylene appear clear from information already presented in the literature: (a) Systematic theoretical studies employing correlated wave functions revealed a substantial electronic effect of different  $\alpha$ -substituents on the singlet–triplet energy gap ( $\Delta E_{S-T}$ ).<sup>3</sup> It has been shown that electronegative substituents increase the S–T gap, whereas electropositive substituents reduce the gap. In addition,  $\pi$ -donor or  $\pi$ -acceptor substituents exert a significant effect on  $\Delta E_{S-T}$ , with the former stabilizing singlets and the latter stabilizing triplets. For example, the <sup>3</sup>B<sub>1</sub> state of SiH<sub>2</sub> is 18–21 kcal/mol (experimental,<sup>4</sup> 19–23 kcal/mol calculated<sup>5</sup>) higher in energy than the <sup>1</sup>A<sub>1</sub> ground state, whereas a much larger gap of 75–77 kcal/mol has been measured for SiF<sub>2</sub>.<sup>6</sup> Likewise, methyl substituents increase the gap to 23–26 kcal/mol in Si(CH<sub>3</sub>)<sub>2</sub>.<sup>7b,c,8</sup> In contrast, the more electropositive SiH<sub>3</sub> group decreases the computed  $\Delta E_{S-T}$  to –5 to –10 kcal/mol in Si(SiH<sub>3</sub>)<sub>2</sub>.<sup>3c,9</sup> With electropositive Li substitution, theory in fact has already predicted that SiLiH and SiLi<sub>2</sub> are ground-state triplets, being by several kcal/mol more stable than the singlet species.<sup>3a,7a,c,8–10</sup> However, although interesting conceptually, it appears questionable if SiLiH or SiLi<sub>2</sub> will become accessible experimentally. (b) Another important factor is the steric control of  $\Delta E_{S-T}$ : the singlet state is continuously destabilized relative to the triplet state upon widening the R–Si–R angle ( $\alpha$ ), eventually the singlet and triplet curves cross, and the order of stability of the two states is reversed, e.g., at  $\alpha \cong 130^\circ$  for the parent SiH<sub>2</sub>.<sup>11</sup> This idea inspired several experimental studies which used bulky carbon substituents R, such as *tert*-butyl,<sup>12</sup> mesityl (2,4,6-trimethylphenyl),<sup>13</sup> or 1-adamantyl,<sup>14</sup> but all of these R<sub>2</sub>Si silylenes were found to be ground-state singlets. Theoretical studies along the same lines culminated in a landmark paper by Grev, Schaefer, and Gaspar,<sup>9</sup> in which it has been clearly shown that the goal of generating a triplet silylene might be easier to achieve if both the electronic effects of  $\alpha$ -electropositive atoms and the steric widening of the R–Si–R angle are combined. Using TCSCF (singlet)–SCF (triplet) calculations, these authors indeed computed a triplet ground state for Si(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> ( $\Delta E_{S-T} = 1.2$  kcal/mol), but from calibration of this theoretical level against results for smaller systems at more sophisticated levels of theory they concluded that the singlet state is by 3–4 kcal/mol more stable than the triplet state.<sup>9</sup> Thus, the question of which substituents reverse the singlet–triplet stability producing a ground-state triplet still remains.

The accurate prediction of singlet–triplet energy differences constitutes a substantial challenge for standard *ab initio* theory because of the need to treat both states in a balanced way, to include both near degeneracy and dynamic electron correlation effects. The answer of post-HF *ab initio* theory to such a problem, the use of a high level of correlation treatment in combination with large and flexible basis sets, is not a practical option for the highly substituted systems representing promising candidates for ground-state triplet silylenes. However, presently, methods based on approximate density functional theory provide a computationally efficient alternative to the rigorous *ab initio* approach.

To gauge the accuracy of the practical computational “workhorse” that we have chosen for the larger systems, the BLYP/DZVP-ECP method,<sup>15</sup> we have studied a number of smaller

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(15) These calculations have been performed with the program DGAUSS 2.3, Cray Research, Inc., 1994. The gradient corrected BLYP functional was used with a standard DZVP valence basis set and an effective core potential (ECP, see Chen, H.; Krasowski, M.; Fitzgerald, G. *J. Chem. Phys.* **1993**, *98*, 8710) on all non-hydrogen atoms. Even with this approximate method the calculations on the larger molecules required several hundred hours of CRAY-J90 time per optimization.

**Table 1.**  $\Delta E_{S-T}$  (kcal/mol) and R–Si–R Bond Angles (Singlet/Triplet, in degrees) Computed at Various Levels of Theory

method	SiH <sub>2</sub>	Si(CH <sub>3</sub> ) <sub>2</sub>	Si(SiH <sub>3</sub> ) <sub>2</sub>	Si(Si(CH <sub>3</sub> ) <sub>3</sub> ) <sub>2</sub>
BLYP/DZVP-ECP	–18.5 90.9/118.3	–23.6 98.8/118.3	–9.3 94.7/124.5	–3.2 100.6/129.1
BLYP/DZP	–20.9 90.9/118.8	–26.5 98.0/119.3	–10.1 93.6/126.2	–4.4 100.9/129.1
B3LYP/DZP	–20.1 91.4/118.4	–25.8 97.8/118.7	–7.6 92.7/126.1	–3.3 100.9/129.6
B3LYP/6-311++G(3d,2p)	–20.7 91.5/118.5	–26.2 97.4/118.1	–9.0 92.3/126.6	–3.1 <sup>c</sup> –3.1 <sup>c</sup>
CCSD(T)/cc-pVQZ	–20.2 <sup>a</sup> 92.4/118.5	–26.6 <sup>b</sup>	–9.8 <sup>b</sup>	

<sup>a</sup> Energy calculations on CCSD(T)/6-311++G(3df,2p) optimized geometries. <sup>b</sup> Energy calculations on B3LYP/6-311++G(3d,2p) optimized geometries. <sup>c</sup> Energy calculations on B3LYP/DZP optimized geometries.

silylenes at various levels of theory,<sup>16</sup> and the results are summarized in Table 1.

As evident from these data, there is an overall good agreement among the various levels of theory for the computed  $\Delta E_{S-T}$  and the optimized bending angle  $\alpha$ . We note a general tendency of the BLYP/DZVP-ECP to overestimate the stability of the triplet by 2–3 kcal/mol compared to the more reliable reference calculations, e.g., for SiH<sub>2</sub> and Si(CH<sub>3</sub>)<sub>2</sub>. A pleasingly low deviation of the BLYP/DZVP-ECP calculations is obtained for the two silyl-substituted silylenes Si(SiH<sub>3</sub>)<sub>2</sub> and Si(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>. There is no obvious reason why the same accuracy should not be present in all other silyl-substituted systems studied. Hence, we conclude that our BLYP/DZVP-ECP calculations overestimate the relative stability of the triplet by 3 kcal/mol at most (including corrections for zero-point energies, which do not exceed 0.5 kcal/mol).

The small energy gap of –3.2 kcal/mol computed at BLYP/DZVP-ECP for Si(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> confirms the best previous theoretical estimate for this species ( $\Delta E_{S-T} = -3$  to  $-4$  kcal/mol)<sup>9</sup> and led us to select the Si–Si–Si unit as the essential building block for finding a ground-state triplet silylene. Inspired by Gaspar's experimental ideas<sup>14</sup> and the theoretical reasonings mentioned above, we first studied Si(1-adamantyl)<sub>2</sub> and Si(1-silaadamantyl)<sub>2</sub>. In agreement with experiment,<sup>14</sup> we found the former to have a singlet ground state. On the other hand, according to the BLYP/DZVP-ECP results, Si(1-silaadamantyl)<sub>2</sub> possesses a triplet ground state. However, given the observed uncertainty of our computational approach of up to –3 kcal/mol, the computed gap of 0.9 kcal/mol is certainly too small to allow for an unequivocal statement with respect to its ground-state multiplicity.

In search of more promising candidates we turned to the Si(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> system and increased the steric bulk of the  $\alpha$ -silicon substituents by consecutively adding alkyl groups.<sup>17</sup> The introduction of one *tert*-butyl group to each silyl substituent causes an opening of  $\alpha$  by 6° in the singlet structure, whereas  $\alpha$  remains

(16) The B3LYP functional has been used as implemented in Gaussian 94, Gaussian, Inc., Pittsburgh, PA, 1995. Very high accuracy CCSD(T) calculations employing the correlation consistent polarized quadruple  $\zeta$  basis set (cc-pVQZ, H. C. Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007; Si: Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358) have been performed with Molpro 96 (see, for example: Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219 and references therein).

(17) The structures of all of these silylenes were first optimized using the semiempirical AM1 method. At this level of theory a systematic search of the conformational space for rotation around the various bonds was carried out, i.e., all Si–Si and Si–C bonds were systematically rotated in steps of 120°, and subsequent geometry optimizations of all geometrical parameters (including dihedral angles) were carried out (several hundred conformations were calculated for each case). The structures lowest in energy for the singlet and for the triplet states of each silylene, which correspond to the global minima at this level of theory, were then submitted to geometry optimization at the DFT level. The conformational analyses were performed using the Spartan 3.0 program (Wavefunction, Inc., 18401 von Karman Ave., Irvine, CA 92715.)

(18) Kira, M. (Tohoku University, Sendai, Japan), personal communication.

(19) Experiments currently being conducted by Gaspar et al. will soon allow to test this prediction. For a preliminary report of detecting a triplet (*i*-Pr<sub>3</sub>Si)<sub>2</sub>Si see: Gaspar, P. P.; Chen, T.; Haile, T.; Lei, D.; Lin, T. S.; Smirnov, A. I.; Winchester, W. R. The 31 Organosilicon Symposium, Tulane University, New Orleans, Louisiana, May 29–30, 1998, C-3.

**Table 2.**  $\Delta E_{S-T}$  (kcal/mol) and Si–Si–Si Bond Angles (Singlet/Triplet) Computed at the BLYP/DZVP-ECP Level of Theory

species	$\Delta E_{S-T}$	$\alpha_{Si-Si-Si}^a$
Si(1-adamantyl) <sub>2</sub>	–15.9	112.7/125.0
Si(1-silaadamantyl) <sub>2</sub>	0.9	116.3/129.4
Si(Si(CH <sub>3</sub> ) <sub>2</sub> ( <i>t</i> -Bu)) <sub>2</sub>	–1.5	106.4/130.1
Si(Si( <i>i</i> -Pr) <sub>3</sub> ) <sub>2</sub>	1.7; 1.4 <sup>b</sup>	119.1/137.2
Si(Si( <i>i</i> -Pr)( <i>t</i> -Bu)) <sub>2</sub>	2.4	121.0/142.2
Si(Si( <i>t</i> -Bu) <sub>3</sub> ) <sub>2</sub>	7.1	130.9/147.5

<sup>a</sup> In degrees. <sup>b</sup> B3LYP/DZP energy calculations on BLYP/DZVP-ECP optimized geometries.

nearly unchanged in the triplet, which is indicative of only minor steric repulsion. Consequently,  $\Delta E_{S-T}$  increases only slightly compared to Si(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, and the ground-state multiplicity remains unchanged (Table 2). This is consistent with recent experimental findings by Kira et al. that (*t*-BuMe<sub>2</sub>Si)<sub>2</sub>Si and (*i*-PrMe<sub>2</sub>Si)<sub>2</sub>Si have singlet ground states,<sup>18</sup> lending support to the reliability of our computational approach. The more bulky Si(*i*-propyl)<sub>3</sub> group as substituent widens  $\alpha$  significantly in both the singlet and the triplet silylenes, and (*i*-Pr<sub>3</sub>Si)<sub>2</sub>Si is computed to be a ground-state triplet at the BLYP/DZVP-ECP level<sup>17</sup> (and the more elaborate B3LYP/DZP calculations confirm this result). However,  $\Delta E_{S-T}$  is small, only 1.4–1.7 kcal/mol making an unequivocal theoretical prediction of its ground state very difficult.<sup>19</sup> A slightly larger gap of 2.4 kcal/mol in favor of the triplet results from the presence of two Si(*i*-propyl)(*tert*-butyl)<sub>2</sub> substituents on the central silicon atom.<sup>17</sup> Exchange of the two remaining *i*-propyl groups by *t*-butyl groups, however, leads to a significant increase in  $\alpha$  and in  $\Delta E_{S-T}$ , with a computed singlet–triplet gap of 7.1 kcal/mol in favor of the triplet. Using even the most conservative error estimate, based on the largest deviation found in our calibration calculations, the lower limit for  $\Delta E_{S-T}$  in this silylene should be 4.1 kcal/mol, and we therefore are confident in predicting that (***t*-Bu<sub>3</sub>Si**)<sub>2</sub>Si has a triplet ground-state multiplicity. In view of the pleasingly low deviations observed in the calibration calculations, especially for Si(SiR<sub>3</sub>)<sub>2</sub>, R = H, CH<sub>3</sub>, we believe that Si((*i*-propyl)(*tert*-butyl)<sub>2</sub>)<sub>2</sub> and Si(Si(*i*-propyl)<sub>3</sub>)<sub>2</sub><sup>19</sup> are also promising candidates for experiment. Our theoretical predictions are awaiting experimental testing and verification.

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