DFT Study on Triplet Ground State Silylenes Revisited: The Quest for the Triplet Silylene Must Go On

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Summary: A DFT study on triplet ground state silylenes was reinvestigated using more precise calculation methods without an effective core potential approximation than that used in a previous study. Despite both the results of the former theoretical prediction and the recent finding of the triplet character of tri-tert-butylsilyl(triisopropylsilyl)silylene, (t-Bu)$_3$Si−Si−Si(i-Pr)$_3$, only bis(tri-tert-butylsilyl)silylene, (t-Bu$_3$Si)$_2$Si, is calculated to have a triplet ground state.

Silylene is one of the most important intermediates in the reaction of organosilicon compounds.[1] The electronic structure of silylenes has attracted much attention, because all known silylene species possess a singlet ground state in contrast to the easily accessible triplet ground state of their carbon analogues, the carbenes. Therefore, the preparation of a triplet ground state silylene has been one of the most challenging issues in modern organosilicon chemistry. Despite the many reported experimental efforts,[2−4] there has been no clear evidence for the existence of the triplet ground state silylene. On the other hand, recent theoretical studies have predicted that the generation of the triplet ground state silylene is achievable using highly bulky silyl groups as appropriate substituents.[5,6] Indeed, Gaspar et al. tried to justify the usefulness of the bulky silyl groups and reported the photochemical generation of bis(triisopropylsilyl)silylene, (i-Pr$_3$Si)$_2$Si (**1**).[7] Although the hydrogen acquisition reaction of **1** plausibly derived from the triplet state was observed, the stereospecific addition of **1** to the *cis*- and *trans*-2-butenes was also observed as a typical characteristic of the singlet ground state silylene. More recently, his group reported the generation of more sterically encumbered tri-*tert*-butylsilyl(triisopropylsilyl)silylene, (t-Bu)$_3$Si−Si−Si(i-Pr)$_3$ (**2**).[8] In the absence of trapping reagents, **2** showed an intramolecular hydrogen transfer providing the four-membered disilacyclobutane compound. This reaction seemed unlikely to arise from a singlet silylene at room temperature, and thus the reaction was regarded as chemical evidence for its triplet ground state. Therefore, the long quest for the triplet silylene was expected to be finally over.[9]

Nevertheless, the direct evidence of the radical character of **2** by the ESR experiment is not yet available due to the absence of a photochemical precursor that will generate the silylene in a glass matrix. More importantly, it has been noticed that the previous DFT calculations[6] strongly supporting Gaspar's experiment include some uncertainties. First, the effective core potentials (ECPs) were used instead of the real DZVP basis set on all the non-hydrogen atoms to reduce the expense of the computational cost. This approximation technique cannot avoid increasing the calculation errors, and it has already been pointed out in the original paper, i.e., "the BLYP/DZVP-ECP method has a general tendency to overestimate the stability of the triplet by 2−3 kcal/mol".[6] The error range covers not only the calculated $\Delta E_{\mathrm{S-T}}$ value of **1** (+1.4−1.7 kcal/mol) but also that of the more bulky bis(di-*tert*-butylisopropylsilyl)silylene, (t-Bu$_2$(i-Pr)Si)$_2$Si (**3**) (+2.4 kcal/mol). Second, semiempirical AM1 calculations were used for the preoptimization of the singlet and triplet states of all the silylenes in the study, and then only the lowest energy structure of the AM1 calculation was submitted to geometry optimization of the DFT level. We have often found, however, that the semiempirical calculation of organosilicon compounds does not always reproduce the energy minimum of the ab initio and DFT calculations.[10] If the AM1 calculation misleads the structure into the local energy minimum, it would be questionable as to whether the optimized structure at the DFT level is the actual lowest energy structure.

In this communication, we recalculated the energies of the corresponding di(silyl)silylenes using the same BLYP/DZVP method as in a previous study, but without an ECP approximation. We also investigated the conformational analyses by rotating the alkyl substituents on silicon at the same DFT level. The optimized structures of BLYP/DZVP level were further examined by the other DFT method with the triple-ζ basis set (BLYP/TZVP). Consequently, we have found that *only bis(tri-tert-butylsilyl)silylene, (t-Bu$_3$Si)$_2$Si (**4**), which has never*

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Table 1. ΔE_{S-T} (kcal/mol) and R−Si−R Bond Angles (singlet/triplet, in deg) Computed at Various Levels of Theory

method	SiH_2	$SiMe_2$	$Si(SiH_3)_2$
BLYP/DZVP	-20.7^a (-21.0^b)	-25.5^a (-26.1^b)	-9.7^a (-10.1^b)
	91.5/118.0	99.1/119.1	92.8/125.2
BLYP/TZVP	-20.4^a (-20.7^b)	-26.0^a (-26.8^b)	-9.1^a (-9.5^b)
	92.1/118.4	99.4/119.3	93.2/125.7
B3LYP/6-311++G(3d,2p)[c]	−20.7	−26.2	−9.0
	91.5/118.5	97.4/118.1	92.3/126.6
BLYP/DZVP-ECP[c]	−18.5	−23.6	−9.3
	90.9/118.3	98.8/118.3	94.7/124.5

[a] Without ZPE correction. [b] With ZPE correction. [c] From ref 6.

Table 2. ΔE_{S-T} (kcal/mol), Destabilization Energies in the Isodesmic Reaction (ΔE_{DS}, ΔE_{DT}, kcal/mol), and R−Si−R Bond Angles (singlet/triplet, $\alpha_{Si-Si-Si}$, in deg) Computed at Various Levels of Theory

species	method	BF[b]	DFF[c]	ΔE_{S-T}[d]	$\alpha_{Si-Si-Si}$	ΔE_{DS}	ΔE_{DT}	$\Delta\Delta E_{DS-DT}$[e]
$Si(SiMe_3)_2$	BLYP/DZVP-ECP[a]			−3.2	100.6/129.1			
	BLYP/DZVP	183	411	−4.2	100.2/125.6	0.0	0.0	0.0
	BLYP/TZVP	291	411	−3.9	99.9/125.5	0.0	0.0	0.0
$Si(SiMe_2(t\text{-}Bu))_2$	BLYP/DZVP-ECP[a]			−1.5	106.4/130.1			
	BLYP/DZVP	297	663	−3.8	102.4/126.7	+1.7	+1.4	+0.3
	BLYP/TZVP	477	663	−3.7	102.1/126.0	+0.9	+0.7	+0.2
$Si(Si(i\text{-}Pr)_3)_2$ (**1**)	BLYP/DZVP-ECP[a]			+1.7	119.1/137.2			
	BLYP/DZVP	411	915	−1.7	106.3/143.2	+8.5	+6.1	+2.4
	BLYP/TZVP	663	915	−1.3	106.2/143.3	+7.8	+5.2	+2.6
$Si(Si(i\text{-}Pr)_3)(Si(t\text{-}Bu)_3)$ (**2**)	BLYP/DZVP-ECP[a]			N/A				
	BLYP/DZVP	468	1041	−0.8	119.5/141.0	+13.1	+9.8	+3.3
	BLYP/TZVP	756	1041	−1.0	119.3/141.0	+11.5	+8.7	+2.8
$Si(Si(i\text{-}Pr)(t\text{-}Bu)_2)_2$ (**3**)	BLYP/DZVP-ECP[a]			+2.4	121.0/142.2			
	BLYP/DZVP	487	1083	−2.4	117.6/148.1	+14.9	+13.2	+1.7
	BLYP/TZVP	787	1083	−2.4	117.5/148.2	+14.1	+12.6	+1.5
$Si(Si(t\text{-}Bu)_3)_2$ (**4**)	BLYP/DZVP-ECP[a]			+7.1	130.9/147.5			
	BLYP/DZVP	525	1167	+4.9	130.6/156.0	+23.8	+14.7	+9.1
	BLYP/TZVP	849	1167	+4.5	130.5/155.9	+21.0	+12.6	+8.4

[a] From ref 6. [b] Number of basis functions. [c] Number of density fitting functions. [d] Without ZPE correction. [e] $\Delta\Delta E_{DS-DT} = \Delta E_{DS} - \Delta E_{DT}$.

been detected,[11,12] *will have a triplet ground state,* while all the other di(silyl)silylenes will adopt *a singlet ground state or almost isoenergetic singlet−triplet ground states.*

The DFT calculations were performed with the program DGauss 4.1 on an IBM RS/6000 SP system.[13] Spin-restricted BLYP and spin-unrestricted UBLYP functionals were used for the singlet and triplet calculations, respectively.[14,15] The calculation results of a few smaller silylenes are summarized in Table 1. Although there is no significant difference in the calculated bond angles of the silylenes, the ΔE_{S-T} values of SiH_2 and $SiMe_2$ calculated by both the BLYP/DZVP and BLYP/TZVP methods showed a better agreement with those of the higher level B3LYP/6-311++G(3d,2p) calculations than the BLYP/DZVP-ECP method. The calculated ΔE_{S-T} values of $Si(SiH_3)_2$ (−9.7 and −9.1 kcal/mol, without zero-point energy (ZPE) correction) by the present BLYP methods are well comparable to that calculated by the MCSCF-CID method ($\Delta E_{S-T} = -8.3$ kcal/mol), which should be one of the most sophisticated computational procedures for singlet−triplet gaps, reported by Kalcher and Sax.[16] From the deviation observed in Table 1, we estimated that the calculation error in the present study should be 1 kcal/mol at most. Using these more precise DFT methods, the structures of the singlet and triplet states of the larger silylenes were calculated. The ΔE_{S-T} value and the bond angles computed at the DFT levels are summarized in Table 2. [17]

Unfortunately, we could not compare the optimized structures to the former results due to the absence of the supplementary geometrical data in a previous study. However, we can at least compare the calculated bond angles. There are large deviations in the recalculated bond angles from the former results, especially for the singlet state of the silylene **1** (^{1}**1**). The computed bond angle of ^{1}**1** (106.3°) at BLYP/DZVP is much smaller than the reported one (119.1°). We found a conformational isomer of ^{1}**1** with the bond angle of 119.4° as a local minimum structure, but which was 3.4 kcal/mol less stable than the lowest energy structure. This discrepancy of the optimized structures of ^{1}**1** should be derived from the AM1 preoptimization in a previous study,

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(11) The silylene **4** has been postulated as a possible intermediate of the dehalogenation reaction of $(t\text{-}Bu_3Si)_2SiBr_2$; see: Wiberg, N. *Coord. Chem. Rev.* **1997**, *163*, 217−252.

(12) Very recently, the photochemical generation of $(t\text{-}Bu_3Si)_2Si$ from the corresponding silacyclopropene and its triplet state ESR spectra at 77 K were preliminarily reported: Tanaka, T.; Ichinohe, M.; Sekiguchi, A.; Akiyama, K. Abstract of 6th Symposium the Society of Silicon Chemistry Japan, Nov 15−16, 2001; p 68.

(13) DGauss 4.1, 1996, available from Oxford Molecular as part of the Unichem 4.1 suite of programs. Semiempirical calculations were performed by the MNDO94 program, which is also a part of the Unichem 4.1.

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(15) Details of the present computational approach are described in the Supporting Information.

(16) Kalcher, J.; Sax, A. F. *J. Mol. Struct. (THEOCHEM)* **1992**, *253*, 287−302.

(17) Due to the limitation of both CPU time and memory size available, ZPE correction could not be applied for most of the larger silylenes in Table 2. However, the ZPE-corrected ΔE_{S-T} value of $Si(SiMe_3)_2$ (−4.9 kcal/mol at BLYP/TZVP) is 1.0 kcal/mol larger (more negative) than that without the ZPE correction. Destabilization of the triplet state resulting in an increase of ΔE_{S-T} by the ZPE correction is consistent with the tendency of the small silylenes shown in Table 1, and thus we suppose it would be general for the other silylenes. Therefore the relative stability of singlet and triplet states of the other larger di(silyl)silylenes in Table 2 would not be affected, even if the ZPE correction can be applied.

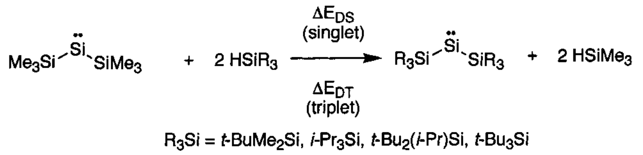

Figure 1. Isodesmic reaction scheme used to estimate the contribution of the bulky silyl group substitution to the stability of the singlet and triplet states of the di(silyl)-silylenes.

because the single-point energy calculation by the AM1 method could not reproduce the relative stability of the two conformational isomers of ^{1}**1**. Using the AM1 method, the large bond angle isomer of ^{1}**1** was calculated to be 0.1 kcal/mol more stable than the true lowest energy structure of ^{1}**1** at the DFT level. On the other hand, the similar single-point energy calculation by the BLYP/DZVP-ECP method kept the relative stability of the two structural isomers of ^{1}**1**. However, the BLYP/DZVP-ECP single point calculation completely failed to reproduce the ΔE_{S-T} of **1**. It was incorrectly suggested that triplet state of **1** (^{3}**1**) became 0.3 kcal/mol more stable than its singlet state by the single-point energy calculation using the BLYP/DZVP-ECP method. Full optimization of ^{1}**1** and ^{3}**1** by the BLYP/DZVP-ECP method from the final structures of the BLYP/DZVP calculation as starting configurations was worse than the single-point calculation for the estimation of ΔE_{S-T} of **1**. ^{3}**1** was incorrectly calculated to be 1.1 kcal/mol more stable than ^{1}**1**. We thus concluded that the use of ECP approximation was a main reason for the overestimation of the stability of the triplet state of **1** in the previous study.[6] Eventually, all the silylenes except for **4** were found to be *a singlet ground state*. Even for the silylene **2** experimentally expected to be a triplet,[8] the singlet state is located slightly lower than its triplet state by 1.0 kcal/mol (at BLYP/TZVP). Only **4** has a triplet ground state, being 4.5 kcal/mol more stable than its singlet state (at BLYP/TZVP).

It has been suggested that, even if the silylene **1** has a *triplet* ground state, the stereospecific addition of **1** to 2-butenes was still explainable if the product of the equilibrium constant for formation of the singlet from the triplet and the rate constant for stereospecific addition of ^{1}**1** is much greater than that for nonstereospecific addition of ^{3}**1**.[7] If this reaction mechanism is correct, however, there must be another dilemma. Even if the silylene **2** has a *singlet* ground state as calculated in the present study, the apparent intramolecular reaction from ^{3}**2** in the absence of trapping reagents will be also explainable in a manner similar to the silylene **1** by the existence of an equilibrium between singlet and triplet states of **2** and the relatively fast rate constant of the intramolecular reaction from ^{3}**2** compared to that for the intermolecular reaction from ^{1}**2**. Therefore, it will be very difficult to determine the ground state multiplicity of sterically encumbered bis(trialkylsilyl)silylenes with a small ΔE_{S-T} value by only the chemical reactivity observed.

A suitable isodesmic reaction (Figure 1) shows the significant nature of the silylene **4** (Table 2).[18] We found that both the singlet and triplet states of the parent bis(trimethylsilyl)silylene, $(Me_3Si)_2Si$, are destabilized by the addition of the bulky substituents. The destabilization energy of the singlet (ΔE_{DS}) is always larger than that of the triplet (ΔE_{DT}) for all the bulky silylenes. This unsymmetrical destabilization tendency is the origin of the decrease in ΔE_{S-T}. However, the difference between ΔE_{DS} and ΔE_{DT} ($\Delta\Delta E_{DS-DT}$) is only +2.8 kcal/mol for **2** (at BLYP/TZVP). On the other hand, the ΔE_{DS} of **4** (+21.0 kcal/mol) is much higher than ΔE_{DT} (+12.6 kcal/mol), and thus the $\Delta\Delta E_{DS-DT}$ (+8.4 kcal/mol) of **4** is 3 times larger than that of **2**. The triplet state of **4** is, therefore, unequivocally more stable than its singlet state due to the large $\Delta\Delta E_{DS-DT}$ value to overcome the ΔE_{S-T} value of the parent bis(trimethylsilyl)silylene.

Although the silylene **2** was predicted to be a singlet by our DFT calculations, the calculated ΔE_{S-T} of **2** was very small. We also have to consider that even our calculations would include some unavoidable errors. We believe the error would be at most 1 kcal/mol as mentioned above, and by taking into account the error, the singlet and triplet state of the silylene **2** should be almost *isoenergetic*. This is the reason the silylene **2** could show a typical reaction from the triplet state even at room temperature.[8] The calculated geometrical data also support a specific and facile switch of the electronic state of the silylene **2**. When the calculated bond angles of the silylenes **1**−**4** in the singlet state by the BLYP/TZVP method are compared, the order is as follows: ^{1}**1** (106.2°) < ^{1}**3** (117.5°) < ^{1}**2** (119.3°) < ^{1}**4** (130.5°). However, careful conformational analyses of the structures showed the order significantly changed in the triplet state as follows: ^{3}**2** (141.0°) < ^{3}**1** (143.3°) < ^{3}**3** (148.2°) < ^{3}**4** (155.9°). Eventually, the bond angle difference of **2** between the singlet and triplet states is only 21.7°, which is the smallest among all the bis(silyl)-silylenes shown in Table 2. In other words, **2** can switch the two electronic states by the least motion of the bond angle. Not only this specific structural character but also the very small ΔE_{S-T} value is important in order to understand the facile accessibility to the triplet state of **2**.

In conclusion, we confirmed that the overestimation of the stability of the triplet state of bis(silyl)silylenes actually occurred in a previous study. We found that only $(t\text{-}Bu_3Si)_2Si$ **4** will have a triplet ground state. We strongly suggest that the quest for the triplet ground state silylene must go on until the direct ESR observation of **2** or the photochemical generation of the unequivocally predicted triplet silylene **4** is accomplished.[12]

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Supporting Information Available: Tables of absolute energies of all the silylenes calculated by two DFT methods and a listing of Cartesian coordinates for all the silylenes optimized at the BLYP/TZVP level. This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] A similar isodesmic reaction was already used for the evaluation of the electronic structure of the long-lived triplet carbenes; see: Woodcock, H. L.; Moran, D.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **2001**, *123*, 4331−4335.