

# Stable silicon-centered localized singlet 1,3-diradicals $\text{XSi}(\text{GeY}_2)_2\text{SiX}$ : theoretical predictions

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**ABSTRACT:** Some localized singlet 1,3- $\sigma$ -diradicals,  $\text{XSi}(\text{GeY}_2)_2\text{SiX}$ , ( $\text{X} = \text{H}, \text{CH}_3, \text{SiH}_3, \text{C}(\text{CH}_3)_3, \text{NH}_2$  for  $\text{X} = \text{F}$ ;  $\text{Y} = \text{H}, \text{CH}_3, \text{OH}, \text{NH}_2, \text{SiH}_3$  for  $\text{X} = \text{H}$ ) are theoretically designed by the orbital phase theory, the density functional theory (DFT) calculations, the second order Møller–Plesset perturbation theory (MP2), and the complete active space self-consistent field (CASSCF) methods. The silicon-centered singlet diradicals are more stable than the lowest triplets and than the bicyclic  $\sigma$ -bonded isomers if the isomers exist. The most stable singlet diradicals are not the  $\pi$ -type diradicals, but the  $\sigma$ -type diradicals where the radicals interact with each other through the Si–Ge bonds in the four-membered rings. Copyright © 2007 John Wiley & Sons, Ltd.

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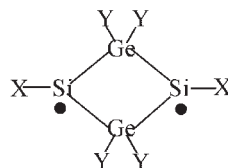
**KEYWORDS:** 1; 3-diradicals; theoretical calculations

## INTRODUCTION

Diradicals are chemical species with two unpaired electrons, which occupy two degenerate or nearly degenerate molecular orbitals. Diradicals play a crucial role in bond-forming and bond-breaking processes, and they are even more ephemeral than monoradicals because the bifunctionality permits both intermolecular and intramolecular couplings. In recent years, localized 1,3-diradicals are of increasing interest in organic chemistry.<sup>1–25</sup> Nevertheless, detections of the localized diradicals are difficult possibly due to the high reactivities and short lifetimes. Singlet states of diradicals usually compete with the triplet states. It is also possible for two radical centers of 1,3-diradicals to form one  $\sigma$  bond. Therefore, the preparation of stable localized singlet 1,3-diradicals is still a challenge.

Some experimental works have shown evidence of long-bond compounds and bond-stretch isomers.<sup>11</sup> The distance between the unpaired electrons provides a qualitative evaluation of the diradical character. For 1,3-disilabicyclo[1.1.0]butane,<sup>11a</sup> the interatomic Si...Si distance (2.412 Å) is longer than the Si–Si single bond

length (2.27–2.33 Å),<sup>26</sup> being taken as an inverted  $\sigma$  bond with diradical character. Some germanium (Ge)- and stannum (Sn)-centered singlet diradicals,  $\text{Ge}_2\text{N}_2$  and  $\text{Sn}_2\text{N}_2$ , were also reported experimentally.<sup>27</sup> It was shown that those Ge- and Sn-centered compounds appear distinct diradical character with much longer distance of Ge...Ge (2.755 Å)<sup>27a</sup> and Sn...Sn (3.398 Å)<sup>27b</sup> than the normal Ge–Ge (2.44 Å)<sup>28</sup> and Sn–Sn (2.81 Å)<sup>29</sup> single bond, respectively. In the present work, we theoretically design some silicon-centered diradicals,  $\text{XSi}(\text{GeY}_2)_2\text{SiX}$  ( $\text{X} = \text{H}, \text{CH}_3, \text{SiH}_3, \text{C}(\text{CH}_3)_3, \text{NH}_2$  for  $\text{Y} = \text{F}$ ;  $\text{Y} = \text{H}, \text{CH}_3, \text{OH}, \text{NH}_2, \text{SiH}_3$  for  $\text{X} = \text{H}$ , **1–11**) with distinct diradical character. The singlet states of these diradicals are predicted to be more stable than the triplet states with appreciable singlet–triplet (S–T) splittings and than the bicyclic  $\sigma$ -bonded isomers, 1,3-disila-2,4-digermbicyclo[1.1.0]butanes. The calculated Si...Si distances between two unpaired electrons (2.9–3.6 Å) are longer than the normal Si–Si single bond.



- 1 X = H, Y = F
- 2 X = CH<sub>3</sub>, Y = F
- 3 X = SiH<sub>3</sub>, Y = F
- 4 X = C(CH<sub>3</sub>)<sub>3</sub>, Y = F
- 5 X = NH<sub>2</sub>, Y = F

- 6 X = H, Y = H
- 7 X = H, Y = CH<sub>3</sub>
- 8 X = H, Y = OH
- 9 X = H, Y = NH<sub>2</sub>
- 10 X = H, Y = SiH<sub>3</sub>
- 11 X = CH<sub>3</sub>, Y = SiH<sub>3</sub>

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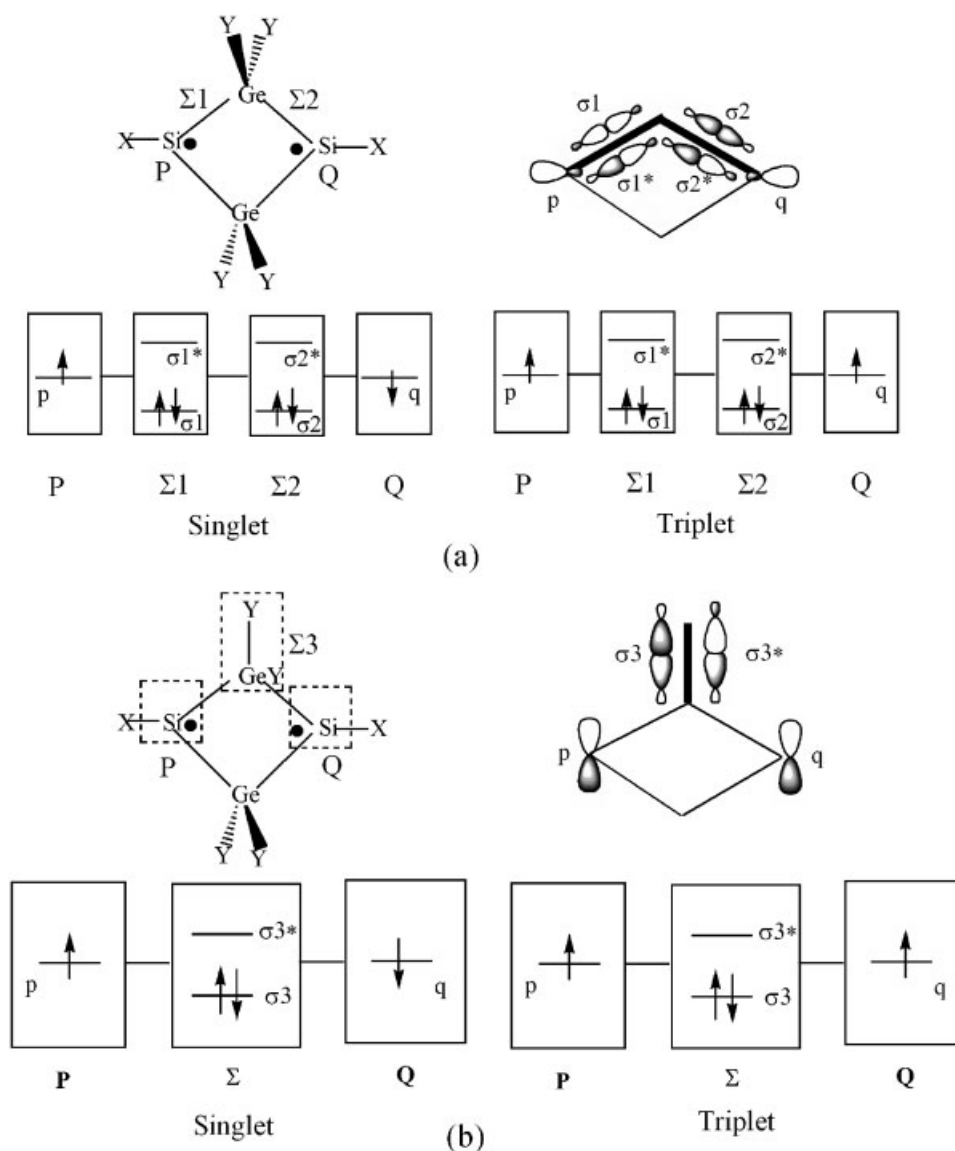
## ORBITAL PHASE DESIGN

The orbital phase theory has been developed for the cyclic orbital interactions underlying various chemical phenomena.<sup>19,25,30–34</sup> The orbital phase is a crucial factor in promoting the cyclic orbital interaction. Here, we employ the orbital phase theory to predict the spin preferences of ground states of the localized 1,3-diradicals, **1–11**.

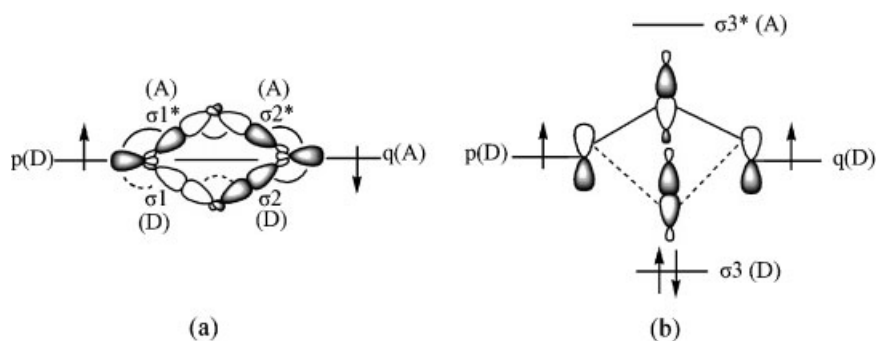
A diradical has two nearly degenerate singly occupied orbitals, p and q, on the two radical centers (P and Q in Fig. 1), respectively. It is possible for the unpaired electrons of diradicals to interact with each other through the bonds or through the space. The through-bond interactions in the singlet and triplet states of localized 1,3-diradicals and  $\pi$ -conjugated diradicals have been addressed from the view point of the orbital phase theory.<sup>19,25,34</sup> The  $\sigma$ -type radical centers interact with each other through the intervening chain of the  $\sigma$  bonds,

$\Sigma_1$  and  $\Sigma_2$  (Fig. 1a).<sup>25</sup> The bonding  $\sigma_1$  and  $\sigma_2$  orbitals are both doubly occupied, and the antibonding  $\sigma_1^*$  and  $\sigma_2^*$  are vacant. The cyclic interaction occurs among the radical orbitals, p and q,  $\sigma_1$  and  $\sigma_2$ , and  $\sigma_1^*$  and  $\sigma_2^*$  orbitals. The  $\pi$ -type radical centers interact with each other through another bond,  $\Sigma_3$  (Fig. 1b). The cyclic interaction occurs among the  $\pi$ -type radical orbitals, p and q with  $\sigma_3$  and  $\sigma_3^*$  orbitals.

The orbital phase properties of the 1,3-diradicals (**1–11**) are depicted in Fig. 2. The electron-donating orbitals are denoted by D, while the accepting orbitals are denoted by A. The effective occurrence of the cyclic orbital interactions requires the simultaneous satisfaction of the following conditions: (1) the electron-donating orbitals (denoted by D–D) are out of phase; (2) the accepting orbitals (denoted by A–A) are in phase; and (3) the donating and accepting orbitals (D–A) are in phase.<sup>19,25,30–34</sup> If the orbital phase meet those require-



**Figure 1.** Models of singlet and triplet localized silicon-centered 1,3-diradicals: (a)  $\sigma$ -type (b)  $\pi$ -type



**Figure 2.** Phase continuity in the (a) singlet  $\sigma$ -type and (b) the triplet  $\pi$ -type 1,3-diradical. The solid and dotted lines indicate in-phase and out-of-phase relations, respectively

ments, the orbital phase is continuous, implying that the delocalization takes place effectively. The system is hence stabilized.

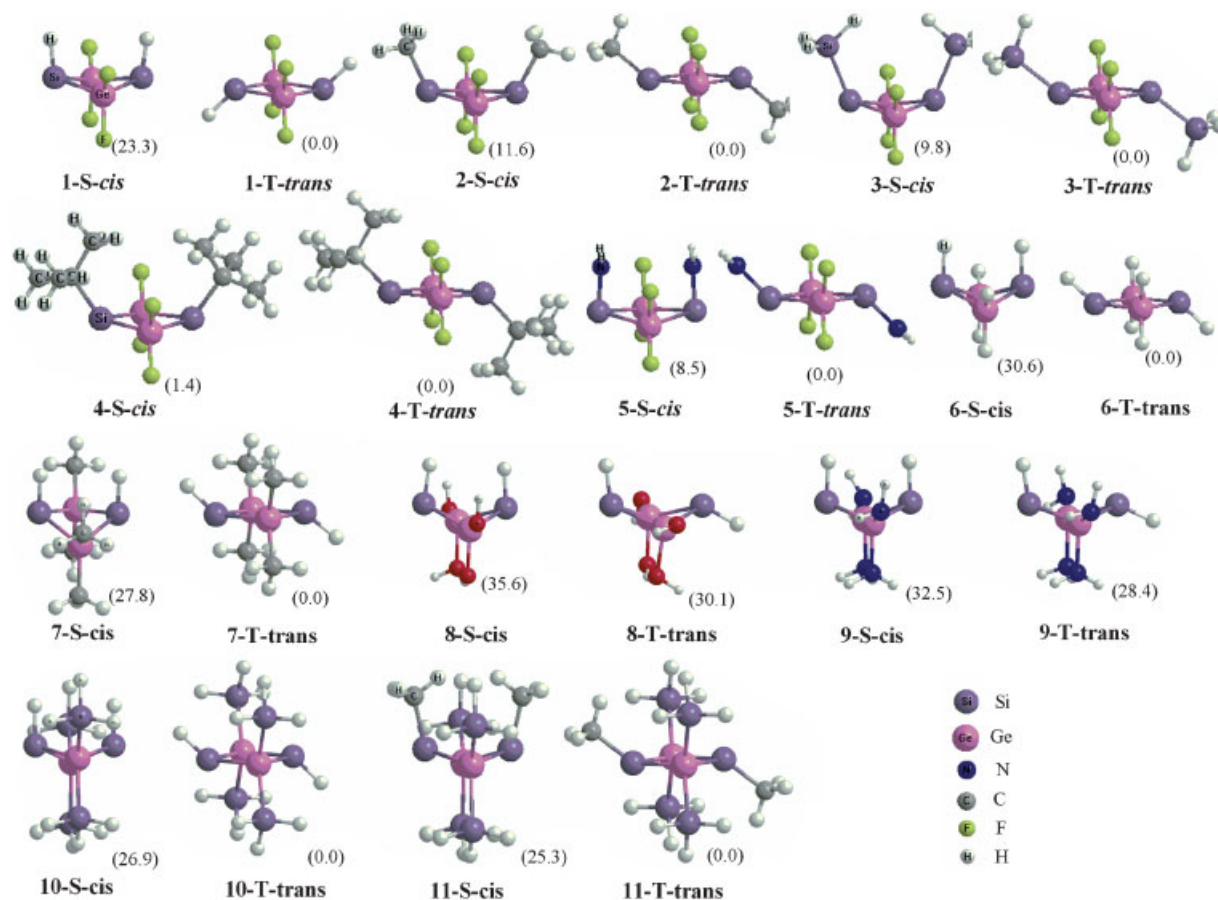
As seen from Fig. 2, the cyclic  $-p-\sigma_1^*-\sigma_2^*-q-\sigma_2-\sigma_1-$  orbital interaction satisfies the continuity requirements in the singlet states of the  $\sigma$ -type diradicals (Fig. 2a): the neighboring orbitals in  $p(D)-\sigma_1^*(A)-\sigma_2^*(A)-q(A)$  are all in phase while those in the sequence  $p(D)-\sigma_1(D)-\sigma_2(D)-q(A)$  are all out of phase. The phase is continuous for the cyclic interaction. Moreover, the radical orbitals,  $p(D)$  and  $q(A)$  are in phase. The direct through-space interaction between the radical centers, that is, the  $p\dots q$  interaction, thermodynamically stabilizes the singlet 1,3-diradicals in addition to the cyclic orbital interactions through the bonds. The extra-stabilization by the through-space interaction increases with the shortening of the distance between the radical centers accompanied by the puckering of the four-membered rings with significant GeSiGeSi dihedral angles. In contrast, the cyclic  $-p-\sigma_3^*-q-\sigma_3-$  orbital interaction is favored by the phase continuity in the triplet states of the  $\pi$ -type diradicals: in phase between the neighboring orbitals in  $p(D)-\sigma_3^*(A)-q(D)$  and out of phase between those in  $p(D)-\sigma_3(D)-q(D)$  for the  $\alpha$ -spins (Fig. 2b). The four-membered rings take planar structures in the  $\pi$ -type diradicals.

The orbital phase theory predicts that the singlet states of the localized 1,3-diradicals thermodynamically prefer the  $\sigma$ -diradicals to the  $\pi$ -diradicals if the interaction through the bond chain is appreciable. This suggests that the  $\sigma$ -bonds ( $\sigma_1$  and  $\sigma_2$ ) should transfer spins to stabilize the singlet diradicals. We choose a heavy atom, Ge, to connect the Si radical centers since the Si—Ge bonds have high  $\sigma$  orbitals and low  $\sigma^*$  orbitals. The Ge atom is larger than the Si atom, keeping the Si radical centers far from each other not to form a bond, or to increase the three-membered ring strain of the  $\sigma$ -bonded isomers, the competitors of the singlet diradicals. In fact, the strain energy (SE) calculated from the homodesmotic<sup>35</sup> reactions of cyclic  $[-SiH_2-GeH_2-SiH_2-]$  is 39.7 kcal/mol at the B3LYP/6-31G\* level, slightly higher than that (38.8 kcal/mol) of cyclotrisilane (cyclic- $Si_3H_6$ ). Furthermore, we choose the four-membered ring structures **1–11**

to multiply the through-bond interactions, to destabilize the transition states of the  $\sigma$ -bond formation by the ring strain, and to strain the  $\sigma$ -bonded isomers by the bicyclic geometries. The substituents Y (=F, H,  $CH_3$ ,  $NH_2$ , OH,  $SiH_3$ ) on the Ge atoms are chosen to stabilize the triplet states of the  $\pi$ -type diradicals by the phase continuity to less extent. The fluorine atom was previously<sup>19</sup> found to lower the polarizability of the C—Y bond due to the large energy gap between the bonding and antibonding orbitals. Polarizable bonds are expected to promote the cyclic  $-p-\sigma_3^*-q-\sigma_3-$  interaction to stabilize the triplet states. Thus, the fluorine atom is suitable for the design of the stable singlet diradicals.

## COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian03 program.<sup>36</sup> We have employed the unrestricted density functional theory (DFT) with B3LYP functional, the unrestricted second order Møller-Plesset perturbation theory (MP2), and the complete active space self-consistent field (CASSCF) method to optimize their geometries, and to investigate spin preferences and energy gaps between the lowest singlet and triplet states ( $\Delta E_{S-T} = E_S - E_T$ ) with both the full electron 6-31G\* basis set and the effective core potential (ECP), LANL2DZ, for Si and Ge. For the silicon-centered 1,3-diradicals, **1–11**, the (6,6) active space was utilized, in which the radical orbitals,  $\pi$  and  $\pi^*$ , and two sets of  $\sigma$  and  $\sigma^*$  orbitals for Si—Ge backbones were involved. To further include effects of dynamical correlation, single-point (6,6)CASPT2N calculations were also carried out at each stationary point obtained by the (6,6)CASSCF calculations. Such calculations have been demonstrated to give rather reasonable predictions on S-T gaps in diradicals.<sup>37</sup> UB3LYP and UMP2 optimized stationary points are demonstrated to be energy minima by frequency analysis. All the reported UB3LYP and UMP2 energies are corrected by the zero-point energies (ZPE). Optimized geometries of the singlet and triplet states of these diradicals and the  $\sigma$ -bonded isomers at various levels can be found in the Figs 3 and 4,



**Figure 3.** The geometries of the lowest singlet (S) and triplet (T) states of the 1,3-diradicals including the *cis* and *trans* isomers optimized at the UB3LYP/6-31G\* level

as well as Figures S1–S5 in Supporting Information. The corresponding values of  $\Delta E_{S-S'}$  ( $\Delta E_{S-S'} = E_S - E_{S'}$ ) and  $\Delta E_{S-T}$  ( $\Delta E_{S-T} = E_S - E_T$ ) at various levels are listed in Table 1 and Tables S1–S6 of Supporting Information. The expectation values of  $\langle S^2 \rangle$  are also given to evaluate the spin contaminations in unrestricted calculations (Tables S1–S5 of Supporting Information).

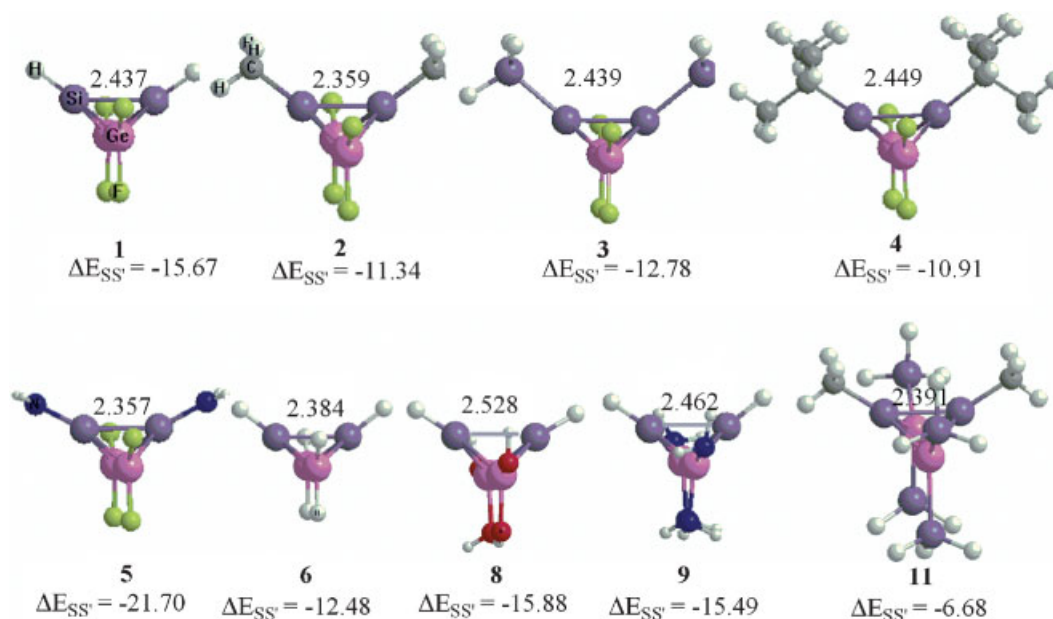
## THE SINGLET PREFERENCE

The lowest singlet diradicals **1–11** were found to have *cis*-conformations with the Si—X bonds significantly bent from the four-membered rings (Figure 3). The radical centers are in conjugation with Si—Ge ring bonds. The geometrical features indicate that the singlet states prefer the  $\sigma$ -type diradicals to the  $\pi$ -type diradicals as have been predicted by the orbital phase theory. The lowest triplet states of **1–7**, **10** and **11** have the  $\pi$ -radical centers at the both Si atoms, which interact with the Ge—Y bonds rather than with the Si—Ge ring bonds. This is in agreement with the orbital phase prediction. The four-membered rings are puckered in the lowest singlet states (S) of **1–11** (with dihedral angles of 1.4–35.6°), and

are planar in the lowest triplet states (T) of **1–11** (except **8** (30.1°) and **9** (28.4°)), *cf.* Fig. 3. The geometries of **8** and **9** imply that these diradicals unexpectedly have the  $\sigma$ -type character on one Si atom and the  $\pi$ -type one on the other. All the lowest triplet states of **1–11** have *trans*-conformations, as expected from the low polarizability of the Ge—Y bonds.

The B3LYP, MP2, CASSCF, and CASPT2 energies of the lowest singlet (S for the diradicals and  $S'$  for the  $\sigma$ -bonded isomers) and the lowest triplet states (T) and the S-T energy gaps,  $\Delta E_{S-T}$  and  $\Delta E_{S-S'}$ , of **1–11** are listed in Table 1. All the singlet diradicals **1–11** are more stable than the triplet states. The UB3LYP results of  $\Delta E_{S-T}$  are close to those obtained by CASSCF calculations. The CASPT2 results show the more significant singlet preference for the ground states of diradicals **1–11**.

All the diradicals calculated here prefer the four-membered ring structures to the bicyclic  $\sigma$ -bonded isomers (Table 1 and Fig. 4). Within the framework of UB3LYP, the lowest singlet diradicals of **1–6**, **8**, **9**, and **11** are predicted to be more stable than the  $\sigma$ -bonded isomers, while we failed to locate the  $\sigma$ -bonded isomers of **7** and **10**. In fact, the  $\sigma$ -bonded isomers of **1–11** have not been located by the MP2 and CASSCF(6,6) calculations.



**Figure 4.** UB3LYP/6-31G\* optimized  $\sigma$ -bonded ( $S'$ ) isomers of **1–6**, **8**, **9** and **11**. The Si–Si bond lengths are shown. Energy gaps ( $\Delta E_{S-S'}$ ) between the lowest singlet ( $S'$ ) and the  $\sigma$ -bonded isomers ( $S'$ ) of 1,3-diradicals calculated are also given

The singlet diradical character can be inspected by the interatomic distance between the radical centers. The non-bonded radical centers Si...Si distances of the lowest singlet diradicals **1–11** are 3.297 Å (**1**), 3.355 Å (**2**), 3.300 Å (**3**), 3.350 Å (**4**), 3.622 Å (**5**), 2.986 Å (**6**), 2.961 Å (**7**), 3.236 Å (**8**), 3.135 Å (**9**), 2.954 Å (**10**), and 3.069 Å (**11**), respectively, at the level of UB3LYP/6-31G\*. These non-bonded distances are considerably longer than the Si–Si bond lengths of known disilranes (2.27–2.33 Å),<sup>26</sup> indicating diradical characters to some extent.

## SUBSTITUENT EFFECTS IN DIRADICALS

The substituent effects on the geometries are also investigated in the lowest singlet and triplet diradicals, as shown in Fig. 3 with the different substitution X on Si atoms (X = H (**1**), CH<sub>3</sub> (**2**), SiH<sub>3</sub> (**3**), C(CH<sub>3</sub>)<sub>3</sub> (**4**), NH<sub>2</sub> (**5**)). The four-membered ring structures of the diradicals **1–5** are puckered in the singlet states and planar in the triplet states. But when we consider the different substitution Y on Ge atoms (Y = H (**6**), CH<sub>3</sub> (**7**), OH (**8**),

**Table 1.** Energies of the lowest singlet ( $S$  for diradicals and  $S'$  for  $\sigma$ -bonded isomers), the lowest triplet states ( $T$ ), and the corresponding relative energy differences ( $\Delta E_{S-T}$ ) of 1,3-diradicals

	X	Y	$\Delta E_{S-S'}$ <sup>a</sup> (kcal/mol)		$\Delta E_{S-T}$ <sup>b</sup> (kcal/mol)			
			UB3LYP /6-31G*	UB3LYP /6-31G*	UB3LYP /LANL2DZ	UMP2 /LANL2DZ	CASSCF <sup>c</sup> /6-31G*	CASPT2 <sup>c</sup> /6-31G*
<b>1</b>	H	F	-15.67	-21.07	-11.61	-9.77	-18.61	-24.03
<b>2</b>	CH <sub>3</sub>	F	-11.34	-17.31	-8.88	-3.98	-14.65	-26.61
<b>3</b>	SiH <sub>3</sub>	F	-12.78	-16.63	-6.77	-9.80	-14.18	-24.09
<b>4</b>	C(CH <sub>3</sub> ) <sub>3</sub>	F	-10.91	-13.16	-7.78	-4.55	-11.57	-21.38
<b>5</b>	NH <sub>2</sub>	F	-21.70	-26.60	-21.47	-25.60	-21.12	-28.62
<b>6</b>	H	H	-12.48	-23.74	-17.17	-22.10	-28.45	-23.74
<b>7</b>	H	CH <sub>3</sub>		-25.24	-19.45	-23.66	-30.57	-25.24
<b>8</b>	H	OH	-15.88	-24.33	-15.82	-25.29	-24.91	-24.33
<b>9</b>	H	NH <sub>2</sub>	-15.49	-26.44	-19.28	-20.99	-30.59	-26.44
<b>10</b>	H	SiH <sub>3</sub>		-20.66	-16.91	-19.90	-26.32	-20.66
<b>11</b>	SiH <sub>3</sub>	SiH <sub>3</sub>	-6.68	-15.35	-13.04	-15.23	-22.70	-15.35

**1** X = H, Y = F; **2** X = CH<sub>3</sub>, Y = F; **3** X = SiH<sub>3</sub>, Y = F; **4** X = C(CH<sub>3</sub>)<sub>3</sub>, Y = F; **5** X = NH<sub>2</sub>, Y = F; **6** X = H, Y = H; **7** X = H, Y = CH<sub>3</sub>; **8** X = H, Y = OH; **9** X = H, Y = NH<sub>2</sub>; **10** X = H, Y = SiH<sub>3</sub>; **11** X = CH<sub>3</sub>, Y = SiH<sub>3</sub> calculated by the UB3LYP, UMP2, (6,6)CASSCF, and (6,6)CASPT2 methods with the 6-31G\* or LANL2DZ basis set. The energies  $E_S$ ,  $E_{S'}$ , and  $E_T$  are given in Tables S1–S3 of the Supporting Information.

<sup>a</sup>  $\Delta E_{S-S'} = E_S - E_{S'}$ .

<sup>b</sup>  $\Delta E_{S-T} = E_S - E_T$ .

<sup>c</sup> CASSCF(6,6)/6-31G\*, CASPT2(6,6)/6-31G\*.

NH<sub>2</sub> (**9**), SiH<sub>3</sub> (**10** and **11**)), the four-membered ring structures of **8** and **9** are puckered both in the singlet and triplet, while the others are puckered in the singlet but planar in the triplet.

As shown in Table 1, the NH<sub>2</sub> groups on the radical centers stabilize the singlet diradical. The high-lying lone pair orbitals on the nitrogen atoms raise the energies of the radical orbitals to promote the p-σ<sub>3</sub>\*-q interaction, weakening the p-σ<sub>3</sub>-q interaction (Fig. 1). Thus, the lone pairs adjacent to the radical centers like **5** stabilize singlet diradicals.

In summary, the singlet preference is appreciable for diradicals **1–11** with the four-membered ring structures. We hope these results may be helpful to prepare some novel diradicals with singlet preference.

## CONCLUSIONS

The orbital phase theory has been applied to the design of a new type of stable diradicals, or the silicon-centered localized 1,3-diradicals, XSi(GeY<sub>2</sub>)<sub>2</sub>SiX (**1–11**). The singlet preferences of **1–11** have been demonstrated by B3LYP, MP2, and CASPT2/CASSCF calculations. The most stable singlet diradicals are the σ-diradicals where the radicals interact with each other through the Si—Ge bonds in the four-membered rings. The most stable triplet diradicals are π-diradicals where the radicals interact with each other through the Ge—Y bonds.

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