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# Theoretical design of singlet localized σ-diradicals: C(MH$_2$)$_3$C (M = Si, Ge, Sn, Pb)

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**Abstract**—Some localized singlet 1,3-σ-diradicals, C(MH$_2$)$_3$C, (M = Si, Ge, Sn, Pb) were theoretically designed by the orbital phase theory and density functional theory calculations. The bicyclic carbon-centered singlet diradicals were more stable than the lowest triplets. Except for M = C, σ-bonded isomers were not located for 1,3-σ-diradicals. 1,4-σ-diradicals, C(M$_2$H$_4$)$_3$C, also had singlet ground states, but they were less stable than σ-bonded isomers.
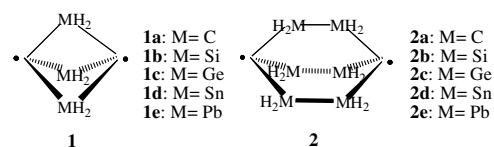© 2005 Elsevier Ltd. All rights reserved.

## 1. Introduction

Localized 1,3-diradicals have evoked intense interest both experimentally and theoretically.[1–31] But detection of localized diradicals are difficult possibly due to their high reactivities and short lifetimes.[1–5] Diradicals have two unpaired electrons in degenerate or nearly degenerate orbitals either with parallel or antiparallel spins in triplet and singlet states, respectively. Singlet diradicals are intermediates in some reactions such as ring opening of strained cycloalkanes,[3–5,12] Cope rearrangements,[32] and bicyclobutane inversion.[33] Up to now, explorations for long-lived singlet localized 1,3-diradicals have been mostly focused on monocyclic four-membered[2,9,12–15,21–25,26a,d,27] and five-membered rings.[1,8–11,33,34] On the other hand, 1,4-diradicals have been investigated as reactive intermediates in numerous chemical reactions both experimentally[31,34–44] and theoretically.[45–54] Localized 1,4-diradicals were measured to have a little longer lifetimes[52–54] than 1,3-diradicals.

Singlet states of diradicals usually compete with triplet states, and also they readily form the corresponding σ-bonded isomers. Preparation of a stable singlet localized diradical remains a challenge. Herein, we theoretically designed singlet localized 1,3-σ-diradicals, C(MH$_2$)$_3$C (**1**) (M = Si, Ge, Sn, and Pb), which were more thermo-

dynamically stable than triplet diradicals, by using the orbital phase theory and density functional theory (DFT). 1,4-σ-Diradicals, C(M$_2$H$_4$)$_3$C (**2**), were also studied for comparison.



2a: M= C
2b: M= Si
2c: M= Ge
2d: M= Sn
2e: M= Pb

1a: M= C
1b: M= Si
1c: M= Ge
1d: M= Sn
1e: M= Pb

## 2. Orbital phase predictions

The orbital phase theory was developed for cyclic orbital interactions[55,56] and has been successfully applied to various molecules and reactions[57,58] including some diradicals.[25,59] Here, we employed the theory to predict spin preference and stabilities of localized 1,3- and 1,4-σ-diradicals. Bicyclic diradicals **1** and **2** were chosen to exclude possibility of π-diradicals by fixing conformation.

A diradical has two singly occupied orbitals, p and q, on radical centers (P and Q in Fig. 1). The unpaired electrons interact with each other through bonds and through space. Through-bond interactions in singlet and triplet states of localized and delocalized diradicals have been studied from the view of orbital phase theory.[25,59] In singlet states, an α-spin electron occupies

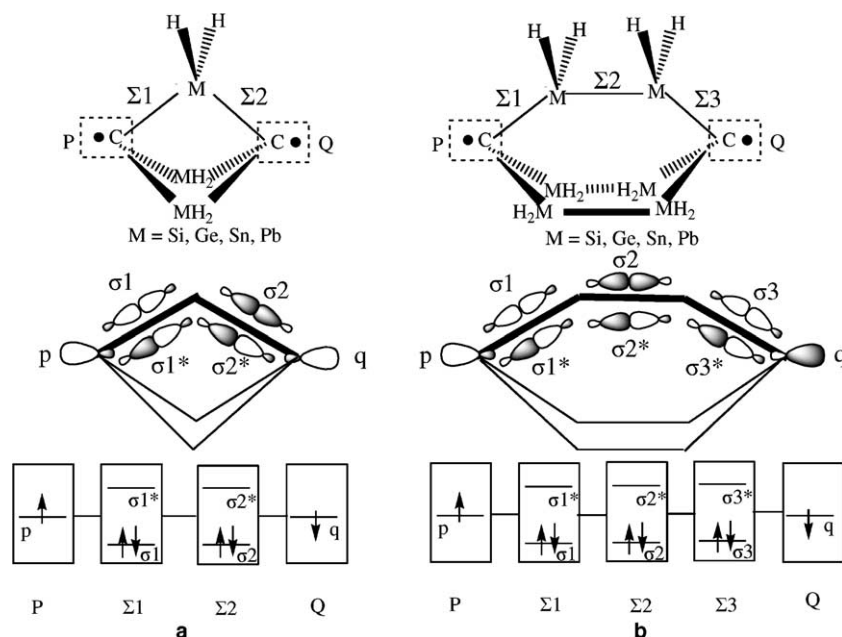* Corresponding authors. Tel.: +86 25 83597408; fax: +86 25 83596131 (J.M.); e-mail: majing@mail.nju.edu.cn

**Figure 1.** Models of (a) 1,3-σ-diradicals (**1**) and (b) 1,4-σ-diradicals (**2**) in singlet states.

one of p and q, and a β-spin electron occupies the other. In 1,3-σ-diradicals (**1**), radical orbitals interacted with each other through σ bond chain, $\Sigma_1$ and $\Sigma_2$. The bonding $\sigma_1$ and $\sigma_2$ orbitals were both doubly occupied, and antibonding $\sigma_1^*$ and $\sigma_2^*$ were vacant. The delocalization and polarization could take place in **1** among p, q, $\sigma_1$, $\sigma_2$, $\sigma_1^*$, and $\sigma_2^*$ orbitals (Fig. 1a), while delocalization in **2** involved p, q, σ1, σ2, σ3, σ1*, σ2*, and σ3* orbitals (Fig. 1b).

Phase properties of 1,3-σ-diradical (**1**) and 1,4-σ-diradical (**2**) are depicted in Scheme 1. When orbital phase relations met the phase continuity requirement (i.e., D–A and A–A interactions are in phase and D–D interaction is out of phase where the electron-donating and accepting orbitals are denoted by D and A, respectively),[25,55–59] the cyclic orbital interaction effectively occurred, leading to stabilization. Cyclic orbital interactions through bonds satisfied the phase continuity requirement in singlet states of **1** and **2** (Scheme 1).[60] Thus, 1,3- and 1-4-σ-diradicals were predicted to prefer singlet ground states. Orbitals, p and q, were in phase in **1** as required but out of phase in **2** (Scheme 1). The through-space interaction between p and q enhanced the stability of singlet state of **1** but not of **2**. This

clear-cut difference predicted that the singlet preference was more outstanding in **1** than in **2**.

### 3. Computational details

All calculations were carried out with the Gaussian03[61] program. We employed the unrestricted DFT with broken symmetry wave functions to investigate geometries, spin preferences, and energy gaps between the lowest singlet and triplet states, S–T gaps ($\Delta E_{S-T} = E_S - E_T$) with B3LYP functional. Calculations were carried out by using various basis sets, including 6-31G*, cc-pVDZ and effective core potentials (ECP) such as LANL2DZ and CEP-121G. All the optimized geometries were compared in Figure 2 (for **1b**) and Figure S1 (for **1** and **2**). The calculated values of $\Delta E_{S-T}$ are listed in Tables 1, 2, S1, and S2. Results computed with ECP basis sets were close to those with 6-31G* and cc-pVDZ basis sets. Thus, we just employed UB3LYP/LANL2DZ results in our following discussions on spin preference and $\Delta E_{S-T}$ of σ-diradicals **1** and **2** containing heavier elements Si, Ge, Sn, and Pb. Expectation values of $\langle S^2 \rangle$ were also given to evaluate extent of spin contaminations in Figure S1 (as well as in Tables S1 and S2). Optimized
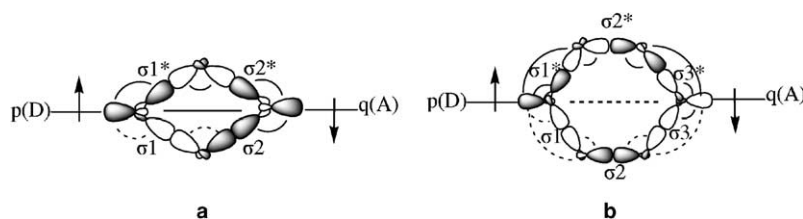


**Scheme 1.** Phase properties of singlet (a) 1,3-σ-diradical (**1**) and (b) 1,4-σ-diradical (**2**). The solid and dotted lines indicate in phase and out phase relations, respectively.
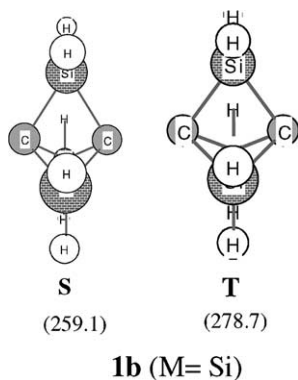
**S** **T**

(259.1) (278.7)

**1b** (M= Si)

**Figure 2.** Optimized geometries of singlet (S) and triplet (T) states of **1b** (M = Si) at the level of UB3LYP/LANL2DZ ($\langle S^2 \rangle = 0.00$ for singlet states).

geometries were demonstrated to be energy minima by confirming that they had no imaginary vibrational frequencies. All the reported energies were corrected by zero-point energies (ZPE).

## 4. 1,3-σ-Diradicals

Energies of the lowest singlet ($E_S$) and triplet ($E_T$) states as well as the corresponding $\Delta E_{S-T}$ ($\Delta E_{S-T} = E_S - E_T$) of 1,3-σ-diradicals (**1a**: M = C, **1b**: M = Si, **1c**: M = Ge, **1d**: M = Sn, **1e**: M = Pd) are listed in Table 1. The lowest singlet states were confirmed by our calculations to be lower in energy than triplet states. For **1a**, C(CH$_2$)$_3$C, energy differences of $\Delta E_{S-T}$ and $\Delta E_{S-S'}$ were −77.13 kcal/mol and 12.72 kcal/mol, respectively (at

the level of UB3LYP/6-31G*). Therefore, when M = C the singlet diradical with the C···C distance of 1.814 Å was less stable than its σ-bonded isomer (in which the length of C–C bond was 1.579 Å). For other higher congeners **1b–e**, distances between radical centers, $r$(C···C), of lowest singlet states fell in the range of 1.972 Å (for **1b**)–2.443 Å (for **1e**), about 28.1–58.6% longer than that (1.54 Å) of a normal C–C single bond (at the level of UB3LYP/LANL2DZ). The singlet preference was shown by $\Delta E_{S-T}$ (**1b**: −55.67 kcal/mol, **1c**: −47.50 kcal/mol, **1d**: −41.78 kcal/mol, **1e**: −40.76 kcal/mol). The σ-bonded isomers were not located for the bicyclic 1,3-σ-diradicals when M = Si, Ge, Sn, Pb, presumably due to high ring strains in polycyclic three-membered rings. Bicyclic 1,3-σ-diradicals **1b–e** were promising candidates for singlet diradicals.

## 5. 1,4-σ-diradicals

At the level of UB3LYP/6-31G*, we failed to locate the singlet state of C(C$_2$H$_4$)$_3$C (**2a**) except for its σ-bonded isomer. The prediction of less remarkable singlet preference of 1,4-σ-diradicals was confirmed by calculations on **2b–e**.[62] The absolute values of $\Delta E_{S-T}$ of 1,4-σ-diradicals (**2b**: 7.91 kcal/mol, **2c**: 6.06 kcal/mol, **2d**: 0.44 kcal/mol, **2e**: 3.13 kcal/mol) were smaller than those of 1,3-σ-diradicals. Distances between carbon atoms, $r$(C···C), in singlet states calculated at the level of UB3LYP/LANL2DZ were of 3.323 Å (**2b**), 3.515 Å (**2c**), 3.904 Å (**2d**), and 4.138 Å (**2e**), which were longer than the non-bonded C···C distances in 1,3-σ-diradicals (**1**). Distances between radical centers were elongated by 97.9–164.9% relative to those in the σ-bonded isomers. But

**Table 1.** The lowest singlet ($E_S$) and triplet ($E_T$) energies and energy differences ($\Delta E_{S-T}$) of 1,3-σ-diradicals (**1**) calculated by UB3LYP method with 6-31G*, cc-pVDZ, LANL2DZ, and CEP-121G basis sets

| | r(C···C)[a] (Å) | | $\Delta E_{S-T}$[b] (kcal/mol) | | | |
| | S | T | 6-31G* | cc-pVDZ | LANL2DZ | CEP-121G |
|---|---|---|---|---|---|---|
| **1a** | 1.814 | 1.814 | −77.13 | | | |
| **1b** | 1.972 | 2.321 | −64.61 | −65.49 | −55.67 | −50.63 |
| **1c** | 2.094 | 2.339 | −59.06 | −59.81 | −47.50 | −48.54 |
| **1d** | 2.271 | 2.551 | | | −41.78 | −40.71 |
| **1e** | 2.443 | 2.617 | | | −40.76 | |

[a] Distance between radical centers at the level of UB3LYP/LANL2DZ except for **1a**. S and T denote singlet and triplet states, respectively.
[b] $\Delta E_{S-T} = E_S - E_T$.

**Table 2.** Energies of the lowest singlet ($E_S$), triplet ($E_T$) and σ-bonded isomers ($E_{S'}$) of 1,4-σ-diradicals (**2**) and energy differences ($\Delta E_{S-S'}$ and $\Delta E_{S-T}$) calculated by UB3LYP methods with 6-31G*, LANL2DZ, and CEP-121G basis sets

| | r(C···C)[a] (Å) | | | $\Delta E_{S-S'}$[b] (kcal/mol) | | | $\Delta E_{S-T}$[c] (kcal/mol) | | |
| | S | S' | T | 6-31G* | LANL2DZ | CEP-121G | 6-31G* | LANL2DZ | CEP-121G |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | | 1.538 | 2.416 | | | | | | |
| **2b** | 3.323 | 1.679 | 3.019 | 4.57 | 8.99 | 9.51 | −8.47 | −7.91 | −7.17 |
| **2c** | 3.515 | 1.663 | 3.165 | 6.75 | 14.33 | 13.79 | −10.77 | −6.06 | −6.96 |
| **2d** | 3.904 | 1.655 | 3.469 | | 21.49 | 23.88 | | −0.44 | 3.69 |
| **2e** | 4.138 | 1.562 | 3.579 | | 31.86 | 39.80 | | −3.13 | −5.94 |

[a] Distance between radical centers at the level of UB3LYP/LANL2DZ except for **2a**. S, T, and S' denote singlet and triplet states of diradicals and the σ-bonded isomers, respectively.
[b] $\Delta E_{S-S'} = E_S - E_{S'}$.
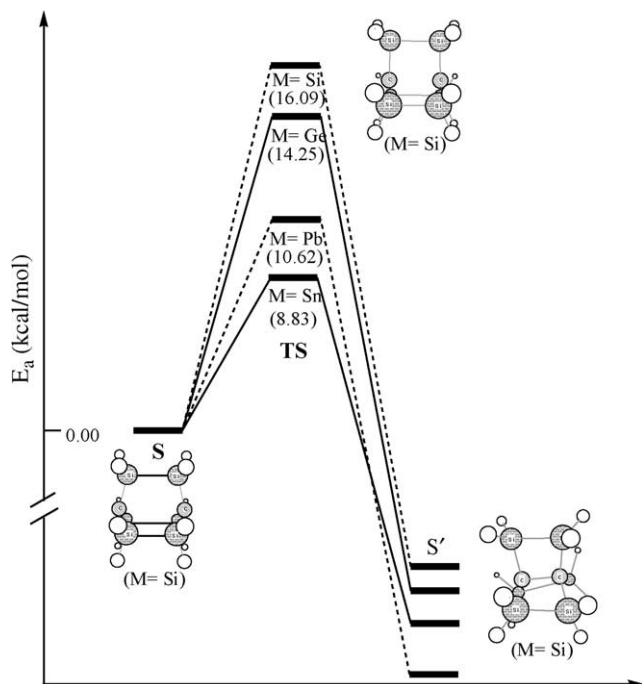[c] $\Delta E_{S-T} = E_S - E_T$.

**Figure 3.** Reaction profiles for transformations from singlet 1,4-diradicals **2** (M = Si, Ge, Sn, Pb) to their σ-bonded isomers at the level of UB3LYP/LANL2DZ.

in those σ-bonded isomers, C–C bonds (1.679 Å in **2b**; 1.663 Å in **2c**; 1.655 Å in **2d**; 1.562 Å in **2e** at the level of UB3LYP/LANL2DZ) were longer than a normal C–C single bond. σ-Bonded isomers were more stable than singlet 1,4–diradicals by 8.99 kcal/mol (**2b**), 14.33 kcal/mol (**2c**), 21.49 kcal/mol (**2d**), and 31.86 kcal/mol (**2e**), respectively (Table 2). In order to survey kinetic stabilities of singlet diradicals, we located transition states (TS) in transformations from singlet states to corresponding σ-bonded isomers of **2b–e** at the level of UB3LYP/LANL2DZ. The results are shown in Figure 3. The activation energies, $E_a$, were found to be 16.09 (**2b**), 14.25 (**2c**), 8.83 (**2d**), and 10.62 (**2e**) kcal/mol, respectively. Thus, singlet diradicals would be easily transformed to corresponding σ-bonded isomers.

In summary, we have theoretically designed some potential singlet localized σ-diradicals. We have predicted by an orbital phase theory and confirmed by DFT calculations that bicyclic 1,3-σ-diradicals **1** (M = Si, Ge, Sn, and Pb) should prefer singlet ground states. Energy gaps between the lowest singlet and triplet states show that the singlet preference is outstanding in **1**. The σ-bonded isomers have not been located for bicyclic 1,3-σ-diradicals when M = Si, Ge, Sn, and Pb. For bicyclic 1,4-σ-diradicals **2**, the singlet preference is less remarkable and the σ-bonded isomers are more stable.

## Supplementary data

Figure S1 depicted geometries of singlet and triplet states of bicyclic 1,3- and 1,4-σ-diradicals and the σ-bonded isomers of **2** optimized at the levels of 6-31G*,

LANL2DZ, cc-pVDZ, and CEP-121G. The ZPE energies, $\langle S^2 \rangle$ values, and $\Delta E_{S-T}$ of **1b–e** and **2b–e** are listed in Tables S1 and S2. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.06.064.

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60. The phase is discontinuous in the triplet states.

61. Frisch, M. J. et. al. Gaussian 03, Reversion B.04; Gaussian, Inc., Pittsburgh PA, 2003. [Full reference is given in Supplementary data.]

62. One exception is that the singlet state (S) for **2d** (M = Sn) is higher in energy than the triplet state (T) at the level of UB3LYP/CEP-121G (Table S2).