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Theoretical Designs of Singlet Localized 1,3-Diradicals

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Spin preference and S−T gaps of localized 1,3-diradicals were studied by an orbital phase theory and theoretical calculations. The orbital phase theory was applied to rationalize thermodynamic and kinetic stabilities of diradicals. We theoretically designed some singlet localized 1,3-diradicals, substituted trimethylenes, which are more stable than the lowest triplets. Some diradicals with the four-membered rings, 2,4-disilacyclobutane-1,3-diyls, were designed and shown to have singlet ground states and to be more stable than the σ-bonded isomers, 2,4-disilabicyclo[1.1.0]butanes. The ab initio calculations supported predictions of the stable carbon-centered localized singlet 1,3-diradicals.

Introduction

Diradicals are even-electron molecules that have one bond less than the number permitted by the standard rule of valence. Localized 1,3-diradicals have evoked intense interest, both experimentally[1−15] and theoretically.[9,12−23] Detections of the localized diradicals are difficult possibly due to their higher reactivities and shorter lifetimes.[1−5] Triplet states of some localized 1,3-diradicals can be observed by electron spin resonance spectroscopy in matrices at very low temperatures.[1,2] But their singlet states are extremely short-lived intermediates that have only recently been observed by femtosecond spectroscopy.[3−5] Several theoretical calculations[18,19,21] predicted a triplet ground state for the simplest localized diradical, trimethylene (TM, **1**), and indicated little or no barrier to ring closure in the singlet state, which was supported by the fast decay time of 120 fs probed for the TM system.[4] (It should be mentioned that the literature of theoretical studies on species **1** collected here is not exhaustive and more related references can be found in refs 18 and 21, and so on.) So substantial efforts have been made to prepare and characterize the persistent, localized singlet 1,3-diradicals for potential applications in the field of molecular materials such as electrical conductors.[11] The 2,2-difluoro and 2,2-diethoxy derivatives of 1,3-diphenyl-1,3-cyclopentanediyl diradicals have longer lifetimes (microseconds).[8,9] Moreover, the biradicaloid form of the 1,2-diphosphinodiboranes with a planar PBPB ring structure and sterically demanding substituents has been found to be stable even at room temperature.[12] Search for the other stable localized singlet diradicals, especially the carbon-centered 1,3-diradicals, remains a challenge to both experimental and theoretical scientists.

Several factors such as substitution effects and the ring strain drawn from the successful experience are helpful to guide the future exploration of some new singlet 1,3-diradicals with the unpaired electrons located at the carbon atoms; even so, theoretical predictions from both the qualitative theory and calculations are desired. Some simple topological rules have been developed to predict the ground spin states and stabilities of π-conjugated diradicals.[24−29] An orbital phase theory[30,31] has been

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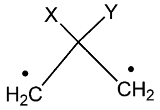
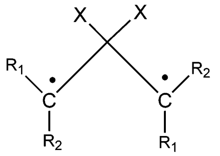
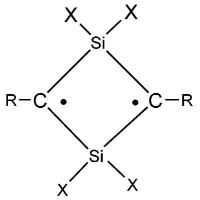


1 X=Y=H
2 X=Y=SiH_3
3 X=Y=F

4 X=H,Y=CH_3
5 X=H, Y=NH_2
6 X=H, Y=OH
7 X=H, Y=F

8 X=H, Y=SiH_3
9 X=H, Y=PH_2
10 X=H, Y=SH
11 X=H, Y=Cl





12 X=SiH_3, R_1= R_2=CN
13 X=SiH_3, R_1= R_2=CF_3
14 X=SiH_3, R_1= CH_3, R_2=CF_3
15 X=SiH_3, R_1=SiH_3, R_2=CF_3
16 X=SiH_3, R_1=NO_2, R_2=NH_2
17 X=CH_3, R_1=R_2=CF_3

18 X=H, R=H
19 X=H, R=F
20 X=H, R=SiH_3
21 X=CH_3, R=F
22 X=NH_2, R=F
23 X=OH, R=F

24 X=F, R=F
25 X=F, R=OH
26 X=F, R=NH_2
27 X=F, R=CH_3

successfully applied to various chemical systems and reactions including π-conjugated diradicals.[27] Here, we employ the orbital phase theory to predict the substitution effects on spin preferences, singlet−triplet (S−T) energy gaps, and stabilities of the localized 1,3-diradicals.

TM (**1**) and its geminally disubstituted diradicals with silyl and fluoro groups (**2** and **3**, respectively) and monosubstituted derivatives **4**−**11** are selected to probe the substituent effects on the S−T gaps. Subsequently, we theoretically design some new acyclic (**12**−**17**) and cyclic (**18**−**27**) carbon-centered singlet 1,3-diradicals with singlet preferences. Especially, the cyclic diradicals are predicted to have appreciable S−T splittings and stabilities relative to the corresponding σ-bonded isomers.

2. An Orbital Phase Theory

The orbital phase theory has been developed for the cyclic orbital interactions underlying various chemical systems.[30−33] The orbital phase is an important factor in promoting the cyclic orbital interaction. The effective occurrence of a cyclic orbital interaction 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.[30−33] When the orbital phase relations meet the requirement, the system is stabilized by the effective delocalization and polarization. Otherwise, the system is less stable. According to the orbital phase continuity requirement, we can predict stabilities of many systems.

A Model of Diradicals. Recently, applications of the orbital phase theory have been successfully extended to some diradicals.[27,33g] It has been demonstrated that the spin preference and stabilities of π-conjugated diradicals[27] and relative stabilities of the crossed vs linear σ-conjugated triplet diradicals E_4H_8 and E_5H_{10} (E = C, Si, Ge, Sn)[33h] are controlled by the orbital phase. Here, an orbital phase theory is developed for localized 1,3-diradicals (Figure 1) to investigate effects of the intramolecular interaction of bonds and unpaired electrons on the spin preference and thermodynamic and kinetic stabilities of the singlet and triplet states. The diradical has two singly occupied orbitals, p and q, of nearly the same energy on two radical centers (P and Q). The radical centers interact with each other through a σ-bond (Σ). In the triplet state, the orbitals, p and q, are singly occupied by α-spin electrons (Figure 1a), whereas in the singlet state, a α-spin electron occupies one of p and q orbitals, and a β-spin electron occupies the other (Figure 1b).

Through-Bond Interactions. The unpaired electrons of diradicals may interact with each other through bonds. The through-bond interactions in triplet states of diradicals have been studied from the viewpoint of the orbital phase theory.[27,33g] As shown in Figure 1a, in the ground configuration, G, radical orbitals of a triplet state are singly occupied by α-spins, the central σ orbital is doubly occupied, and the σ^* orbital is empty. The delocalization of excessive α-spins and the bond polarization can take place among radical orbitals, p and q, and the central σ and σ^* orbitals, resulting in the electron-transferred configurations (T) and locally excited configurations (E) (Figure 2a). When one α-spin electron in p shifts to vacant σ^* through the interaction of the ground configuration G with the transferred configuration T_1, the electron delocalization from the radical center to the middle σ bond takes place by the mixing of the transferred configuration. This configuration interaction is approximated by the p−σ^* orbital interaction. The resulting hole in the radical orbital p is then supplemented by another α-spin electron from the bonding σ orbital via an interaction between the transferred configuration, T_1, and the locally excited configuration, E, which is approximated by the σ−p interaction. The mixing of the excited configuration polarizes the central σ bond. In short, G−T_1−E or σ−p−σ^* interaction is involved in the electron delocalization−polarization process between radical centers and the σ bond. The similar delocalization−polarization process through another radical orbital q

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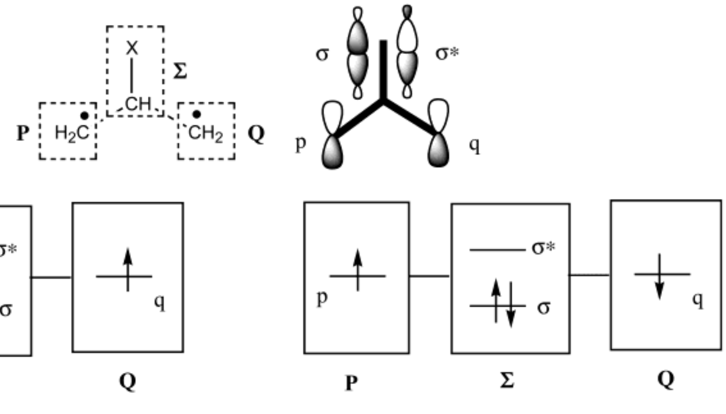

(a) Triplet (b) Singlet

FIGURE 1. Models of (a) triplet and (b) singlet localized 1,3-diradicals.

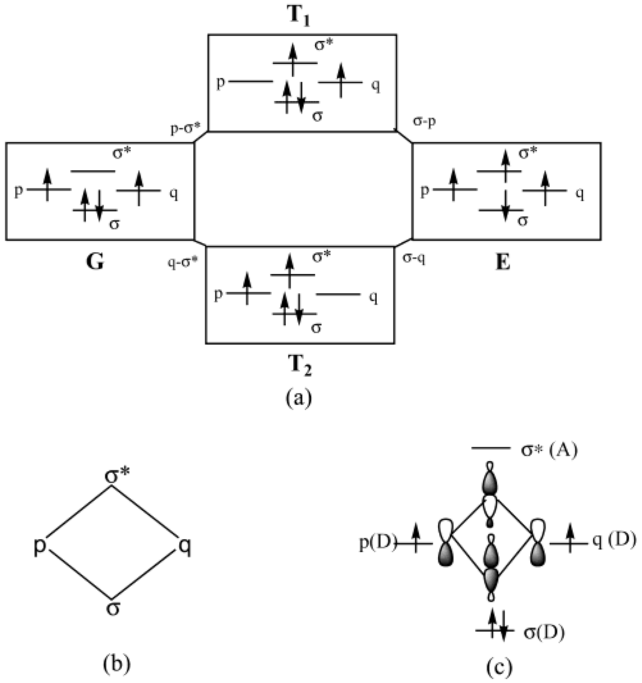

FIGURE 2. Through-bond interactions in the triplet state of 1,3-diradicals: (a) the mechanism of electron delocalization and polarization of α-spin electrons, (b) the cyclic orbital interaction, and (c) the orbital phase continuity.

contains the $G-T_2-E$ or $\sigma-q-\sigma^*$ interaction. Consequently, the cyclic $-G-T_1-E-T_2-$ configuration (Figure 2a) or $-\sigma-p-\sigma^*-q-$ orbital interaction (Figure 2b) occurs in the triplet state. For the triplet, the radical orbitals, p and q, and bonding σ orbital are donating orbitals (labeled by D in Figure 2c) for α-spin electrons, while the antibonding σ^* orbital (marked by A) is electron accepting. It can be clearly seen in Figure 2c that the electron-donating radical orbitals (D's), p and q, can be in phase with the accepting σ^* orbital (A) and out of phase with the donating orbital, σ (D), at the same time for the triplet state. So the orbital phase is continuous in the triplet 1,3-diradical and the triplet state is stabilized by the effective cyclic orbital interactions.[34]

However, the delocalization−polarization mechanism in the singlet state is more complicated (Figure 3a).

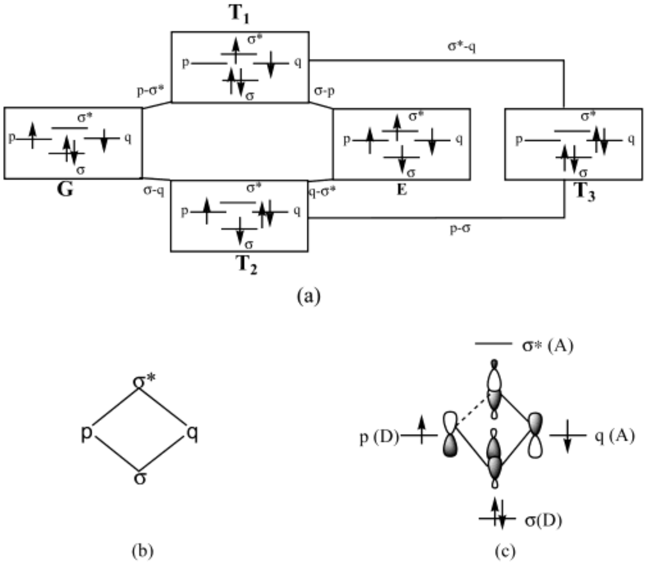

FIGURE 3. Through-bond interactions in the singlet state of 1,3-diradicals: (a) the mechanism of electron delocalization and polarization of α-spin electrons, (b) the cyclic orbital interaction, and (c) the orbital phase discontinuity.

Similar to the triplet state, there also exists a cyclic $-G-T_1-E-T_2-$ configuration or $-\sigma-p-\sigma^*-q-$ orbital interaction in the singlet (Figure 3a).[35] However, the radical orbital q is an electron-accepting orbital (A) for the α-spin electron (rather than the donating orbital) in the singlet state. Thus, there is an additional path of α-spin electron delocalization, $-G-T_1-T_3-T_2-$ or $-p-\sigma^*-q-\sigma-$, in the singlet state.[36] In this case, orbital phase continuity conditions cannot be satisfied simultaneously (denoted by the dashed line in Figure 3c). In contrast with the triplet state, the singlet 1,3-diradical suffers from the

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(34) In addition, for the β-spin, the delocalization−polarization mechanism and the phase continuity property are similar to those for the α-spin electrons. The only difference lies in that the radical orbitals, p and q, are electron accepting (A) for β-spin electrons in the triplet states.

(35) The G denotes the ground-state configuration, in which the central σ orbital is doubly occupied, the σ^* is empty, and the radical orbitals p and q are singly occupied by the α- and β-spin electrons, respectively. T_1, T_2, and T_3 are the electron transferred configurations raised by the delocalization of α-spins. The locally excited configuration is labeled by E, which corresponds to the polarization of the σ bond.

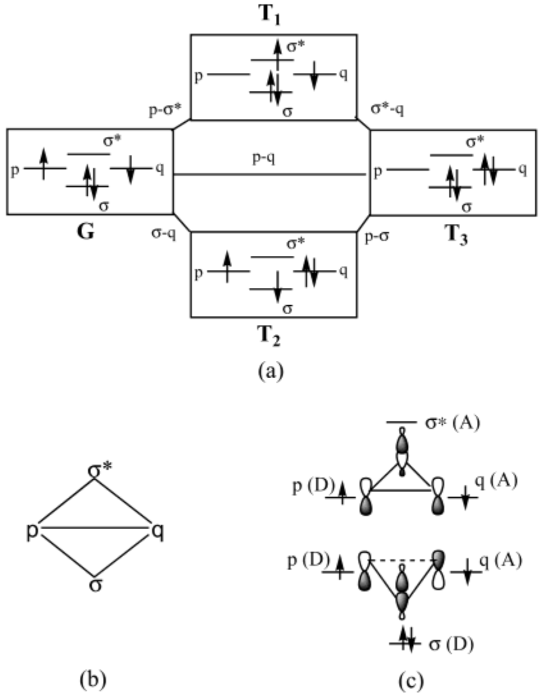

FIGURE 4. Through-space interactions in the singlet state of 1,3-diradicals: (a) the mechanism of electron delocalization of α-spin electrons, (b) the cyclic orbital interactions, and (c) the orbital phase properties.

orbital phase discontinuity. Therefore, the triplet state of the TM (**1**) diradical is predicted to be more stable than the singlet state by the orbital phase theory, which is in agreement with that from Hund's rule.[37]

Through-Space Interactions. In the singlet state of 1,3-diradical, there may also exist the through-space interaction between radical centers, i.e., p···q interaction (Figure 4), in addition to the previously addressed cyclic $-p-\sigma^*-q-\sigma-$ orbital interactions (Figure 3). The through-space interaction is indispensable for the bond formation between the radical centers. The corresponding delocalization of the α-spin electron is shown in Figure 4a. Clearly, the involvement of the through-space p···q interaction gives rise to two cyclic orbital interactions, $-p-\sigma^*-q-$ and $-p-\sigma-q-$.[38] From Figure 4c, one can find that the cyclic $-p-\sigma^*-q-$ orbital interaction can satisfy the phase continuity requirements: for the α-spin electron the electron-donating radical orbital, p (D), could simultaneously be in phase with the σ^* antibonding orbital (A) and the other accepting radical orbital, q (A), which are in phase with each other. The tendency of ring closure through the p···q interaction is thus promoted by the effective cyclic $-p-\sigma^*-q-$ orbital interaction. The other cyclic orbital interaction, $-p-\sigma-q-$, does not obey the phase continuity requirements, since the electron-donating radical orbital, p (D), cannot be out of phase with the σ bonding orbital (D) and in phase with the other radical orbital, q (A), at the same time for the α-spin, while σ (D) and q (A) are in phase with each other.

The cyclic orbital interaction of p and q with σ^* or with σ can significantly occur at the transition state of the ring closure of 1,3-diradicals. The continuous orbital phase for the cyclic orbital interaction with σ^* implies effective stabilization of the transition states when the σ bonds are electron acceptors. *Electron-withdrawing substituents X (e.g., X = F or Cl) at C_2 kinetically destabilize the 1,3-diradicals to facilitate the ring closure.* Electron-releasing groups (e.g., X = SiH_3) do not exhibit such kinetic effects due to the discontinuous orbital phase for the cyclic orbital interaction of p and q with σ.

Effects of Donor and Acceptor Substituents. In addition to the orbital phase, the relative energy between the electron-donating and -accepting orbitals is another important factor for the effective cyclic orbital interaction. Energies of σ and σ^* orbitals are changed by substitutions at the C_2. Replacement of C−H bonds by strongly electron-donating groups X raises the energy of the σ_{C-X} orbital (Figure 5a). The increase in the energy of σ_{C-X} strengthens interactions of radical center orbitals, p and q, with the σ orbital (shown by bold lines in Figure 5a). The $p-\sigma_{C-X}-q$ interaction becomes more effective than the $p-\sigma_{C-X}{}^*-q$ one. These interactions are important for the electron delocalization between radical centers through σ bonds in singlet states. The phase discontinuity in the singlet state (Figure 3c) is mitigated by the more effective $p-\sigma_{C-X}-q$ interaction, so that the singlet diradicals gain some stabilizations. This contributes to a decrease in

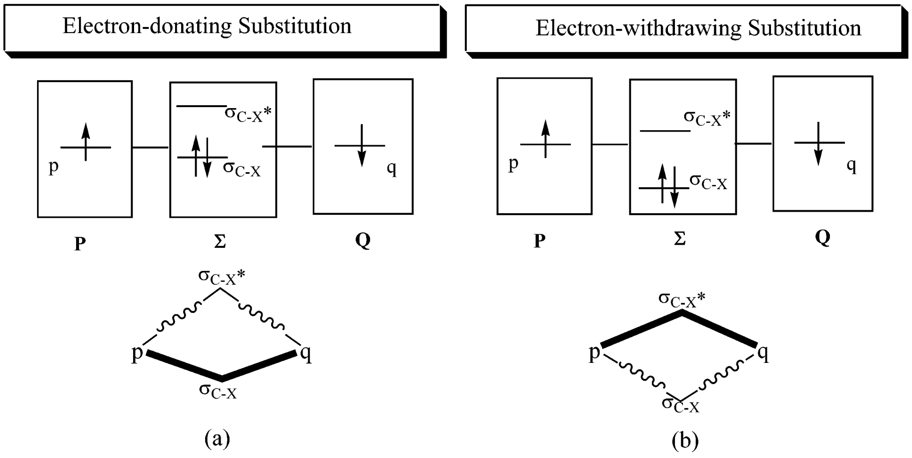

FIGURE 5. Electron-donating and -withdrawing substitutents change the effective orbital interaction from the cyclic $-p-\sigma^*-q-\sigma-$ orbital interaction to acyclic (a) $p-\sigma-q$ and (b) $p-\sigma^*-q$ interactions, respectively. The bold line means the interaction is strengthened by substitutions, and the wavy line denotes the weakened orbital interaction.

ΔE_{ST} or even to a reversion of the spin preference (i.e., the singlet preference). Strongly electron-accepting substituents will lower σ_{C-X}^*, leading to the much stronger $p-\sigma_{C-X}^*-q$ interaction than the $p-\sigma_{C-X}-q$ interaction (Figure 5b). The singlet stabilization also occurs in this case, contributing to a reduction of ΔE_{ST} or a singlet preference.

Substitution with Polarizable Bonds. The triplet stabilization is related to the polarization of the C−X bonds, i.e., the $\sigma_{C-X}-p-\sigma_{C-X}^*$ and $\sigma_{C-X}-q-\sigma_{C-X}^*$ interactions. Thus, the energy gap between σ_{C-X} and σ_{C-X}^* is important for evaluating the polarizability of a C−X bond. The triplet states are stabilized with the increase in the bond polarizability or with the decrease in the $\sigma_{C-X}-\sigma_{C-X}^*$ energy gap.

3. Computational Results

Computational Details. Predictions of the substituent effects on both singlet and triplet states and the tendency of the ring closure with the strong electron-accepting substituents were confirmed by the complete active space self-consistent field (CASSCF) method as implemented in GAUSSIAN98[39] with the basis set of 6-31G*. For the parent and substituted 1,3-diradicals **1**−**11**, the (6,6) active space was utilized for optimizations and frequency analysis, where the radical orbitals, π and π^*, and two sets of σ and σ^* orbitals for C_1-C_2 and C_2-C_3 backbones were involved. To further include effects of dynamical correlation, single-point CASPT2 calculations were also carried out at each stationary point. In addition, we have carried out both CASSCF and CASPT2 calculations with the 6-311G** basis sets on TM (**1**) and its silyl monosubstituted derivate (**8**) to assess the influence of the basis sets. It has been found that the choice of more flexible basis sets may impose small effects on the optimized geometries and S−T gaps (ΔE_{S-T}) for the studied systems (cf. Table 1).

It is still quite expensive to carry out the (6,6)CASSCF optimizations on some novel diradicals **12**−**27**, which are the more complicated derivatives of 1,3-diradicals. Therefore, we employed the unrestricted density functional theory (DFT) to investigate their geometries, spin preferences, and S−T gaps (ΔE_{S-T}) with the B3LYP functional and 6-31G* basis set. The optimized geometries of the singlet and triplet states of these diradicals can be found in the Supporting Information. All the reported energies were corrected by the zero-point energies (ZPE). The expectation values of S^2, $\langle S^2\rangle$, were also given to evaluate the spin contaminations, from which the corrected values of ΔE_{S-T} can be obtained by using Yamaguchi's formula, $\Delta E_{S-T}^{corr} = \langle S^2{}_T\rangle/(\langle S^2{}_T\rangle - \langle S^2{}_S\rangle) \times \Delta E_{S-T}$.[40] Although the performance of UB3LYP calculations on the ΔE_{S-T} of some 1,3-diradicals has already been investigated in comparison with the CASPT2 results,[41−43] we conducted single-point (6,6)CASSCF calculations at the UB3LYP-optimized singlet and triplet geometries for compounds **14** and **24**. Both methods predict singlet preferences for **14** and **24** and the calculated ΔE_{S-T} values are close to each other (for **14**, $\Delta E_{S-T} = -3.56$ (by UB3LYP), −5.71 (by corrected formula[40]), and −4.94 kcal/mol (by (6,6)-CASSCF); and for **24**, $\Delta E_{S-T} = -19.1$ (by UB3LYP), −21.1 (by corrected formula[40]), and −19.9 kcal/mol (by (6,6)CASSCF[44]), cf. Tables 3 and 4). However, it should be noticed that usually the broken symmetry UB3LYP descriptions do not represent pure open-shell singlet states but suffer from spin contaminations. Hence the good agreement in ΔE_{S-T} values between the UB3LYP and CASSCF for **24** may be a consequence of the relatively small spin pollution ($\langle S^2{}_S\rangle = 0.19$).[44]

TM and Its Disubstituted Derivatives. The CASSCF and CASPT2 energies of singlet (E_S for diradicals and $E_{S'}$ for the σ-bonded isomers) and the lowest triplet diradicals (E_T) and their relative energy differences, $\Delta E_{S-S'}$ and ΔE_{S-T}, of TM (**1**) and its substituted derivatives (**2**−**11**) are listed in Table 1. The present (6,6)-CASSCF and previous (2,2)CASPT2N calculations[21] of TM (**1**) indicate that both the singlet and triplet states prefer conrotatory conformers (**b** in Scheme 1), where the terminal methylene groups are rotated in a conrotatory manner out of the plane defined by the three carbon atoms. Since radical centers interact with different C−H bonds, there is no cyclic orbital interaction. The more favored conrotatory conformation of the singlet state is

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[36] The electron in σ^* coming from p further delocalizes into q via an interaction between T_1 and another transferred configuration T_3 (approximated as σ^*-q interaction). When the electron hole in bonding σ orbital of T_2 is supplied with a α−spin electron by p through $p-\sigma$ interaction, we can also arrive at T_3, resulting in another cyclic $-p-\sigma^*-q-\sigma-$ interaction.

[37] A diradical has two nearly degenerate orbitals for two unpaired electrons. The triplets are more stable than the singlets according to Hund's rule, which also may be applicable when the nearly degenerate orbitals overlap each other to a small degree. Even if there is the perturbation by substituents, the triplet preference of typical 1,3-diradicals is still expected, because the orbital phase continuity stabilizes the triplet states, while the discontinuity does not stabilize the singlet states.

[38] The α-spin electron in p can shift into the vacant σ^* orbital via the through-bond interaction. On the other hand, the through-space p···q interaction allows the α-spin electron in p to delocalize directly to the other radical orbital q where the ground configuration G interacts with the transferred configuration T_3, which is approximated by $p-q$ interaction. Consequently, the cyclic orbital interaction, $-p-\sigma^*-q-$, results from the interactions among G, T_1, and T_3 configurations. Similarly, there is another cyclic $-p-\sigma-q-$ orbital interaction as shown in the lower cycle of Figure 4b.

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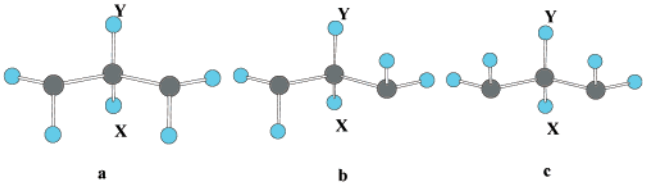
[44] (a) The (6,6)CASSCF values for **24** were first calculated by one reviewer of our original manuscript. (b) As addressed by this reviewer, the studied singlets with zero (or nearly zero) $\langle S^2\rangle$ values may not be typical diradicals with the unpaired electrons perfectly localized at each radical center. Instead, the singlet "diradicals" with long "nonbonded" distances in the present work have weak through-space interactions but relatively strong through-bond interactions to make the unpaired electrons delocalizing around the radical centers. Figures 2 and 3 in ref 12 are helpful in understanding such singlet "diradicals".

TABLE 1. Energies of the Singlet (E_S for Diradicals and $E_{S'}$ for σ-Bonded Isomers), the Lowest Triplet (E_T) States, and the Corresponding Relative Energy Differences ($\Delta E_{S-S'}$ and ΔE_{S-T}) of the Trimethylene-Based 1,3-Diradicals Calculated by (6,6)CASSCF and (6,6)CASPT2 Methods with the 6-31G* (and 6-311G) Basis Sets[a]**

	conformer[b] (r(C···C), Å)		$\Delta E_{S-S'}$, kcal/mol			ΔE_{S-T}, kcal/mol		
geminal substitutions	S/S′	T	CASSCF	CASPT2	ref	CASSCF[c]	CASPT2[c]	ref
X = Y = H (**1**)	**b** (2.518/1.530)	**b**	54.5	64.8	63.9[d]	0.90 (0.91)	1.05 (0.89)	0.7[d]
disubstituted TM								
X = Y = SiH_3 (**2**)	**a** (2.570/1.484)	**a**	50.3	58.8	50.9[d,e]	−5.09	−11.2	−11.9[d,f]
X = Y = F (**3**)	NL[g]	**b**						
monosubstituted TM								
X = H, Y = CH_3 (**4**)	**b** (2.513/1.533)	**a**	52.4	66.1			1.45	1.09
X = H, Y = NH_2 (**5**)	**b** (2.495/1.538)	**a**	45.2	62.7			1.54	1.81
X = H, Y = OH (**6**)	**a** (2.495/1.546)	**b**	42.1	70.5			−0.03	−0.44
X = H, Y = F (**7**)	NL[g]	**a**						
X = H, Y = SiH_3 (**8**)	**c** (2.566/1.489)	**c**	50.7	53.4			−0.88 (−0.84)	−10.5 (−15.8)
X = H, Y = PH_2 (**9**)	**b** (2.501/1.491)	**c**	54.8	61.6			1.83	1.79
X = H, Y = SH (**10**)	**b** (2.519/1.503)	**c**	43.4	66.9			0.36	5.86
X = H, Y = Cl (**11**)	NL[g]	**c**						

[a] The (6,6)CASSCF and (6,6)CASPT2 energies E_S, $E_{S'}$, and E_T are given in Tables S1 and S2 of the Supporting Information. [b] The most stable conformations of singlets (S) and triplets (T) are roughly described by **a**, **b**, and **c** (Scheme 1).The disrotatoty conformers, **a** and **c**, are identical to each other for TM (**1**) and its disubstituted derivatives **2** and **3**. The separations between the terminal carbon atoms, r(C···C) for diradicals (S) and σ-bonded isomers (S′), are presented in parentheses. The dihedral angles of conformers can be found in Table S1 of the Supporting Information. [c] The 6-311G** results are given in parentheses. [d] The (2,2)CASPT2N results, ref 21. [e] The CASSCF(10,10)/6-31G* and CASPT2N(10,10)/6-31G* calculations gave results of 54.0 and 51.4 kcal/mol, respectively.[21] [f] The (10,10)CASPT2N result is −11.1 kcal/mol.[21] [g] Not located as the local minimum.

SCHEME 1



in agreement with the orbital phase discontinuity for the cyclic orbital interaction in the disrotatory conformers. The similar conformation of the triplet suggests that energies of σ and σ* of C−H bonds are too low and high, respectively, to polarize the C−H bonds. Primary stabilization in the triplet comes from the interaction between the pair of p (q) and σ* orbitals. So, there are no effects of cyclic orbital interaction on the preference of the singlet and triplet states. This is confirmed by a very small gap ($\Delta E_{S-T} = 0.7-1.05$ kcal/mol as shown in Table 1) with the singlet lying slightly above the triplet state. In addition, our (6,6)CASSCF and CASPT2 calculations with both 6-31G* and 6-311G** basis sets produce similar S−T gaps of around 0.90 kcal/mol, which are close to the 0.7 kcal/mol value obtained from the (2,2)-CASPT2N calculation.[21]

The singlet and triplet states of the 2,2-disubstituted silyl derivative **2** are found to be in favor of a slightly disrotatory conformation (**a** in Scheme 1), where the radical orbitals interact with the same C−Si bond (cf. Supporting Information). Such a conformation provides a chance for the cyclic orbital interaction to occur in **2**. The conformational change in the triplet states from **b** for **1** to **a** for **2** can be understood in terms of the polarizability of C−X bonds. As mentioned before, the energy gap between σ_{C-X} and σ_{C-X}* is a measure of the polarizability of a C−X bond. We calculated the σ_{C-X} and σ_{C-X}* energies of the model molecule, CH_3−X, (X = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl) by the bond model analysis (BMA)[45,46] and the natural bond orbital (NBO) program[47] at the RHF/6-31G* and B3LYP/6-31G* levels with results shown in Table 2. Since those NBO results of the relative orbital energies are parallel with the BMA values, we just use the BMA results in the following discussions. The energy gap is smaller for C−Si (1.22 au) than for C−H (1.45 au), suggesting the C−Si bond is more polarizable than the C−H bond. The disrotatory conformation allows **2** to gain the stabilization due to the cyclic orbital interaction favored by the phase continuity

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(45) For the current version of the bond model analysis, see: (a) Iwase, K.; Inagaki, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2781. (b) Inagaki, S.; Ikeda, H. *J. Org. Chem.* **1998**, *63*, 7820. (c) Inagaki, S.; Yamamoto, T.; Ohashi, S. *Chem. Lett.* **1997**, 977. For the applications, see: (d) Ikeda, H.; Naruse, Y.; Inagaki, S. *Chem. Lett.* **1999**, 363. Inagaki, S.; Ohashi, S.; Kawashima, T. *Org. Lett.* **1999**, *1*, 1145. (e) Inagaki, S.; Ikeda, H.; Kawashima, T. *Tetrahedron Lett.* **1999**, *40*, 8893. (f) Ikeda, H.; Ushioda, N.; Inagaki, S. *Chem. Lett.* **2001**, 166. (g) Ikeda, H.; Kato, T.; Inagaki, S. *Chem. Lett.* **2001**, 270. (h) Naruse, Y.; Hayashi, A.; Sou, S.; Ikeda, H.; Inagaki, S. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 245. (i) Ohwada, T.; Miura, M.; Tanaka, H.; Sakamoto, S.; Yamaguchi, K.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **2001**, *123*, 10164.

(46) For the original version of the bond model analysis, see: (a) Inagaki, S.; Goto, N. *J. Am. Chem. Soc.* **1987**, *109*, 3234. (b) Inagaki, S.; Goto, N.; Yoshikawa, K. *J. Am. Chem. Soc.* **1991**, *113*, 7144. (c) Inagaki, S.; Yoshikawa, K.; Hayano, Y. *J. Am. Chem. Soc.* **1993**, *115*, 3706. (d) Inagaki, S.; Ishitani, Y.; Kakefu, T. *J. Am. Chem. Soc.* **1994**, *116*, 5954. (e) Inagaki, S.; Kakefu, T.; Yamamomto, T.; Wasada, H. *J. Phys. Chem. A* **1996**, *100*, *23*, 9615. For another method of the bond model analysis, see: (f) Ikeda, H.; Inagaki, S. *J. Phys. Chem. A* **2001**, *47*, 10711.

(47) *NBO*, Version 3.1; Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.

TABLE 2. Energies of σ and σ^* Orbitals, and the $\sigma-\sigma^*$ Energy Gaps (in units of au) of C−X Bonds in CH_3X Obtained from Bond Model Analysis (BMA)[a] at the RHF/6-31G* Level and from Natural Bond Orbital (NBO) Analysis[b] at Both RHF/6-31G* and B3LYP/6-31G* Levels

			$\Delta E(\sigma-\sigma^*)$		
X	$E(\sigma)$	$E(\sigma^*)$	BMA:RHF	NBO:RHF	NBO:B3LYP
H	−0.713	0.737	1.450	1.411	0.954
CH_3	−0.794	0.679	1.473	1.440	0.982
NH_2	−0.899	0.698	1.596	1.574	1.058
OH	−0.973	0.643	1.616	1.673	1.096
F	−1.068	0.629	1.697	1.748	1.139
SiH_3	−0.714	0.508	1.221	1.084	0.708
PH_2	−0.779	0.410	1.189	1.109	0.707
SH	−0.815	0.162	0.977	1.163	0.737
Cl	−0.882	0.192	1.074	1.198	0.759

[a] Reference 45. [b] Reference 47.

in the triplet state. On the other hand, the disrotatory conformation **b** of the singlet state may be ascribed to the strong donating capability of silyl groups in **2**. The high σ_{C-Si} energy strengthens the $p-\sigma_{C-Si}-q$ interaction relative to the $p-\sigma_{C-Si}{}^*-q$ interaction (cf. Figure 5). The effect of the acyclic $p-\sigma_{C-Si}-q$ interaction free from the phase requirements is predominant over that of the cyclic $-p-\sigma_{C-Si}-q-\sigma_{C-Si}{}^*-$ orbital interaction disfavored by the phase discontinuity. Thus the singlet state may be stabilized by the acyclic $p-\sigma_{C-Si}-q$ interaction. In fact, both the (6,6)CASSCF and CASPT2 results for 2,2-disilyl-substituted TM, **2** (Table 1), show that the singlet ground state is favored, which agrees with other calculations.[21] In addition, the separation between the terminal carbon atoms (2.570 Å by CASSCF) in the singlet of **2** is longer than that of the parent **1** by 0.052 Å and is about 68% longer than the typical C−C single bond (1.530 Å).

All attempts at searching for the singlet 2,2-difluoro-TM (**3**) led to the collapse to the σ-bonded isomers, 1,1-difluorocyclopropane. This is in agreement with kinetic instability of the singlet for strong acceptors at C_2 due to the through-space p···q interaction favored by the orbital phase continuity for the cyclic $-p-\sigma^*-q-$ interaction. The triplet is found to have a conrotatory conformation **b**, which is similar to the parent diradical **1** but in contrast to the disrotatory one, **a**, of 2,2-disilyl-TM (**2**). This is consistent with the weak bond polarizability of the C−F bond. The $\sigma-\sigma^*$ energy gap is larger for C−F (1.67 au) than for C−H (1.45 au) and C−Si (1.22 au). The acyclic $\sigma_{C-F}-p(q)-\sigma_{C-F}{}^*$ and hence the cyclic $-p-\sigma_{C-F}-q-\sigma_{C-F}{}^*-$ interactions are less effective in **3**. Then, the diradical **3** chooses stabilization by the $p(q)-\sigma^*$ interactions.

Monosubstituted 1,3-Diradicals. There are two disrotatory conformers, **a** and **c**, in addition to a conrotatory conformer, **b**, for monosubstituted TM diradicals (Scheme 1). In the disrotatory conformers, **a** and **c**, two radical centers are in conjugation with C−X (X = H) and C−Y (Y = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl) bonds, respectively.

The most stable conformations of the monosubstituted 1,3-diradicals exhibit interesting trends. Most of the singlet conformers of the substituted 1,3-diradicals have conrotatory conformations (denoted as **b** in Table 1), where the cyclic orbital interaction is not effective. The cyclic orbital interactions in the disrotatory conformers, **a** and **c**, are disfavored by the orbital phase discontinuity in singlets. An exception is a disrotatory conformation **a** for **6** with an electron-withdrawing substitution, Y = OH. In the conrotatory conformation, at least one of the radical orbitals interacts with a σ^*_{C-O} orbital, which is quite low in energy. This may lead finally to the kinetic instability of the conrotatory conformer of **6** (Figure 4b). Another exception is a disrotaotory conformation **c** for **8** with X = SiH_3. The strong donating group SiH_3 reduces the disadvantage by the phase discontinuity in the disrotatory conformer **c** by enhancing the $p-\sigma-q$ path of the cyclic interaction, relative to the other part, $p-\sigma^*-q$ (cf. Figure 5a).

Most of the triplet diradicals have disrotatory conformations. The cyclic orbital interactions are favored by the phase continuity, and occur in the disrotatory conformations. 1,3-Diradicals with the second-row substitutions, **4**−**7**, prefer conformer **a** with the central C−H bond in conjugation (except for the conrotatory conformation **b** in **6**), whereas those substituted with the third-row groups, **8**−**11**, favor the disrotatory conformation **c** with the C−Y bond in the conjugation. Two radical orbitals prefer to interact with a more polarizable σ bond at C_2 to effect the cyclic orbital interaction favored by the phase continuity in the triplet.

The ΔE_{S-T} values (Table 1) calculated by both the CASSCF and CASPT2 methods show the triplet preference for the monosubstituted TM diradicals **4** (Y = CH_3), **5** (Y = NH_2), and **9** (Y = PH_2).[48] Their S−T gaps are very small and close to that of the parent species **1** (Y = H), implying that negligible perturbations are introduced by those substituents. However, the ΔE_{S-T} values of **6** (Y = OH), **8** (Y= SiH_3), and **10** (Y = SH) appear to be strongly method dependent due to extremely narrow energy gaps between the singlet and triplet states. It is still a big challenge for theoretical chemists to obtain the accurate ΔE_{S-T} values for those open-shell systems with subtle S−T energy differences such as −0.03, −0.88, and 0.47 kcal/mol (obtained from (6,6)CASSCF calculations) for **6** (Y = OH), **8** (Y= SiH_3), and **10** (Y = SH), respectively. The CASSCF is a necessary starting point for those diradicals with distinct multireference characteristics. The CASPT2, a widely used multireference many-body perturbation method, is assumed to further improve the accuracy of the calculated ΔE_{S-T} values by considering the dynamical electron correlation. But this method fails whenever there are "intruder states", which are outside the model space but with eigenvalues falling below one that is inside.[49] It is recognized that in CASSCF calculations some highly excited configurations in the active space will be higher in energy than some single excitations from orbitals in the active set to orbitals outside that set.[49] The CASPT2 results can depend on the choice of the CAS space. This may account for the remarkable difference in ΔE_{S-T} values of **8** (Y = SiH_3) between the CASSCF and CASPT2 methods.

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(48) The trend of the triplet preference of these monosubstituted diradicals cannot be explained by the orbital phase properties in a unified manner yet, since the most stable conformers are different between the singlet and triplet states.

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TABLE 3. Energies of the Singlet (E_S for Diradicals and $E_{S'}$ for σ-Bonded Isomers), the Lowest Triplet (E_T) States, and the Corresponding Relative Energy Differences ($\Delta E_{S-S'}$ and ΔE_{S-T}) of Acyclic 1,3-Diradicals Calculated at the UB3LYP/6-31G(d) Level[a]

species	X	R		E_S, au (r(C···C), Å)	$E_{S'}$, au (r(C···C), Å)	$\Delta E_{S-S'}$, kcal/mol	E_T, au	$\Delta E_{S-T}{}^{corr}$,[b] kcal/mol
		R_1	R_2					
12	SiH_3	CN	CN	−1068.06960 (2.522)	−1068.09184(1.568)	14.0	−1068.06389	−3.58 (−5.62)
13	SiH_3	CF_3	CF_3	−2047.19712 (2.476)	−2047.25184 (1.539)	34.3	−2047.19045	−4.19 (−6.96)
14	SiH_3	CH_3	CF_3	−1451.73124 (2.529)	−1451.79883 (1.519)	42.4	−1451.72557	−3.56 (−5.71)[c]
15	SiH_3	SiH_3	CF_3	−1954.51130 (2.511)	−1954.57155 (1.529)	37.8	−1954.50352	−4.88 (−7.79)
16	SiH_3	NH_2	NO_2	−1218.81633 (2.506)	−1218.82097 (1.487)	2.9	−1218.81539	−0.59 (−1.12)
17	CH_3	CF_3	CF_3	−1544.40967 (2.469)	−1544.47018 (1.549)	38.0	−1544.40824	−0.89 (−1.69)

[a] The expectation values of S^2, $\langle S^2\rangle$, for the singlet (triplet) states are 0.74 (2.04) for **12**, 0.80 (2.01) for **13**, 0.76 (2.01) for **14**, 0.75 (2.01) for **15**, 0.95 (2.01) for **16**, and 0.95 (2.01) for **17**, respectively. [b] The corrected values, $\Delta E_{S-T}{}^{corr}$, given in parentheses, are obtained by using Yamaguchi's formula (ref 40), $\Delta E_{S-T}{}^{corr} = \langle S^2{}_T\rangle/(\langle S^2{}_T\rangle - \langle S^2{}_S\rangle) \times \Delta E_{S-T}$, to account for the effects of spin contamination. [c] The (6,6)CASSCF value is −4.94 kcal/mol.

TABLE 4. Energies of the Lowest Singlet (E_S) and Triplet (E_T) States and Their Energy Differences (ΔE_{S-T}) of 2,4-Disilacyclobutane-1,3-diyls (2,4-Disilabicyclo[1.1.0]butanes) Calculated at the UB3LYP/6-31G(d) Level

species	X	R	E_s, au (r(C···C) distance, Å)	$\langle S^2\rangle$[c]	E_T, au	$\langle S^2\rangle$[d]	$\Delta E_{S-T}{}^{corr}$,[e] kcal/mol
18	H	H	−658.65632 (1.664)[a]	0.0	−658.62049	2.01	−22.5
19	F	H	−1055.89706 (1.996)[a]	0.0	−1055.87025	2.01	−16.8
20	SiH_3	H	−1821.38769 (1.601)[a]	0.0	−1821.35824	2.01	−18.5
21	F	CH_3	−1134.47922 (2.286)[a]	0.0	−1134.45629	2.01	−14.4
22	F	NH_2	−1166.61024 (2.509)[b]	0.0	−1166.57090	2.01	−24.7
23	F	OH	−1206.32758 (2.448)[b]	0.0	−1206.29246	2.01	−22.0
24	F	F	−1254.35686 (2.388)[b]	0.19	−1254.32644	2.01	−19.1 (−21.1)[f]
25	OH	F	−1158.16701 (2.344)[b]	0.10	−1158.13584	2.01	−19.6 (−20.6)
26	NH_2	F	−1078.58258 (2.042)[a]	0.0	−1078.55684	2.01	−16.2
27	CH_3	F	−1014.30882 (1.715)[a]	0.0	−1014.28292	2.01	−16.3

[a] The puckered conformation. [b] The planar conformation. [c] The expectation values of S^2 for the singlet states to evaluate the spin contaminations. [d] The expectation values of S^2 for the triplet states. [e] The corrected values, $\Delta E_{S-T}{}^{corr}$, given in parentheses, are obtained by using Yamaguchi's formula (ref 40), $\Delta E_{S-T}{}^{corr} = \langle S^2{}_T\rangle/(\langle S^2{}_T\rangle - \langle S^2{}_S\rangle) \times \Delta E_{S-T}$, to diminish effects of spin contamination. [f] The (6,6)CASSCF value is −19.9.[44]

The Singlet Diradical Characteristics. As shown in Table 1, all the singlet diradicals **1**−**11** are less stable than their σ-bonded isomers with the corresponding relative energy differences, $\Delta E_{S-S'}$, larger than 40 kcal/mol. The σ-bonded isomer represents one strong-coupling limit of the singlet state with the through-space interactions strong enough to form a covalent bond. On the other hand, the "ideal" singlet diradical corresponds to a model with the unpaired electrons completely localized on the distal atoms without any through-space interactions. The real singlet diradicals lie between these two extremes with weak through-space interactions. The singlet diradical character can be inspected by the ΔE_{S-T}, the interatomic distance between the radical centers, and the electron density of the unpaired spins.[50] Especially, the distance between the unpaired electrons provides a direct evaluation of the diradical character. Many significant experimental and theoretical works have shown evidence of long-bond compounds and bond-stretch isomers,[13−15,22,23] which exhibited diradical characteristics to some extent. It is our aim to find some singlet diradicals with distinct diradical characteristics such as the appreciable ΔE_{S-T} and long interradical distances.

From the above theoretical predictions and the numerical results of the 1,3-diradicals, we can conclude that substitutions at the central carbon atom could tune the S−T gaps. The disubstitution on C_2 of TM with strongly electron-donating groups stabilizes singlet states to a significant degree. Therefore, the 2,2-disilyl-TM (**2**) is a promising motif for designing acyclic localized 1,3-diradicals with the singlet preference. On the other hand, the low polarizability of C−Y bonds (for example, Y = F) stabilizes the triplet states of 1,3-diradicals to a lesser extent. Due to electron acceptability of such substituents, however, the singlet states suffer from the kinetic destabilization and easily undergo ring closure to form the σ-bonded isomers. Thus, difluorination on the carbons between the radical centers also can be chosen for designing 1,3-diradicals with the singlet preference if we can take advantage of other factors (e.g., the ring strain) to prevent ring closure.

4. Designs of 1,3-Diradicals

As addressed above, the competitive species of a singlet 1,3-diradical is not only a triplet state but also a σ−bonded isomer. Here, we employ theories of orbital phase and ring strain to design more stable singlet 1,3-diradicals than the triplet diradicals and the σ−bonded isomers. Energies of the singlet and triplet states as well as the S−T gaps of the localized 1,3-diradicals are calculated at the UB3LYP/6-31G(d) level with the results listed in Tables 3 and 4 for acyclic and cyclic diradicals, respectively. The optimized geometries of the singlet states of these 1,3-diradicals (**12**−**27**) are given in Figures 6 and 7 (the dihedral angles are listed in Tables S3 and S4 of the Supporting Information).

Acyclic Diradicals. The substitution by two electron-donating groups at C_2 in TM has been recognized to

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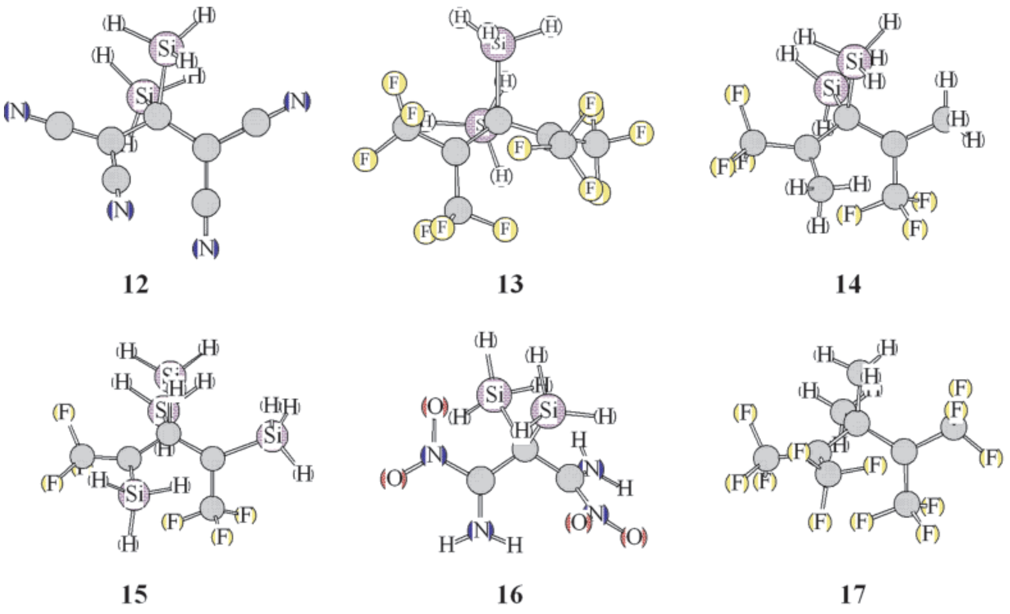

12 13 14 15 16 17

FIGURE 6. The optimized geometries of the singlet acyclic 1,3-diradicals **12**−**17**.

kinetically and thermodynamically stabilize the singlet state. We choose silyl groups as 2-substituents. The singlet state of 2,2-disilyl-TM (**2**) is more stable than the triplet, but much less stable than the σ−bonded isomer, 1,1-disilylcyclopropane. We further employ substituent effects to increase stabilities of the 1,3-diradicals relative to the cyclopropane isomers.

In Table 3, we present calculation results of 2,2-disilyl-TM derivatives **12** and **13** with electron-withdrawing substituents (CN and CF_3) and those (**14**−**16**) with captopdative substituents on the radical centers. It has been pointed out that UB3LYP calculations generally give too small values of ΔE_{S-T} in comparison with those obtained from high-level ab initio calculations.[41,42] Thus, the single-point (6,6)CASSCF calculations also have been performed at the UB3LYP-optimized geometries to assess the amounts of ΔE_{S-T} underestimated by UB3LYP computations. For **14**, the UB3LYP predicts the S−T gap of −3.56 kcal/mol, while the CASSCF gives a value of −4.94 kcal/mol. The underestimate of ΔE_{S-T} by UB3LYP calculations has been ascribed to the mixing of wave functions for triplet state into the singlet state.[41,42] In other words, the “singlet” wave function given by unrestricted methods is not a pure singlet wave function but is contaminated by the higher energy triplet wave functions, which can be reflected by the nonzero values of $\langle S^2 \rangle$ in Table 3. A correction formula proposed by Yamaguchi et al.[40] may alleviate this problem to some extent by scaling off spin contaminations in the singlet. The corrected ΔE_{S-T} values are also tabulated in parentheses in Table 3. Since we are only interested in the qualitative trend in the singlet preference and do not pursuit the quantitative values of ΔE_{S-T}, for simplicity, just the uncorrected values are employed in the following discussions.

Electron-withdrawing groups at the terminal carbons in TM relatively increase the electron-donating ability of the C−Si bonds on C_2 to stabilize the singlet diradicals kinetically and thermodynamically according to theoretical results. The singlet diradicals of **12** and **13** are found to be 3.58 and 4.19 kcal/mol more stable than the triplets. In addition, captodative substituents are expected to stabilize the radical centers. We evaluate the captodative substituent effects by saturated substituents, i.e., CH_3 or SiH_3 groups as donors and CF_3 groups as acceptors in **14** and **15**. Singlet diradicals **14** and **15** are 3.56 and 4.88 kcal/mol more stable than the lowest triplets. The π-conjugated substituents, NH_2 groups as donors and NO_2 groups as acceptors, in **16** lower the singlet preference ($\Delta E_{S-T} = -0.59$ kcal/mol). The lowering may be due to the strong captodative effect, which stabilizes the radical centers too much to interact with each other through σ bonds. Furthermore, the low singlet preference ($\Delta E_{S-T} = -0.89$ kcal/mol) of **17** with CH_3 groups in place of SiH_3 supports the significance of SiH_3 groups at C_2.

The singlet diradicals are more stable than the triplets for all species examined here. However, the expected enhancement of the singlet preference was not found in comparison with that of 2,2-disilyl-TM (**2**). Steric crowding between the terminal substituents hinders the geometry for forming the disrotatory conformations necessary for the effective through-bond interaction. In fact, the optimized conformations are conrotated to a considerable degree (Figure 6).

Stabilities of the singlet 1,3-diradicals relative to the cyclopropane isomers are much improved. The 2,2-disilyl-TM diradical is 54.0 (51.4) kcal/mol less stable than 1,1-disilylcyclopropane at the CASSCF(10,10)/6-31G* (CASPT2N(10,10)/6-31G*) level.[21] The instablities of the singlet diradicals (**12**, **13**, **14**, **15**, and **17**) relative to the cycolpropane isomers are reduced to 14.0, 34.3, 42.4, 37.8, and 38.0 kcal/mol, respectively, but are still large. In contrast, the energy difference between two singlet isomers of **16** is very small (2.9 kcal/mol). Consequently, the singlet diradical **16** is expected to be stable enough to exist in equilibrium with its σ-bonded isomer.

As mentioned before, the long C···C distances for **12**−**17** also reveal the singlet diradical characteristics. The separations between the unpaired electron centers are enlarged by around 60−69% relative to the corresponding

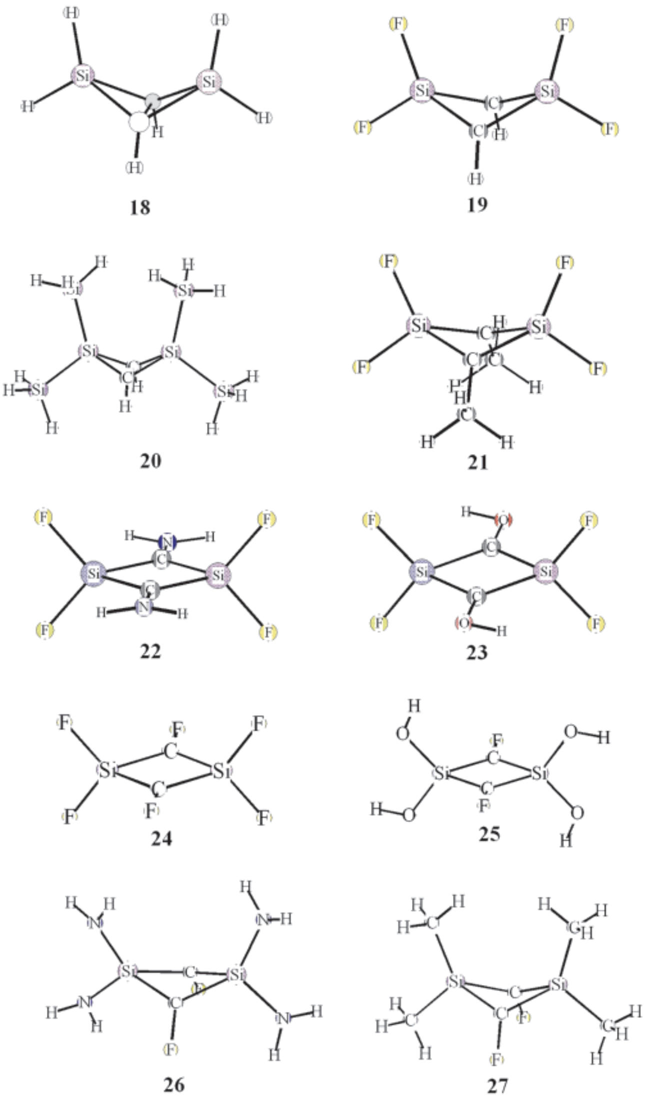

FIGURE 7. The optimized geometries of the singlet cyclic 1,3-diradicals **18**−**27**.

C−C bond lengths in their σ-bonded isomers, exhibiting some singlet diradical character.

Cyclic Diradicals. Considering the factor that the ring strain disfavors the formation of a covalent σ bond between radical centers, we take the four-membered rings as alternative promising motifs for designing stable localized 1,3-diradicals. Four-membered rings prevent the formation of the σ-bonded isomers more effectively than larger rings. It is well-recognized that the σ-bonded isomer with the bicyclo[1.1.0]butane framework has a higher strain than the three-membered ring. Local energy minima have not been located for the singlet diradicals, cyclobutane-1,3-diyl and its derivatives with electron-donating (SiH_3) and -accepting groups (F) on the saturated carbon atoms (C_2 and C_4), but for the σ-bonded isomers, bicyclo[1.1.0]butanes. Silirane is about 10 kcal/mol more strained than cyclopropane. The strain energies estimated from homodesmotic reactions at the MP2/6-31G** level are 35.9 kcal/mol[32c] for silirane and 25.7 kcal/mol for cyclopropane.[51] Silicon atoms introduced into the four-membered ring can further enhance the strain effects. So, it is natural for us to search for the stable singlet diradicals on the basis of the 2,4-disilaclyobutane-1,3-diyl (**18**) motif where the saturated carbon atoms are replaced with silicon atoms. The lowest singlet of **18** is a σ-bonded isomer, 2,4-disilabicyclo[1.1.0]butane with an unusually weak C−C bond (bond length is 1.664 Å).

We need to further elongate the C−C bond in **18** to design stable singlet diradicals. Electron-withdrawing groups on the saturated carbon atoms (C_2 and C_4) were previously reported to elongate the C_1−C_3 bond between the bridgeheads in bicyclo[1.1.0]butane.[46d] Electron-withdrawing groups have been predicted in section 2 to stabilize the triplet diradicals to a lesser extent due to the low polarizability of the C−X bonds. We introduce fluorine substitutions at silicon atoms in **18** to build a new diradical **19**. In fact, the nonbonded C···C distance in **19** (puckered) is long (1.996 Å) enough to be taken as a "diradical" (Table 4).[44b] The singlet is 16.8 kcal/mol more stable than the lowest triplet. On the contrary, electron-donating silyl groups are expected to shorten the C···C distance relative to the parent species **18**. Indeed, radical **20**, another derivative of 2,4-disilabicyclobutane, has shorter (1.601 Å) C···C separation than that (1.664 Å) in **18** (Table 4). Thus, 2,4-disilacyclobutane-1,3-diyls with electron-withdrawing groups on the silicon atoms are candidates for stable singlet diradicals.

Electron-donating groups on the radical centers are predicted from the orbital phase theory to stabilize the singlet diradicals, 2,4-disilacyclobutane-1,3-diyls, with electron-withdrawing groups on the silicon atoms.[52] The orbital phase discontinuity for the delocalization between radicals is mitigated by the enhanced donating ability of the radicals by substituents. We calculated CH_3-, NH_2-, OH-, and F-derivatives (**21**−**24**) with the results shown in Table 4. Local energy minima were not located for the σ-bonded isomers but for the singlet diradicals. The four-membered rings are planar for R = NH_2 (**22**), OH (**23**), and F (**24**), and puckered for R = CH_3 (**21**). The nonbonded C···C distance increases in the order of R = CH_3 (2.286 Å) < R = F (2.388 Å) < R = OH (2.448 Å) < R = NH_2 (2.509 Å). The singlet preference increases in the same order, i.e., R = CH_3 (ΔE_{S-T}= −14.4 kcal/mol) < R = F (−19.1 kcal/mol) < R = OH (−22.0 kcal/mol) < R = NH_2 (−24.7 kcal/mol). These trends are in parallel with the tendency in the π-donating ability of substituents. 2,4-Disilacyclobutane-1,3-diyls with electron-withdrawing groups on the silicon atoms and π-electron-donating groups on the carbon atoms are stable localized singlet 1,3-diradicals.

We then calculated the effects of the substituents (X = CH_3, NH_2, OH, and F) on the silicon atoms in 2,4-disilacyclobutane-1,3-diyls with R = F. The nonbonded C···C distance (1.715 Å for X = CH_3 < 2.042 Å

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(51) For reviews on the small ring strain see: (a) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. (b) Hengge, E.; Janoschek, R. *Chem. Rev.* **1995**, *95*, 1495. (c) Gimarc, B. M.; Zhao, M. *Coord. Chem. Rev.* **1997**, *158*, 3385.

(52) When the cyclic −σ−p−σ*−q− orbital interaction is favored by the phase continuity in the triplet states of acyclic diradicals (with one bridge), there are four cyclic orbital interactions in cyclic diradicals with four-membered rings (with two bridges, called σ_1 and σ_2). As the p−σ−q and p−σ*−q interactions are strengthened by electron-donating and -accepting substituents in the singlet states of acyclic diradicals, the singlet states of the four-membered rings substituted by electron-donating and -accepting groups are stabilized by the cyclic −p−σ_1−q−σ_2− and −p−σ_1*−q−σ_2*− interactions, respectively, which are favored by the orbital phase.

for X = NH_2 < 2.344 Å for X = OH < 2.388 Å for X = F) increases with the electron-withdrawing ability of substituents, which is in agreement with our predictions. The long C···C distances in systems of X = NH_2 (**26**), OH (**25**), and F (**24**) exhibit singlet diradical characteristics. The four-membered rings are planar for X = OH (**25**) and F (**24**), and puckered for X = NH_2 (**26**) and CH_3 (**27**). The singlet preference is greater for 1,3-diradicals with stronger electron-withdrawing groups ($\Delta E_{S-T} = -19.1$ kcal/mol for X = F and $\Delta E_{S-T} = -19.6$ kcal/mol for X = OH) than that for those with the weaker withdrawing groups ($\Delta E_{S-T} = -16.3$ kcal/mol for X = CH_3 and $\Delta E_{S-T} = -16.2$ kcal/mol for X = NH_2). This trend supports the predicted substitution effects on S−T gaps. Among the species in Table 4, we can find that the stable localized singlet 1,3-diradicals are built on 2,4-disilacyclobutane-1,3-diyls with electron-withdrawing groups on the silicon atoms and π-electron-donating groups on the carbon atoms (**19**, **21**−**26**), especially **22**−**25** of planar geometry.

In summary, the singlet preference is appreciable for **12**−**17** (Table 3) and more appreciable for the four-membered ring diradicals **18**−**27** (Table 4). Despite the small lowest S−T gaps of around −4 kcal/mol, acyclic localized diradicals **12**−**15** are still interesting, because 2,2-dihydroxyl-1,3-diphenyl-1,3-cyclopentanediyl of the comparable singlet preference (4 kcal/mol calculated at the same theoretical level) was studied as a model of the long-lived diradicals.[9]

5. Conclusions

The orbital phase theory has been applied to develop a theoretical model of localized 1,3-diradicals, to predict the substitution effects on the spin preference and S−T gaps, and to design stable localized carbon-centered 1,3-diradicals.

Several predictions on the relative stabilities of singlet and triplet states have been drawn from the orbital phase theory: (1) the triplet is more stabilized by the cyclic orbital interaction than the singlet for TM (where X = H); (2) both strong electron-donating and -accepting substituents X (or Y) give rise to the thermodynamic stabilization for the singlet and even to a reversion of the spin preference (i.e., the singlet preference); (3) strong electron-withdrawing groups (−F and −Cl) on C_2 reduce the kinetic stability of the singlet while donating groups do not have such a destabilization effect; and (4) electronegative atom substituents are better for designing the localized 1,3-diradicals with the singlet preference due to the low polarizability of the C_2−X (or C_2−Y) bonds (e.g., X or Y = F, OH) and hence stabilize the triplet less to some extent. These predictions have been confirmed by CASSCF and CASPT2 calculations on **1**−**11**.

We have also investigated some acyclic 1,3-diradicals **12**−**17** on the basis of the 2,2-disilyl-TM (**2**) motif, which has been shown by the orbital phase property to be kinetically and thermodynamically stable in the singlet state. The present calculations (UB3LYP/6-31G*) showed their ground states are all singlet with small lowest S−T spacing. These acyclic diradicals are, however, less stable than the σ-bonded isomers, cyclopropanes.

Furthermore, effects of the ring strain have been included in the four-membered ring systems to enhance the stability of the singlet diradicals relative to σ-bonded isomers. The singlet states of 2,4-disilacyclobutane-1,3-diyls **22**−**25** with F or OH groups on Si_2 and Si_4 and NH_2 or OH groups on C_1 and C_3 have been found to be more stable than triplets and not to have the corresponding σ-bonded isomers, 2,4-disilabicyclo[1.1.0]butanes, as local minima. The F or OH substituents on Si_2 and Si_4 thermodynamically stabilize the singlet 1,3-diradicals by weakening effects of the orbital phase discontinuity, and stabilize the triplet states less due to low polarizabilities of C−X bonds. The strong π-donating NH_2 or OH groups on C_1 and C_3 promote the delocalization of unpaired electrons through the acceptor Si−R bonds (R = F or OH). The cyclic species **22**−**25** are suggested to be promising targets for future experimental synthesis of persistent localized singlet diradicals. The present work may stimulate the realization of stable carbon-centered localized singlet 1,3-diradicals.

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Supporting Information Available: Optimized geometries and energies for all the studied species. This material is available free of charge via the Internet at http://pubs.acs.org.

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