

DFT Prediction of Ground-State Spin Multiplicity of Cyclobutane-1,3-diyls: Notable Effects of Two Sets of Through-Bond Interactions

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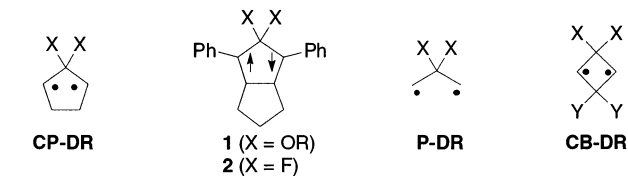
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Abstract: DFT calculations (UB3LYP/6-31+G**) have been performed to predict the substituent effect on the ground-state spin-multiplicity and the singlet–triplet energy gap in cyclobutane-1,3-diyls, **CB-DR**. The ground state is calculated to be largely dependent on the substituents (X, Y) at the C2 and C4 positions. The substituent effects can be reasonably explained by the two sets of through-bond (TB) interactions which result from the coupling between the symmetric nonbonding molecular orbital (Ψ_S) and the C–X (Y) σ and σ^* orbitals.

The effect of substituents on ground-state spin multiplicity has attracted much attention in diradical chemistry.¹ Borden² and our group³ have computationally found a notable substituent (X) effect at the C2 position on the ground-state spin-multiplicity of cyclopentane-1,3-diyls, **CP-DR**. Thus, the electron-withdrawing C2–X (X = F, OR) bonds cause the singlet state to lie below the triplet state, which is the ground state for X = H, alkyl.⁴ These theoretical predictions have been recently confirmed by generating the kinetically stabilized singlet diradicals **1**⁵ ($\tau_{293K} \sim \mu\text{s}$) and **2**⁶ ($\tau_{293K} \sim 80\text{ ns}$). The strongly electron-donating C2–SiR₃ bonds may also produce a singlet ground state, as has been reported computationally for 2,2-disilyl-1,3-propanediyl **P-DR** (X = SiH₃).^{2c}

The ground-state spin-multiplicity and the singlet–triplet energy gap are largely dependent on the energy difference between the symmetric (Ψ_S) and antisymmetric (Ψ_A) nonbonding molecular orbitals (NBMOs, see Figure 1) in which the two electrons are located. The qualitative molecular orbital interaction diagram that accounts for the substituent effect is shown in Figure 1. The through-space (TS) overlap of the two radical p orbitals leads to two formally nonbonding molecular orbitals (NBMOs), in which the symmetric MO (Ψ_S) lies energetically below the antisymmetric MO (Ψ_A). In principle, the TS interaction favors a singlet ground state, although the interaction is largely dependent on the distance between the two radical sites.⁷ In 1,3-diradicals, the through-bond (TB) interaction plays an important role in determining the energies of Ψ_S and Ψ_A .⁸ The Ψ_A MO is prevented by symmetry from mixing with either of the intervening C–X σ and σ^* orbitals at the C2 position, but Ψ_S can mix with both. The interaction (TB1) with the C–X σ orbital (X = H, SiH₃) increases the energy of Ψ_S (left side in Figure 1), while the interaction (TB2) with the C–X σ^* orbital (X = F, OR) decreases the energy (right side in Figure 1). Thus, the magnitude of the TB interaction determines the ground-state spin-multiplicity. When two hydrogen atoms are introduced at the C2 position (**CP-DR1**, X = H), the weak interaction of Ψ_S with the C–H σ orbital (σ_{C-H}) increases slightly the energy of Ψ_S . Thus, the triplet is predicted to be the ground state, which has been experimentally confirmed by Closs.⁴ When the C–X σ orbital (X = e.g., SiR₃, σ_{C-Si}) interacts more efficiently with Ψ_S , the orbital interaction (TB1) places Ψ_S above Ψ_A with a larger energy spacing. Thus, the singlet is the preferred spin state, which has been already calculated for 2,2-disilyl-1,3-propanediyl (**P-DR**) by Borden.^{2c} A strong TB2 interaction becomes important to locate Ψ_S far below Ψ_A , when the energy of the C–X σ^* orbital is lowered by the introduction of electron-withdrawing groups (X = F, OR) at the C2 position.^{2b,3}



In the present study, we are interested in the substituent (X, Y) effects at the C2 and C4 positions on the ground-state spin-multiplicity and the singlet–triplet energy gap ($\Delta E_{ST} = E_S - E_T$) in cyclobutane-1,3-diyls **CB-DR**. Two sets of the TB interaction, i.e., TB1 + TB1, TB2 + TB2, or TB1 + TB2, would be expected for the cyclobutane-ring system, but only one set of the TB interaction, i.e., TB1 or TB2, is possible for the five-membered ring system **CP-DR** (Figures 1 and 2). How do the two sets of TB interactions in **CB-DR** affect the ground-state spin-multiplicity and the singlet–triplet energy gap? To this end, a variety of substitution patterns in **CB-DR1–11** have been investigated (Table 1).

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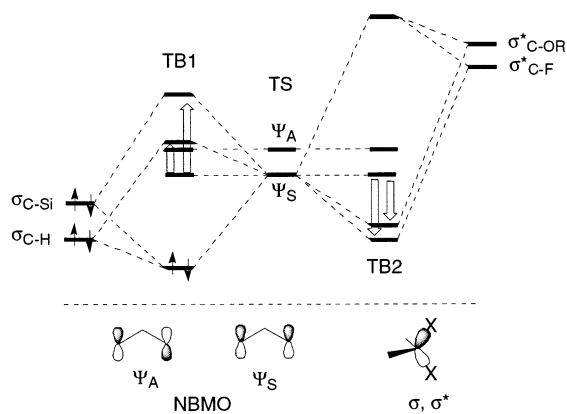


FIGURE 1. Orbital interaction diagram: TS, through-space interaction between the two radical p orbitals; TB1, through-bond interaction between the σ_{C-X} orbital and the symmetric NBMO (Ψ_S); TB2, through-bond interaction between the σ_{C-X}^* orbital and the symmetric NBMO (Ψ_S).

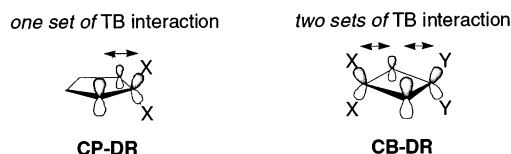


FIGURE 2. Through-bond (TB) interaction in the five-membered ring system **CP-DR** and in the four-membered ring system **CB-DR**: comparison of *one set* of TB interaction with *two sets* of TB interactions.

TABLE 1. Substituent (X, Y) Effects on the Singlet–Triplet Energy Gaps in Cyclobutane-1,3-diyls **CB-DR**^a

entry	CB-DR	X	Y	ΔE_{ST}^b	S^2	$\Delta E_{ST,corr}^d$	E_{rel}^e	ΔE^W
1	CB-DR1	H	H	+1.3	1.01	+2.7	0	-0.95
2	CB-DR2	SiH ₃	SiH ₃	-7.4	0.00	-7.4	+10.1	+2.76
3	CB-DR3	F	F	-17.6	0.37	-21.7	+24.4	-3.55
4	CB-DR4	OH	OH	-9.1	0.64	-13.3	+16.0	-2.90
5	CB-DR5	OMe	OMe	-7.8	0.71	-12.1	+14.8	-2.62
6	CB-DR6	SiH ₃	H	-1.2	0.90	-2.1	+4.8	+1.87
7	CB-DR7	F	H	-3.8	0.82	-6.5	+9.2	-2.29
8	CB-DR8	OH	H	-1.5	0.91	-2.2	+4.9	-1.92
9	CB-DR9	OMe	H	-0.7	0.93	-1.2	+3.9	-1.82
10	CB-DR10	F	SiH ₃	+1.3	0.99	+2.6	+0.1	-1.16
11	CB-DR11	OH	SiH ₃	+1.3	1.01	+2.5	+0.2	+1.19

^a The calculations were performed at the UB3LYP/6-31+G (d,p) level of theory. The geometry optimizations were performed in the following symmetries: **CB-DR1–3** (D_{2h}), **CB-DR4,5** (D_2), **CB-DR6,7,11** (C_{2v}), **CB-DR8–10** (C_2). ^b ΔE_{ST} (kcal/mol) = $E_S - E_T$, before spin corrections. ^c S^2 values are for the singlet state. The S^2 values for the triplet state were calculated to be ca. 2.0; see the Supporting Information. ^d The energy gaps, $\Delta E_{ST,corr}$, were calculated after spin correction according to Yamaguchi's method (ref 14); $\Delta E_{ST,corr}$ (kcal/mol) = $S^2[T]/(S^2[T] - S^2[S])\Delta E_{ST}$. ^e The relative energy differences from **CB-DR1** (X = Y = H), E_{rel} (kcal/mol) = $2.7 - \Delta E_{ST}$. ^f ΔE^W (eV) = $\Psi_S - \Psi_A$. The energies were calculated for the singlet state at RB3LYP/6-31+G(d,p).

Density functional theory (DFT)⁹ has been shown to produce reasonable results for open-shell as well as closed-shell molecules.^{3,10,11} Because of the relatively low computational cost, we have chosen to calculate the substituent effects on the singlet–triplet energy spacing ($\Delta E_{ST} = E_S - E_T$) for **CB-DR** at the UB3LYP/6-31+G

(d,p) level¹² of theory with the Gaussian 98 package.¹³ The geometries of both the singlet and triplet states were optimized in D_{2h} , D_2 , C_{2v} , or C_2 symmetry, depending on the structure of **CB-DR**, see footnote *a* in Table 1. The substituent effects on ΔE_{ST} (kcal/mol) are listed in Table 1 (entries 1–11). Considerable spin-contamination was found for all the singlet states (i.e., S^2 0.37–1.01) except **CB-DR2** (X = Y = SiH₃, entry 2). A pure singlet ($S^2 \approx 0.00$) was calculated for **CB-DR2** at this level of theory. For the triplet states, excellent spin expectation values, $S^2 \approx 2.0$, were obtained for all of the calculations. To estimate the pure singlet–triplet energy differences, the spin-corrected energy gap, $\Delta E_{ST,corr}$, was calculated according to the method reported by Yamaguchi and co-workers.¹⁴

As shown in Table 1, the ground-state spin-multiplicity and the energy gap were largely dependent on the substituents (X, Y) at the C2 and C4 positions. A triplet ground state, $\Delta E_{ST,corr} = +2.7$ kcal/mol, was calculated for cyclobutane-1,3-diyl **CB-DR1** (X = Y = H, entry 1). A triplet ground state ($\Delta E_{ST} = +1.7$ kcal/mol) has been already reported at the GVB level of theory by Dougherty,^{7,15} which was confirmed by an EPR measurement.¹⁶ Thus, the DFT calculations reproduced well the ground state of **CB-DR1**. The triplet ground state suggests that the magnitude of the TB interaction between the weakly electron-donating C–H σ orbitals and the Ψ_S orbital is nearly equal to that of the TS interaction in **CB-DR**, cf. Figure 1. As reported for 1,3-diyls **P-DR**^{2c} and **CP-DR**,^{2a,b,3} the strongly electron-donating C–SiH₃ (X = Y = SiH₃) bonds or electron-withdrawing C–X(Y) (X = Y = F, OR) bonds promoted the singlet as the ground state (entries 2–5). It should be noted, as expected, that the energy gaps were found to be much larger than those calculated for the five-membered 1,3 diradicals **CP-DR** at the same level of theory (Table 2). To compare the substituent effects, the relative energies, E_{rel} (kcal/mol) = $\Delta E_{ST,corr}$ (for X = Y = H) – $\Delta E_{ST,corr}$, were calculated for **CB-DR** and **CP-DR** (Tables 1–2). The substituent effect on the energy gap in **CB-DR** (entries 2–5 in Table 1) is nearly twice as large as that calculated in **CP-DR** (entries 2–5 in Table 2). The results clearly indicate

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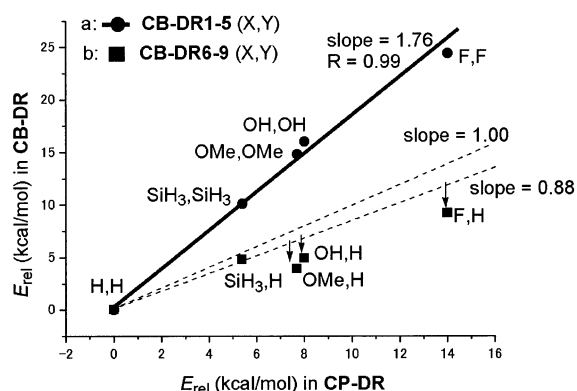
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TABLE 2. Substituent (X) Effect on the Singlet–Triplet Energy Gaps in Cyclopentane-1,3-diyls CP-DR

entry	CP-DR	X	lit.	ΔE_{ST}^a			E_{rel}^b
				this work ^c		$\Delta E_{ST,corr}$	
1	CP-DR1	H	+1.2 ^d	+0.6	1.00	+1.3	0
2	CP-DR2	SiH ₃	<i>e, f</i>	-2.3	0.87	-4.1	+5.4
3	CP-DR3	F	-9.8 ^g	-8.1	0.72	-12.7	+14.0
4	CP-DR4	OH	-7.4 ^h	-3.8	0.85	-6.7	+8.0
5	CP-DR5	OMe	<i>e</i>	-3.6	0.87	-6.4	+7.7

^a ΔE_{ST} (kcal/mol) = $E_S - E_T$. ^b E_{rel} (kcal/mol) = $1.3 - \Delta E_{ST,corr}$ (this work). ^c The calculations were performed in C_{2v} symmetry for CP-DR1–3 and in C_2 symmetry for CP-DR3–4 at the UB3LYP/6-31+G(d,p) level of theory. S^2 values are for the singlet state. The S^2 values for the triplet state were calculated to be ca. 2.0; see the Supporting Information. The energy gaps, $\Delta E_{ST,corr}$, were calculated after spin correction. ^d In C_2 symmetry at the CISD level of theory, ref 4c. ^e The energy gaps have not been reported previously. ^f The energy gaps, $\Delta E_{ST} = -6.2$ kcal/mol at the CASSCF and -11.9 kcal/mol at the CASPT2N level of theory, were reported for 2,2-disilyl-1,3-propanediyl P-DR (X = SiH₃), ref 2c. ^g In C_{2v} symmetry at the CASPT2N level of theory, ref 2b. ^h In C_2 symmetry at the UB3LYP/6-31G(d), ref 3.

**FIGURE 3.** Plots of the substituents effects (E_{rel}) in CB-DR against the substituent effect (E_{rel}) in CP-DR.

that the double through-bond interaction (TB1 + TB1 for CB-DR1–2 or TB2 + TB2 for CB-DR3–5, Figures 1 and 2) plays an important role in the energy spacing.

To get more information on the role of the through-bond interaction in CB-DR, the ground-state spin-multiplicity and the energy gap were calculated for the unsymmetrically substituted diradicals (X ≠ Y, entries 6–11 in Table 1). Singlet ground states, $\Delta E_{ST} < 0$, were found for CB-DR6–9 (X = SiH₃, F, OH, OMe, Y = H), entries 6–9 in Table 1. However, the relative energies (E_{rel}) were less than half of the values found in the symmetric diradicals (entries 2–6 in Table 1). The relative energies for CB-DR7–9 (entries 7–9 in Table 1) were also much smaller than those in CP-DR3–5 (entries 3–5 in Table 2). In contrast, the relative energy of the silyl-substituted diradical CB-DR6 (X = SiH₃, Y = H, entry 6 in Table 1) was nearly equal to that calculated for CP-DR2 (X = SiH₃, entry 2 in Table 2). Interestingly, a triplet ground state was calculated for CB-DR10 (X = F, Y = SiH₃) and CB-DR11 (X = OH, Y = SiH₃), entries 10 and 11 in Table 1. The competitive substituent effect is also quite informative for understanding the role of through-bond interaction on the ground-state spin-multiplicity in CB-DR.

The orbital interaction diagrams shown in Figure 1 can rationalize the substituent effects on the spin multiplicity and the singlet–triplet energy gap in CB-DR. First, we will discuss the cooperative substituent effect (X = Y, TB1 + TB1 or TB2 + TB2, entries 1–5 in Table 1, Figure 1). The weak electron-donating σ_{C-H} bonds (TB1 + TB1) are not enough to separate energetically the two NBMOs (Ψ_S and Ψ_A), but instead diminish the energy gap caused by the through space interaction (TS) between the two 2p orbitals (left side in Figure 1, the interaction between σ_{C-H} and Ψ_S). Thus, the triplet was calculated to be the ground state (entry 1 in Table 1). The TB interaction between the electron-donating σ_{C-Si} orbital and Ψ_S is stronger than in the C–H case and increases the energy of Ψ_S far above that of Ψ_A (left side in Figure 1, interaction between σ_{C-Si} and Ψ_S). Thus, the two electrons preferably occupy the Ψ_A orbital, resulting in a singlet ground state (entry 2 in Table 1).

A more quantitative assessment can be made by calculating the energy gap, ΔE^W (eV) = $\Psi_S - \Psi_A$, between Ψ_S and Ψ_A for the singlet state at the RB3LYP/6-31+G(d,p) level of theory (entries 1 and 2 in Table 1).¹⁷ For CB-DR1 (X = Y = H), the energy of Ψ_S was calculated to be lower than that of Ψ_A by 0.95 eV (entry 1 in Table 1). In contrast, for CB-DR2 (X = Y = SiH₃), the energy of Ψ_S was found to be above the energy of Ψ_A by 2.76 eV (entry 2 in Table 1).

The double TB2 interaction (TB2 + TB2, right side of Figure 1) explains reasonably the remarkable effect of the electron-withdrawing C–F (X = Y = F, entry 3 in Table 1) and C–OR (X = Y = OR, entries 4,5 in Table 1) bonds on the singlet preference. Namely, the MO interaction results in lowering the symmetric Ψ_S , and enhancing the energy difference between the two NBMOs. The TB2 interaction of the C–F σ^* orbital should be larger than that of C–OR σ^* orbital, since the electronegativity of a fluorine atom is larger than that of an oxygen atom. Thus, the energy difference between Ψ_S and Ψ_A in CB-DR3 (X = Y = F) is predicted to be larger than that in CB-DR4,5 (X = Y = OR).

The larger the energy difference ($|\Delta E^W|$) between the Ψ_S and Ψ_A NBMOs, the more likely it is that the singlet will fall below the triplet in energy. The qualitative MO prediction has been again assessed by the calculated ΔE_{ST} and ΔE^W values; compare entry 3 with entries 4, 5 in Table 1. As has been mentioned before, the cooperative substituent effects on the singlet–triplet energy spacing ΔE_{ST} in CB-DR is nearly twice as large as that calculated for CP-DR system. To assess more quantitatively the cooperative substituent effect, the E_{rel} values for CB-DR were plotted against those for CP-DR (Figure 3). For the symmetrically substituted CB-DR2–5 (X = Y = SiH₃, OH, OMe, F, Figure 3a), a linear correlation ($R = 0.99$) with the substituent effect in CP-DR2–5 (X = SiH₃, OH, OMe, F) was obtained with a slope of 1.76. This indicates that one set of the substituent effect in CB-DR2–5 is in proportional to the substituent effect in CP-DR2–5, although the effect in CB-DR is about 0.88 times as large

(17) RB3LYP calculations do not produce accurately the absolute energies of the two NBMOs, since the two spins are supposed to be perfectly occupied in the lower NBMO. However, as shown in Table 1, the $|\Delta E^W|$ values are roughly in proportion to the singlet preference. Thus, we feel that the values, at least in this study, are reliable for discussion.

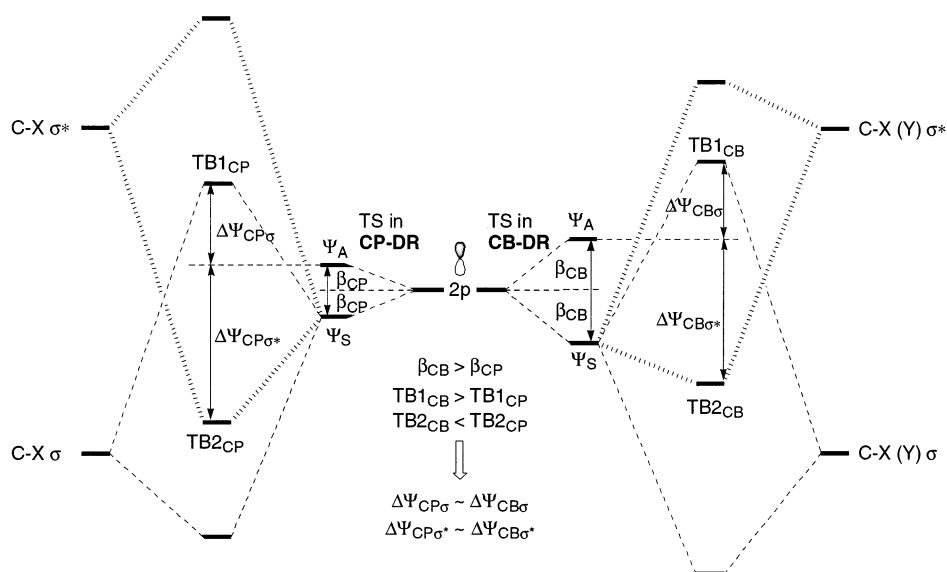


FIGURE 4. Comparison of the orbital interactions, through-space (TS) and through-bond (TB), between **CP-DR** and **CB-DR**.

as that in **CP-DR**. The correlation is not so easy to understand, since the magnitude of the TS and TB interactions should be different in the two systems.

A plausible explanation for this correlation is shown in Figure 4. The TS interaction is dependent on the distance between the two 2p orbitals;⁷ thus, the energy gap between the Ψ_S and Ψ_A NBMOs should be different between the two diradicals. Namely, since the distance between the two radical carbons in **CB-DR** is shorter than that in **CP-DR**, the energy separation caused by the TS interaction in **CB-DR** (β_{CB}) is larger than that in **CP-DR** (β_{CP}); $\beta_{CB} > \beta_{CP}$. Consequently, the TB1 interaction of Ψ_S with the C–X (Y) σ orbital in **CB-DR** ($TB1_{CB}$) is greater than that in **CP-DR** ($TB1_{CP}$); $TB1_{CB} > TB1_{CP}$, since the energy gap between the interacting two orbitals in **CB-DR** is smaller than that in **CP-DR**. Conversely, the TB2 interaction of Ψ_S with C–X (Y) σ^* orbital in **CB-DR** ($TB2_{CB}$) should be smaller than that in **CP-DR** ($TB2_{CP}$); $TB2_{CB} < TB2_{CP}$. Thus, it is possible to predict that the one set of TB interactions in **CB-DR** is in proportion to the **CP-DR** case; $\Delta\Psi_{CP\sigma} \sim \Delta\Psi_{CB\sigma}$ and $\Delta\Psi_{CP\sigma^*} \sim \Delta\Psi_{CB\sigma^*}$. This orbital interaction is the best for understanding the linear correlation of the substituent effect between the two diradical systems.

Next, we will discuss the substituent effects for the unsymmetrically substituted **CB-DR6–9** (X = SiH₃, OH, OMe, Y = H). As shown in Figure 3b, the substituent effect in **CB-DR6** (X = SiH₃, Y = H) is almost the same as the effect in **CP-DR2** (X = SiH₃). In contrast, for the other diradicals **CB-DR7–9** (X = OMe, OH, F, Y = H), the substituent effects are far below the line of the slope of 0.88. The substituent effects can be explained by the two sets of TB interactions (Figures 1 and 2). For the diradical **CB-DR6** (X = SiH₃, Y = H), the cooperative effect of the weakly electron-donating C–H bonds and the strongly electron-donating C–SiH₃ bonds pushes up the symmetric Ψ_S orbital in the same direction (left side in Figure 1). Since the substituent effect in **CB-DR** is slightly smaller than that in **CP-DR**, the cooperative effect of the weakly electron-donating C–H bonds and the strongly electron-donating C–SiH₃ bonds in **CB-DR6**

is nearly equal to that calculated for **CP-DR2** (X = SiH₃). For the diradicals **CB-DR7–9** (X = F or OR, Y = H), the electron-withdrawing C–F and C–OR bonds pull down the Ψ_S orbital (TB 2) while the weakly electron-donating C–H bonds increase the energy of the orbital (TB1). Thus, the substituent effect of the hydrogen atoms (Y = H) partially cancels the effect of the fluorine atoms (X = F) or the oxygen atoms (X = OR). This competitive substituent effect is the best for explaining the deviation from the line of slope 0.88 (Figure 4b).

Finally, we will explain the reason for the triplet ground state of the diradicals **CB-DR10–11** (entries 10–11 in Table 1). Again, the two sets of TB interactions rationalize the substituent effect on the ground state spin multiplicity. The strongly electron-donating C–SiH₃ bonds effectively push up the energy of Ψ_S while the electron-withdrawing C–F and C–OR bonds pull down the energy of the orbital. Thus, the competitive TB interaction cancels the TS interaction so that the triplet is predicted to be the ground state in the MO calculations.

In the present study, we have found an unprecedented effect of the two sets of through-bond interactions on the ground state spin-multiplicity and the singlet-triplet energy gap in the **CB-DR** system. The cooperative substituent effects (X = Y) increased the singlet-triplet energy gap, compared with the **CP-DR** system. The competitive substituent effects (X \neq Y) decreased the singlet preference, and in some cases the substitution pattern changed the ground state spin multiplicity.

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Supporting Information Available: Computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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