

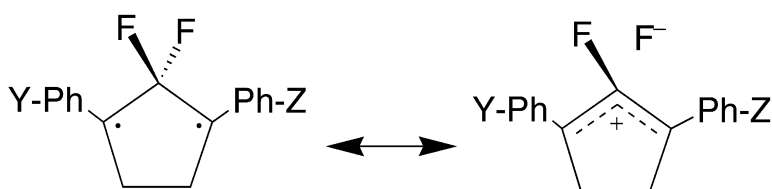
Article

**DFT Calculations on the Effects of *Para* Substituents on the Energy Differences between Singlet and Triplet States of 2,2-Difluoro-1,3-diphenylcyclopentane-1,3-diyls**

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### DFT Calculations on the Effects of *Para* Substituents on the Energy Differences between Singlet and Triplet States of 2,2-Difluoro-1,3-diphenylcyclopentane-1,3-diyls

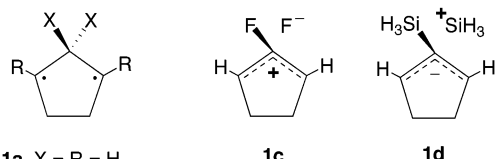
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**Abstract:** UB3LYP/6-31g\* calculations have been performed on a series of *para*-substituted 2,2-difluoro-1,3-diphenylcyclopentane-1,3-diyls (**4**). The singlet is computed to be the ground state for each of the diradicals, regardless of the nature of the *para* substituents, which range from strongly  $\pi$ -electron-donating (amino) to strongly  $\pi$ -electron-withdrawing (nitro). In the symmetrically *para*-disubstituted diradicals, the size of the singlet–triplet energy gap ( $\Delta E_{ST}$ ) increases with the  $\pi$ -electron-donating ability of the substituents, but in the unsymmetrically substituted diradicals, large values of  $\Delta E_{ST}$  are calculated even when one of the substituents is a  $\pi$  electron acceptor. The origins of the competitive and cooperative substituent effects, predicted for diradical **4**, are discussed in light of the calculated effects of the same substituents on the singlet and triplet states of diradical **6**, which lacks the geminal fluorines at C-2 that are present in **4**.

Experiments by Closs and Buchwalter established that cyclopentane-1,3-diyl (**1a**) has a triplet ground state.<sup>1</sup> Subsequent experimental studies by Dougherty, Adam, Wirz, and their co-workers showed that the 1,3-diphenyl derivative (**1b**) has a triplet ground state too.<sup>2</sup> In agreement with these experimental results, ab initio calculations by Schaefer and co-workers predicted the triplet to be the ground state of **1a**.<sup>3</sup>

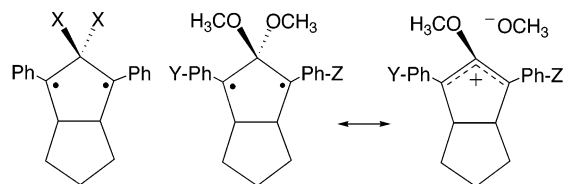


- 1a**, X = R = H  
**b**, X = H, R = Ph  
**c**, X = F, R = H  
**d**, X = SiH<sub>3</sub>, R = H

In contrast, CASPT2 calculations have predicted that hyperconjugation can make the singlet the ground state of cyclopentane-1,3-diyls that are geminally substituted at C-2 with either fluorines (**1c**)<sup>4</sup> or silyl groups (**1d**).<sup>5</sup> The hyperconjugated

resonance structure drawn for **1c** depicts the manner in which the geminal fluorines are predicted to stabilize the lowest singlet state, and the hyperconjugated resonance structure drawn for **1d** shows how the geminal silyl substituents are predicted to stabilize this state.

The prediction of a singlet ground state for **1c** has been confirmed experimentally in a bicyclic derivative of 2,2-difluoro-1,3-diphenylcyclopentane-1,3-diyl (**2a**).<sup>6</sup> Although C–O bonds are expected to be poorer hyperconjugative electron acceptors than C–F bonds, Abe, Adam, and co-workers have found that the analogous derivative of 2,2-diethoxy-1,3-diphenylcyclopentane-1,3-diyl (**2b**) not only has a singlet ground state but is also longer lived than the difluoro derivative (**2a**).<sup>7</sup>



- 2a**, X = F  
**b**, X = OC<sub>2</sub>H<sub>5</sub>  
**3a**, Y = Z = H  
**b**, Y = *p*-CN, Z = H  
**c**, Y = *p*-OCH<sub>3</sub>, Z = H  
**d**, Y = Z = *p*-CN  
**e**, Y = Z = *p*-OCH<sub>3</sub>  
**f**, Y = *p*-CN, Z = *p*-OCH<sub>3</sub>

Most recently, Abe, Adam, and co-workers have studied *para* substituent effects on the lifetimes of bicyclic derivatives of

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singlet 2,2-dimethoxy-1,3-diphenylcyclopentane-1,3-diyls (**3**).<sup>8</sup> Diradical **3a**, with unsubstituted phenyl groups, was the shortest lived ( $\tau = 320$  ns). The half-lives measured for the monosubstituted singlet diradicals were 470 ns for **3b** and 600 ns for **3c**. For the disubstituted diradicals the half-lives were  $\tau = 625$  ns for **3d**,  $\tau = 1050$  ns for **3e**, and  $\tau = 740$  ns for **3f**. The effects of substituents on extending the half-life of **3a** seem to be roughly multiplicative, so the substituent effects on the activation energies for ring closure appear to be approximately additive.

Cyano is a better radical-stabilizing substituent than methoxyl,<sup>9</sup> so the effect of the methoxyl group on the singlet diradical lifetime is, at first sight, surprising. However, to the extent that the hyperconjugated resonance structure shown for **3** is important, the  $\pi$ -electron-donating *p*-methoxyl substituents in **3c** and **3e** should have a stronger effect on extending the lifetimes of the singlet diradicals than the  $\pi$ -electron-withdrawing cyano substituents in **3b** and **3d**. The lifetimes measured by Abe, Adam, and co-workers are, indeed, consistent with this expectation.<sup>8</sup>

The substituent effects on the lifetimes of **3** are small. The largest substituent effect, that due to the pair of methoxyl substituents in **3e**, makes the lifetime of this singlet diradical only a little more than a factor of 3 greater than that of **3a**. A factor of 3 at room temperature corresponds to only a 0.6 kcal/mol difference between the activation energies for ring closure of **3a** and **3e**. The factor of 1.7 greater lifetime of **3e**, relative to **3f**, corresponds to a difference of only 0.3 kcal/mol in the activation energies for ring closure.

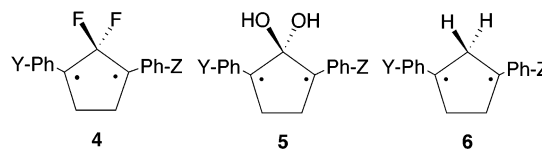
Presumably, the substituent effects on the lifetimes of **3** are small, because the substituents stabilize not only the singlet diradicals but also the transition structures (TSs) for their ring closure. The TSs for ring closure are expected to be early, so it is reasonable to suppose that they too should have substantial diradical character. Therefore, the substituent effects on the activation energies for ring closure are likely to be only a small fraction of the substituent effects on the thermodynamic stabilization energies of the singlet diradicals, relative to the energies of the ring-closed products formed from them.

Not only are the substituent effects on the singlet diradical lifetimes small, but they also contain contributions from the abilities of the substituents to stabilize both the radical centers in the first resonance structure for **3** and the positive charge at C-1 and C-3 in the second resonance structure. Consequently, it is impossible to know exactly how much of the 0.3 kcal/mol difference between the energies of activation for ring closure of **3e** and **3f** is actually due to the expected difference between the abilities of methoxyl and cyano substituents to stabilize the positive charge in the hyperconjugated resonance structure, and how much is contributed by the difference between the radical-stabilizing abilities of these two substituents.

A good indicator of the ability of *para* substituents to stabilize the positive charge in the hyperconjugated resonance structure

for **3** should be the effect of the substituents on the singlet–triplet splitting in these diradicals. Radical stabilization by *para* substituents should affect the lowest singlet and triplet states of **3** about equally, but only the energy of the singlet should be affected by how well the *para* substituents stabilize the positive charge in the hyperconjugated resonance structure for **3**.

Singlet–triplet energy differences are much easier to calculate than to measure.<sup>10</sup> Therefore, we carried out calculations of the singlet–triplet energy differences ( $\Delta E_{ST}$ ) in monocyclic diradicals **4–6**. The results of these calculations are reported and discussed in this paper.



**a**, Y = Z = H; **b**, Y = *p*-NH<sub>2</sub>, Z = H; **c**, Y = *p*-OH, Z = H; **d**, Y = *p*-CN, Z = H; **e**, Y = *p*-NO<sub>2</sub>, Z = H; **f**, Y = Z = *p*-NH<sub>2</sub>; **g**, Y = Z = *p*-OH; **h**, Y = Z = *p*-CN; **i**, Y = Z = *p*-NO<sub>2</sub>; **j**, Y = *p*-NH<sub>2</sub>, Z = *p*-NO<sub>2</sub>; **k**, Y = *p*-OH, Z = CN

## Computational Methodology

CASPT2 calculations have been shown to give rather accurate values of singlet–triplet splittings in diradicals.<sup>10</sup> Unfortunately, even for diradicals **4a–6a**, which have no *para* substituents, (14/14)CASPT2 calculations are required to provide variational correlation for just the  $\pi$  electrons. For Y = Z = CN, (18/18)CASPT2 would have to be performed for this purpose. Since we wanted to compute  $\Delta E_{ST}$  for more than 30 diradicals, we decided to perform calculations based on unrestricted density functional theory (UDFT). Although UDFT calculations were certain to give less accurate values of  $\Delta E_{ST}$  than CASPT2 calculations (vide infra), we were able to carry out UDFT calculations on **4–6**, whereas CASPT2 calculations on these diradicals would have been beyond the computational resources available to us.

All calculations were performed with the 6-31G\* basis set.<sup>11</sup> Calculations based on density functional theory were carried out with the three-parameter functional of Becke<sup>12</sup> and the correlation functional of Lee, Yang, and Parr.<sup>13</sup> Geometries were optimized and vibrational analyses were performed at the unrestricted (U)B3LYP level of theory. Optimized geometries were demonstrated to be energy minima by confirming that they had no imaginary vibrational frequencies. The harmonic frequencies were used, without scaling, to compute zero-point energies. All of the calculations were carried out with the Gaussian 98 suite of programs.<sup>14</sup>

## Results and Discussion

Symmetrically disubstituted derivatives of **4** (i.e., those with Y = Z) were found to have equilibrium geometries with only C<sub>2</sub> symmetry. The unsymmetrically substituted diradicals (Y ≠ Z) were found to have equilibrium geometries with no

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**Table 1.** UB3LYP/6-31G\* Singlet–Triplet Energy Differences ( $\Delta E_{ST}$ )<sup>a</sup> in Diradicals **4a–k** (kcal/mol), before and after Correction for Spin Contamination,<sup>b</sup> and the  $\langle S^2 \rangle$  Values for the Singlet States That Were Used To Make the Corrections<sup>c</sup>

Y, Z	$\langle S^2 \rangle$	$\Delta E_{ST}$	$\Delta E_{ST}^{corr}$
H, H ( <b>4a</b> )	0.80	4.5	7.4
<i>p</i> -NH <sub>2</sub> , H ( <b>4b</b> )	0.75	4.9	7.8
<i>p</i> -OH, H ( <b>4c</b> )	0.77	4.7	7.7
<i>p</i> -CN, H ( <b>4d</b> )	0.80	4.2	7.1
<i>p</i> -NO <sub>2</sub> , H ( <b>4e</b> )	0.80	4.2	7.0
<i>p</i> -NH <sub>2</sub> , <i>p</i> -NH <sub>2</sub> ( <b>4f</b> )	0.72	5.1	7.9
<i>p</i> -OH, <i>p</i> -OH ( <b>4g</b> )	0.75	4.9	7.8
<i>p</i> -CN, <i>p</i> -CN ( <b>4h</b> )	0.83	3.8	6.5
<i>p</i> -NO <sub>2</sub> , <i>p</i> -NO <sub>2</sub> ( <b>4i</b> )	0.83	3.7	6.2
<i>p</i> -NH <sub>2</sub> , <i>p</i> -NO <sub>2</sub> ( <b>4j</b> )	0.69	5.0	7.7
<i>p</i> -OH, <i>p</i> -CN ( <b>4k</b> )	0.76	4.6	7.4

<sup>a</sup>  $\Delta E_{ST}$  values were calculated as  $E_T - E_S$ , where  $E_T$  and  $E_S$  are the computed electronic energies at optimized geometries, with zero-point energies included. Thus, a positive sign indicates that the singlet is the ground state. <sup>b</sup> The corrected values,  $\Delta E_{ST}^{corr}$ , were obtained by scaling the singlet electronic energies, to account for the effects of spin contamination,<sup>20</sup> as described in the text. <sup>c</sup> Values of  $\langle S^2 \rangle_T$  were all in the range of 2.05–2.06.<sup>16</sup>

element of symmetry. The geometries of the stationary points and their UB3LYP electronic energies are available as Supporting Information.

The zero-point-inclusive, singlet–triplet energy differences ( $\Delta E_{ST}$ ) are given in Table 1 for diradicals **4a–k**. As expected, the better hyperconjugatively electron-accepting C–F bonds at C-2 in **4** give larger  $\Delta E_{ST}$  values than the C–OH bonds at C-2 in **5**. Although the values of  $\Delta E_{ST}$  computed for **5** are smaller in size, they vary with substituents in the same way as the  $\Delta E_{ST}$  values in **4**. Therefore, the values of  $\Delta E_{ST}$  for **5a–k** are not given in Table 1 but are available as Supporting Information.

In agreement with the experiments on **2a**,<sup>6</sup> **2b**,<sup>7</sup> and **3**,<sup>8</sup> the singlet is predicted to be the ground state of **4** and **5** for all the substituents that were investigated. The values of  $\Delta E_{ST}$  for **4** were found to be smaller at the fully optimized UB3LYP singlet and triplet geometries than at  $C_s$  or  $C_{2v}$  geometries, in which all the carbons were constrained to lie in the same plane. However, the difference in each case amounted to no more than 0.2 kcal/mol.<sup>15</sup>

**Effect of Spin Contamination on the “Singlet” UB3LYP Wave Functions.** Also given in Table 1 are the values of  $\langle S^2 \rangle$  for the unrestricted “singlet” wave functions for **4**.<sup>16</sup> The deviations of these  $\langle S^2 \rangle$  values from the value of  $\langle S^2 \rangle = 0$  for a pure singlet wave function show that there are substantial amounts of triplet spin contamination in the singlet UB3LYP wave functions. To the extent that the singlet UB3LYP wave functions for **4** are contaminated by the higher energy triplet wave functions, the UB3LYP values of  $\Delta E_{ST}$  in Table 1 are expected to be smaller than those that would be computed by multiconfigurational methods, which actually do give pure singlet wave functions with  $\langle S^2 \rangle = 0$ .

To assess the amounts by which the  $\Delta E_{ST}$  values for **4** are underestimated by the UB3LYP values in Table 1, we performed single-point (14/14)CASSCF and CASPT2<sup>17</sup> calculations of  $\Delta E_{ST}$  in **4a** at UB3LYP-optimized singlet and triplet geometries

(15) Therefore, for the sake of computational economy, calculations on **5** and **6** were performed at  $C_{2v}$  and  $C_s$  geometries that were constrained to have a plane of symmetry, and vibrational analyses were not performed.

(16) The  $\langle S^2 \rangle$  values for the UB3LYP triplet wave functions were all very close to the value of  $\langle S^2 \rangle = 2.0$  for a pure triplet. The individual  $\langle S^2 \rangle$  values for the UB3LYP triplet wave functions are available in the Supporting Information.

that were both constrained to have  $C_{2v}$  symmetry. In these calculations the 14  $\pi$  electrons were distributed among the 6 bonding, 2 nonbonding, and 6 antibonding  $\pi$  orbitals. These calculations were carried out with the MOLCAS package of ab initio programs.<sup>18</sup>

At the (14/14)CASSCF level of theory  $\Delta E_{ST} = 3.5$  kcal/mol was obtained for **4a**. This value is actually 1.0 kcal/mol smaller than the UB3LYP value that is computed when the optimized singlet and triplet geometries of this diradical are both constrained to have  $C_{2v}$  symmetry. However, when dynamic electron correlation was included<sup>19</sup> by performing (14/14)-CASPT2 calculations, the ionic terms in the CASSCF wave function (e.g., those represented by the hyperconjugated resonance structure for **4a**) were stabilized, and the singlet–triplet energy difference increased to  $\Delta E_{ST} = 6.4$  kcal/mol.

The UB3LYP value of  $\Delta E_{ST} = 4.5$  kcal/mol at the optimized  $C_{2v}$  singlet and triplet geometries for **4a** is about two-thirds the CASPT2 value, computed at these same geometries. As expected, the spin contamination in the singlet UB3LYP wave function does lead to the energy of the singlet state being overestimated, so that the size of  $\Delta E_{ST}$  is underestimated.

Yamaguchi, Houk, and co-workers have proposed that singlet electronic energies, computed from unrestricted wave functions, should be scaled to correct for spin contamination in the singlet.<sup>20</sup> After the singlet electronic energies are scaled, the singlet–triplet electronic energy difference ( $\Delta E_{ST}^{elec}$ ) becomes  $\Delta E_{ST}^{scaled} = \Delta E_{ST}^{elec} \langle S^2 \rangle_T / (\langle S^2 \rangle_T - \langle S^2 \rangle_S)$ . Adjustment of the  $\Delta E_{ST}^{scaled}$  values for zero-point energy differences gives the corrected values,  $\Delta E_{ST}^{corr}$ , shown in Table 1.

The value of  $\Delta E_{ST}^{corr} = 7.4$  kcal/mol that is obtained for **4a** is closer to the CASPT2 singlet–triplet splitting of 6.4 kcal/mol than is the uncorrected UB3LYP value of  $\Delta E_{ST} = 4.5$  kcal/mol. Therefore, the following discussion is based on the corrected energies. However, Table 1 shows that the differences between the calculated singlet–triplet splittings in **4a–k** are nearly the same, whether the corrected or uncorrected UB3LYP values of  $\Delta E_{ST}$  are used.

**Calculated Substituent Effects on  $\Delta E_{ST}$  in **4**.** The substituent effects in **4** result in zero-point-inclusive UB3LYP values of  $\Delta E_{ST}^{corr}$  that range, after correction, from highs of  $\Delta E_{ST}^{corr} = 7.9$  kcal/mol for the *p,p'*-diamino-substituted diradical (**4f**) and 7.8 kcal/mol for the *p,p'*-dihydroxy-substituted diradical (**4g**) to lows of  $\Delta E_{ST}^{corr} = 6.5$  kcal/mol for the *p,p'*-dicyano-substituted diradical (**4h**) and 6.2 kcal/mol for the *p,p'*-dinitro-substituted diradical (**4i**). The differences between  $\Delta E_{ST}^{corr}$  values range over only 1.7 kcal/mol, but the differences have significance. For example, the  $\pi$ -electron-donating amino and hydroxyl substituents give the largest values of  $\Delta E_{ST}^{corr}$ , and the  $\pi$ -electron-withdrawing cyano and nitro groups give values

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**Table 2.** Computed (UB3LYP/6-31G\*) Energy Changes (kcal/mol) for the Reactions in Eqs 1 and 4<sup>a</sup> in the Singlet<sup>b</sup> and Triplet States of **4** for Four Different Substituents

Y, Z	singlet	triplet	Y, Z	singlet	triplet
<i>p</i> -NH <sub>2</sub> , H	-0.5	-0.3	<i>p</i> -NO <sub>2</sub> , H	-1.4	-1.0
<i>p</i> -OH, H	-0.2	-0.1	<i>p</i> -NH <sub>2</sub> , <i>p</i> -NO <sub>2</sub>	-3.8	-2.6
<i>p</i> -CN, H	-0.9	-0.7	<i>p</i> -OH, <i>p</i> -CN	-1.5	-1.1

<sup>a</sup> Eq 4 is the same as eq 1, when Z = H. <sup>b</sup> The energy changes for the singlet were obtained by scaling the singlet electronic energies, to account for the effects of spin contamination.<sup>20</sup> However, when the unscaled singlet energies were used, the energy changes were the same as those in the table to within 0.1 kcal/mol.

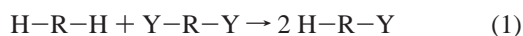
that are even smaller than that of  $\Delta E_{ST}^{corr} = 7.4$  kcal/mol for diradical **4a** with unsubstituted phenyl groups.

As shown in Table 1, there is in general an inverse correlation between both the  $\Delta E_{ST}$  and  $\Delta E_{ST}^{corr}$  values and the  $\langle S^2 \rangle$  values. This inverse correlation is understandable because the largest values of  $\Delta E_{ST}$  and  $\Delta E_{ST}^{corr}$  are found for those diradicals with substituents that most strongly lift the near degeneracy of the two nonbonding orbitals. The larger the gap between these two orbitals, the more closely the value of  $\langle S^2 \rangle$  for the UB3LYP singlet wave function approaches that of  $\langle S^2 \rangle = 0$  for a pure singlet.

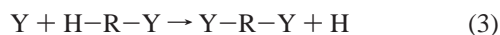
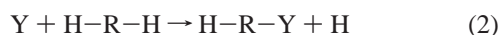
Given the results in Table 1 for the symmetrically substituted diradicals, it is very surprising that the third highest value of  $\Delta E_{ST}^{corr} = 7.7$  kcal/mol in Table 1 and the lowest value of  $\langle S^2 \rangle$  are those for the unsymmetrically substituted diradical with one *p*-amino and one *p*-nitro substituent (**4j**). On the basis of the average of the values of  $\Delta E_{ST}^{corr} = 7.9$  and 6.2 kcal/mol, respectively, for **4f** and **4i**,  $\Delta E_{ST}^{corr} = 7.1$  kcal/mol would have been expected for **4j**.

The higher-than-expected value of  $\Delta E_{ST}^{corr} = 7.7$  kcal/mol for **4j** shows that the effects of the *p*-amino and the *p*-nitro substituent on  $\Delta E_{ST}$  in this diradical are cooperative, rather than competitive. However, as discussed in the next section, the effects of the substituents on  $\Delta E_{ST}$  in the symmetrically substituted diradicals deviate from additivity in a way that shows these substituent effects are competitive.

**Substituent Effects in Symmetrically Substituted 4.** One way to determine whether the effects of two identical substituents, Y, on a molecule, R, are cooperative or competitive is to calculate the energy change for the disproportionation reaction

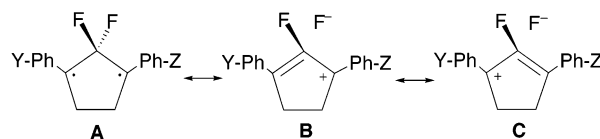


The energy of the reaction in eq 1 is equal to the difference between the energy changes for the hypothetical substitution reactions in eqs 2 and 3.



If the effects of the substituents in Y-R-Y are cooperative, the reaction in eq 3 will always be more energetically favorable than the reaction in eq 2, so the reaction in eq 1 will be endothermic. Conversely, if the effects of the substituents in Y-R-Y are competitive, then the reaction in eq 2 will be more energetically favorable than the reaction in eq 3, so the reaction in eq 1 will be exothermic.

Table 2 tabulates the energies of the reaction in eq 1 for both the singlet and triplet states of diradical **4** for four different *para* substituents. Reaction 1 is exothermic for both electronic states



**Figure 1.** Three resonance structures for 1,3-diaryl derivatives of 2,2-difluorocyclopentane-1,3-diyl (**4**). Only structure **A** contributes to the triplet state, but all three structures contribute to the singlet state. For Y = Z structures **B** and **C** must contribute equally, but for Y ≠ Z the resonance structure that allows the positive charge to be stabilized by the more electron-donating substituent will contribute more.

of **4** for all of the substituents. Therefore, in both states of **4** the substituent effects are competitive for Y = Z. However, for all four substituents, the reaction in eq 1 is slightly more exothermic for the singlet state than for the triplet state. Therefore, the substituent effects on  $\Delta E_{ST}$  in **4** are competitive for Y = Z.

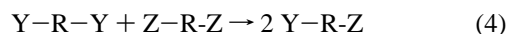
The consequences of this fact are shown in Table 1. For  $\pi$ -electron-donating *para* substituents (e.g., Y = NH<sub>2</sub> and OH), which increase the size of  $\Delta E_{ST}$ , relative to that in the diradical without any *p*-phenyl substituents (**4a**), the first substituent increases the size of  $\Delta E_{ST}$  by slightly more than the second substituent does. For  $\pi$ -electron-withdrawing *para* substituents (e.g., Y = NO<sub>2</sub> and CN), which decrease the size of  $\Delta E_{ST}$ , relative to that in **4a**, the first substituent decreases the size of  $\Delta E_{ST}$  by slightly less than the second substituent does.

**Substituent Effects in Triplet 4.** For understanding why the reaction in eq 1 is exothermic for the triplet states, but slightly more exothermic for the singlet states of diradicals **4a–k**, the three resonance structures shown in Figure 1 are helpful. In the triplet state of **4**, there is some delocalization of the electron in the in-phase combination of 2*p*- $\pi$  AOs at C-1 and C-3 into the low-lying C-F  $\sigma^*$  orbital with the correct symmetry. However, for the sake of simplicity, it is convenient to represent the triplet by resonance structure **A**. Resonance structures **B** and **C** do not contribute to the triplet but only to the singlet, because in these two structures all the electrons are paired.

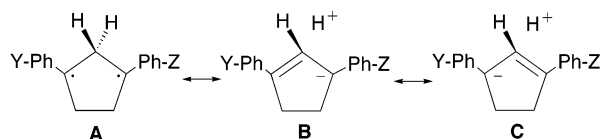
A *para* substituent, Y, in structure **A** can stabilize the unpaired electron at C-1, either by donating a  $\pi$  electron through the benzene ring and into the singly occupied 2*p*- $\pi$  AO at this carbon or by delocalizing the unpaired electron in this AO into a low-lying antibonding  $\pi$  orbital. Consequently,  $\pi$ -electron-donating substituents, such as Y = NH<sub>2</sub> and OH, will result in a net negative charge in the 2*p*- $\pi$  AO at C-1, whereas  $\pi$ -electron-withdrawing substituents, such as Y = NO<sub>2</sub> and CN, will result in a net positive charge in this AO.

If **4** is symmetrically disubstituted (Y = Z ≠ H), the identical charges at C-1 and C-3 will result in Coulombic repulsion between these carbons that is absent when one phenyl group is unsubstituted (Z = H). This repulsion makes the disproportionation reaction in eq 1 energetically favorable, because this reaction places the substituents, Y, in two triplet diradicals, thus relieving the Coulombic repulsion that they engender when they are both in the same triplet diradical.

If Y is a  $\pi$ -electron-donating substituent and Z is a  $\pi$ -electron-withdrawing substituent, then for triplet **4** the disproportionation reaction in eq 4 should be even more exothermic than the



disproportion reaction in eq 1. Not only does the reaction in eq 4 relieve the Coulombic repulsion, engendered by the identical



**Figure 2.** Three resonance structures for 1,3-diphenyl derivatives of cyclopentane-1,3-diyl (**6**). Only structure **A** contributes to the triplet state, but all three structures contribute to the singlet state. However, the contributions of structures **B** and **C** to the singlet state are so small that the triplet is both calculated and found<sup>2</sup> to be the ground state of **6a**.

**Table 3.** Computed (UB3LYP/6-31G\*) Energy Changes (kcal/mol) for the Reactions in Eqs 1 and 4<sup>a</sup> in the Singlet and Triplet States of **6** for Four Different Substituents

Y, Z	singlet	triplet	Y, Z	singlet	triplet
<i>p</i> -NH <sub>2</sub> , H	−0.3	−0.3	<i>p</i> -NO <sub>2</sub> , H	−1.1	−1.1
<i>p</i> -OH, H	0.0	0.0	<i>p</i> -NH <sub>2</sub> , <i>p</i> -NO <sub>2</sub>	−2.8	−2.7
<i>p</i> -CN, H	−0.7	−0.7			

<sup>a</sup> Eq 4 is the same as eq 1, when Z = H.

**Table 4.** UB3LYP/6-31G\* Singlet–Triplet Energy Differences ( $\Delta E_{ST}$ )<sup>a,b</sup> in Diradicals **6a–j** (kcal/mol) and the  $\langle S^2 \rangle$  Values for the Singlet States of These Diradicals

Y, Z	$\langle S^2 \rangle$	$\Delta E_{ST}$	Y, Z	$\langle S^2 \rangle$	$\Delta E_{ST}$
H, H ( <b>6a</b> )	1.05	−0.2	<i>p</i> -NH <sub>2</sub> , <i>p</i> -NH <sub>2</sub> ( <b>6f</b> )	1.04	−0.1
<i>p</i> -NH <sub>2</sub> , H ( <b>6b</b> )	1.04	−0.1	<i>p</i> -OH, <i>p</i> -OH ( <b>6g</b> )	1.04	−0.1
<i>p</i> -OH, H ( <b>6c</b> )	1.04	−0.2	<i>p</i> -CN, <i>p</i> -CN ( <b>6h</b> )	1.06	−0.2
<i>p</i> -CN, H ( <b>6d</b> )	1.05	−0.2	<i>p</i> -NO <sub>2</sub> , <i>p</i> -NO <sub>2</sub> ( <b>6i</b> )	1.05	−0.3
<i>p</i> -NO <sub>2</sub> , H ( <b>6e</b> )	1.05	−0.2	<i>p</i> -NH <sub>2</sub> , <i>p</i> -NO <sub>2</sub> ( <b>6j</b> )	1.03	−0.1

<sup>a</sup>  $\Delta E_{ST}$  values are calculated as  $E_T - E_S$ , where  $E_T$  and  $E_S$  are the computed electronic energies at optimized geometries with  $C_{2v}$  ( $Y = Z$ ) and  $C_s$  ( $Y \neq Z$ ) symmetries. Thus, the negative sign indicates that the triplet is the ground state. <sup>b</sup> Because  $\langle S^2 \rangle \approx 1.0$  in **6**, the singlet is nearly a 1:1 mixture of the  $\langle S^2 \rangle = 0$  singlet and the triplet. Consequently, the values of  $\Delta E_{ST}^{\text{corr}}$  are about twice the uncorrected values of  $\Delta E_{ST}$  in this table.

substituents in both Y–R–Y and Z–R–Z, but this reaction also forms two molecules of Y–R–Z, in which the opposite charges engendered by Y and Z should stabilize each other by their Coulombic attraction. In fact, Table 2 does show that in triplet **4**, with Y = NH<sub>2</sub> and Z = NO<sub>2</sub>, the reaction in eq 4 is much more exothermic than the reaction in eq 1 with Y = NH<sub>2</sub> or with Y = NO<sub>2</sub>. Indeed, the reaction in eq 4 is twice as exothermic as the sum of the energies for the reaction in eq 1 with this pair of substituents. Similarly, in triplet **4**, with Y = OH and Z = CN, the reaction in eq 4 is 40% more exothermic than the sum of the energy changes for the reaction in eq 1 with Y = OH and with Y = CN.

**Substituent Effects in 6.** To the extent that structure **A** in Figures 1 and 2 satisfactorily describes the triplet state of, respectively, fluorocarbon diradical **4** and hydrocarbon diradical **6**, the substituent effects on the exothermicity of the reaction in eq 1 should be the same for the triplet state of both diradicals. Comparison of the results contained in Tables 2 and 3 confirms that our UB3LYP calculations do, in fact, find this to be the case.

Table 3 also shows that the *para* substituent effects in **6** on the energy of the reaction in eq 1 are nearly the same for the singlet as for the triplet state. Therefore, in contrast to the values of  $\Delta E_{ST}$  for diradical **4** in Table 1, the values of  $\Delta E_{ST}$  for diradical **6** in Table 4 are nearly independent of the nature of *para* substituents that are attached to the phenyl groups.

The reason for this difference between **4** and **6** is the same as the reason for the difference between their predicted ground states. Unlike the geminal C–F bonds at C-2 of **4**, which are

strong, hyperconjugative,  $\pi$  electron acceptors, the C–H bonds at C-2 of **6** are very weak, hyperconjugative,  $\pi$  electron donors.<sup>4,21</sup> The C–H bonds at C-2 of cyclopentane-1,3-diyls are, in fact, such weak electron donors that, as already noted, calculations predict and experiments have found a triplet ground state for **1a**<sup>1,3</sup> and **1b**.<sup>2</sup> In addition, consistent with the results of our calculations on **6**, experiments have found that the triplet is also the ground state of a derivative of 1,3-diphenylcyclopentane-1,3-diyl for over 30 different *meta* and *para* substituents.<sup>22</sup>

Explained in terms of the resonance structures, the difference between the ground states of diradicals **4** and **6** is due to the fact that structures **B** and **C** in Figure 1 make a substantial contribution to the singlet state of **4**, but the analogous pair of structures in Figure 2 make a much smaller contribution to the singlet state of **6**. To the extent that structure **A** in Figure 2 adequately describes not only the triplet but also the singlet state of **6**, both states would be expected to be stabilized similarly by *para* substituents. Thus, the small contribution of structures **B** and **C** to the singlet state of **6** is responsible not only for the triplet ground state of these diradicals but also for the predicted insensitivity of  $\Delta E_{ST}$  in **6** to *para* substituents.

**Substituent Effects in Singlet 4.** It is clearly the importance of resonance structures **B** and **C** in Figure 1 for singlet **4** that makes the singlet the ground state of this diradical.<sup>23</sup> It is also the importance of these resonance structures that makes the size of  $\Delta E_{ST}$  in **4** substituent-dependent.

For Y = Z, symmetry demands that structures **B** and **C** in Figure 1 contribute equally to singlet **4**. However, for Y  $\neq$  Z, the resonance structure in which the positive charge is stabilized by the more  $\pi$ -electron-donating phenyl group should make the greater contribution. Consequently, for singlet **4** the reaction in eq 4 should be more exothermic, the more different the substituents Y and Z are in their ability to stabilize a positive charge. The results in Table 2 confirm that this is, indeed, the case.

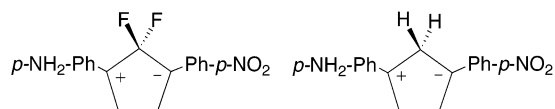
To the extent that structures **B** and **C** contribute to the lowest singlet state of **4**, the energies of the reaction in eq 4 should be more exothermic for the singlet states than for the triplet states of **4**. The results in Table 2 again show that this is, indeed, the case. For example, for Y = NH<sub>2</sub> and Z = NO<sub>2</sub> the exothermicity of the disproportionation reaction in eq 4 is nearly 50% larger for the singlet than for the triplet.

If the energy change for the reaction in eq 4 for the singlet ( $\Delta E_S$ ) is subtracted from that for the triplet ( $\Delta E_T$ ), the difference must be equal to twice the difference between  $\Delta E_{ST}$  in Y–R–Z and the average of  $\Delta E_{ST}$  in Y–R–Y and Z–R–Z.

$$\Delta E_T - \Delta E_S = 2\{\Delta E_{ST}(\text{Y-R-Z}) - [\Delta E_{ST}(\text{Y-R-Y}) + \Delta E_{ST}(\text{Z-R-Z})]/2\} \quad (5)$$

For example, using the results in Tables 1 and 2 for Y = NH<sub>2</sub> and Z = NO<sub>2</sub>, it is easy to confirm that the difference of 1.2 kcal/mol between the energy changes of the reaction in eq 4 for the singlet and triplet states of **4f**, **4i**, and **4j** is equal (within

- (21) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689. In fact, the effect of the substituents on  $\Delta E_{ST}$  in Table 4, although very small, makes it appear that the hydrogens are acting as weak electron acceptors in diradical **6**.  
 (22) Kita, F.; Adam, W.; Jordan, P.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc.* **1999**, *121*, 9265 and references therein.  
 (23) Review: Borden, W. T. *Chem. Commun.* **1998**, 1919.



**Figure 3.** Ionic resonance structures that might contribute to the singlet states of heterosymmetric diradicals **4j** and **6j**, respectively.

0.1 kcal/mol, due to rounding of energy differences) to twice the difference between  $\Delta E_{ST}$  in **4j** and the average of  $\Delta E_{ST}$  in **4f** and **4i**.

$\Delta E_{ST}$  in **4j** is 0.6 kcal/mol larger than the average of  $\Delta E_{ST}$  in **4f** and **4i**, because in singlet **4j** the positive charge in resonance structures **B** and **C** in Figure 2 can localize at the ring carbon to which the *p*-amino-substituted phenyl group is attached, and the pair of electrons in the  $\pi$  bond can be preferentially conjugated with the *p*-nitro-substituted phenyl group. In contrast, although in **4f** the positive charge in **B** and **C** appears only at ring carbons to which the *p*-amino-substituted phenyl group is attached, in **4i** the positive charge appears only at ring carbons to which the *p*-nitro-substituted phenyl group is attached. Thus, on average, in **4f** and **4i** the positive charge in **B** and **C** is distributed equally between the two types of substituted ring carbons, whereas in **4j** the positive charge can be more localized at the ring carbon to which the *p*-amino-substituted phenyl group is attached.<sup>24</sup>

Another possible explanation for the large value of  $\Delta E_{ST}$  in **4j** is that ionic structures, such as that shown in Figure 3, can contribute to the ground states of heterosymmetric diradicals.<sup>25</sup> Indeed, such a contribution was proposed by Abe, Adam, and co-workers to explain the effect of a methoxyl substituent on one phenyl ring and a cyano substituent on the other on extending the lifetime of diradical **3f**.<sup>8</sup>

However, if such a contribution were important, it should lead to a large value of  $\Delta E_{ST}$ , not only in fluorocarbon diradical **4j** but also in hydrocarbon diradical **6j**. Table 4 shows clearly that this is not the case for **6j**. Therefore, it seems unlikely that resonance structures, such as those shown in Figure 3, contribute significantly to either **4j** or **6j**. Consequently, we conclude that the large value of  $\Delta E_{ST}$  in **4j** may be understood as having its origin in a strong contribution to the lowest singlet state from the energetically favorable resonance structure **C** in Figure 1 with  $Y = \text{NH}_2$  and  $Z = \text{NO}_2$ .

## Conclusions

Our UB3LYP calculations confirm that, as expected from resonance structures **B** and **C** in Figure 1, a pair of  $\pi$ -electron-donating *para* substituents stabilize the lowest singlet state of diradical **4** and thus provide larger values of  $\Delta E_{ST}$  for **4** than a

pair of  $\pi$ -electron-accepting *para* substituents.<sup>26a</sup> Our computational results, confirming the stabilization of the lowest singlet state of **4** by  $\pi$ -electron-donating *para* substituents, are consistent with the lifetimes of singlet diradicals **3a–f**, measured by Abe, Adam, and co-workers.<sup>8</sup>

Our calculations predict a large singlet–triplet energy difference, not only in **4f**, where both *para* substituents are  $\pi$ -electron-donating amino groups, but also in **4j**, where one *para* substituent is amino but the other is a  $\pi$ -electron-accepting nitro group. This rather unexpected finding is not due to a contribution from the resonance structure shown in Figure 3 for **4j**. If this structure were important in **4j**, it should be equally important in **6j**, but Table 4 shows that  $\Delta E_{ST}$  in **6j** is very close to that in **6a**, which lacks any *para* substituents.

Instead, we attribute the large value of  $\Delta E_{ST}$  in **4j** to the dominance in the singlet state of resonance structure **C** over **B** for  $Y = \text{NH}_2$  and  $Z = \text{NO}_2$  in Figure 1.<sup>26b</sup> The dominance of structure **C** makes the UB3LYP value of  $\Delta E_{ST}^{\text{corr}} = 7.7$  kcal/mol in this diradical almost as large as that of  $\Delta E_{ST}^{\text{corr}} = 7.9$  kcal/mol in **4f**, despite the fact that in the latter diradical the positive charge in structures **B** and **C** appears at ring carbons that are both substituted with  $\pi$ -electron-donating *p*-aminophenyl groups.

In contrast to the case in fluorocarbon diradical **4**, our calculations predict both a triplet ground state and very small substituent effects on  $\Delta E_{ST}$  in hydrocarbon diradical **6**. Both of these differences between **4** and **6** can be explained by the greater strength of the C–F hyperconjugative interactions in **4**, compared to the C–H hyperconjugative interactions in **6**.<sup>21</sup>

**Acknowledgment.** We thank the National Science Foundation for support of this research at the University of Washington.

**Supporting Information Available:** Optimized UB3LYP/6-31G\* geometries and energies of the singlet and triplet states of diradicals **4–6** (a–k). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0355067

(24) Thus, the unexpectedly large value of  $\Delta E_{ST}$  in **4j**, relative to the average of the values in **4f** and **4i**, can be attributed to the same type of effect that almost always makes the reaction  $A_2 + B_2 \rightarrow 2AB$  exothermic. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 3.

(25) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(26) (a) The effects of the substituents on  $\Delta E_{ST}$  in **4** can also be explained in terms of the effects that the substituents have on the energies of what are in the singlet the HOMO and the LUMO. In the triplet one electron is excited from the HOMO to the LUMO, so the relative energies of these two orbitals modulate the size of  $\Delta E_{ST}$ . The LUMO has a node at C2; consequently, it has larger coefficients at C1 and C3 than the HOMO, which mixes with the orbitals of the C–F bonds at C2. Therefore, the LUMO is more affected than the HOMO by substituents on the phenyl groups that are attached to these two carbons. Substituents that are  $\pi$  electron donors raise the energy of the LUMO more than that of the HOMO, thus increasing the size of  $\Delta E_{ST}$ . Substituents that are  $\pi$  electron acceptors lower the energy of the LUMO more than that of the HOMO, thus decreasing the size of  $\Delta E_{ST}$ . (b) Unsymmetrical phenyl substitution allows the HOMO and the LUMO of the symmetrically substituted diradicals to mix. This mixing lowers the energy of the HOMO and raises the energy of the LUMO, thus increasing the size of  $\Delta E_{ST}$ . The mixing is strongest when the substituents differ most in their  $\pi$ -electron-donating and -accepting abilities. This is why the energy difference in eq 5 is always positive and is largest when one substituent is a strong  $\pi$  electron donor and the other is a strong  $\pi$  electron acceptor.