

## Why Does Perfluorination Render Bicyclo[2.2.0]hex-1(4)-ene Stable toward Dimerization? Calculations Provide the Answers

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**Abstract:** B3LYP calculations with two different basis sets have been performed to understand why bicyclo[2.2.0]hex-1(4)-ene (**1a**) undergoes dimerization with  $\Delta H^\ddagger = 11.5$  kcal/mol, but dimerization of perfluorobicyclo[2.2.0]hex-1(4)-ene (**1b**) has never been observed. The former reaction is computed to be exothermic by 37.2 kcal/mol, whereas the latter is calculated to be endothermic by 7.4 kcal/mol. The 44.6 kcal/mol difference between the enthalpies of these two reactions can be dissected into contributions of 24.5 kcal/mol for the difference between the enthalpies for forming diradical intermediates **2a** and **2b** and 20.1 kcal/mol for cyclization of **2a** and **2b** to, respectively, **3a** and **3b**. The latter enthalpy difference is largely attributable to repulsions between the *endo*-fluorines in the dimer, although the *exo*-fluorines also are found to contribute. The former enthalpy difference is attributable to the difference between the dissociation enthalpies of the  $\pi$  bonds in **1a** and **1b**, which is shown to amount to  $16 \pm 1$  kcal/mol. About 25% of the stronger  $\pi$  bond in fluoroalkene **1b** is found to be due to hyperconjugation of the eight C–F bonds in **1b** with the filled  $\pi$  orbital. However, the major contributor to the stronger  $\pi$  bond in **1b** is shown to be the unfavorable interaction that results when a pyramidalized radical center is syn to a C–F bond. Both of these effects, which contribute to the greater strength of the  $\pi$  bond in **1b**, relative to that in **1a**, are analyzed and discussed.

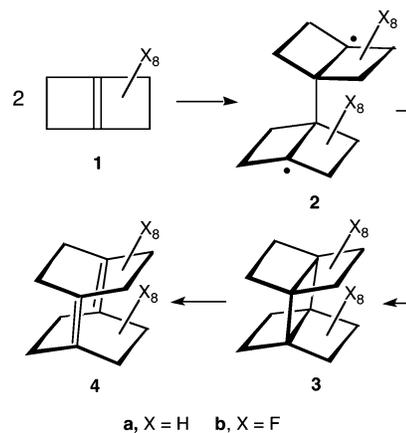
### Introduction

Bicyclo[2.2.0]hex-1(4)-ene (**1a**) has been generated and studied by Wiberg and co-workers.<sup>1</sup> The unusual bonding in the  $\sigma$  skeleton of **1a** results in a large strain energy,<sup>2</sup> which makes **1a** highly reactive. In fact, **1a** undergoes dimerization to **4a**, presumably via the mechanism in Scheme 1, with an enthalpy of activation of only  $\Delta H^\ddagger = 11.5$  kcal/mol.<sup>1</sup>

The very low enthalpy of activation for dimerization is indicative of the ease of breaking the  $\pi$  bond in **1a**. In the absence of a  $\pi$  bond between C1 and C4, these carbons can pyramidalize,<sup>3</sup> and this rehybridization relieves a large amount of the strain in the  $\sigma$  system of **1**.<sup>2</sup>

Perfluorination frequently has a dramatic effect on the reactivities of hydrocarbons,<sup>4</sup> and Lemal and co-workers have found that octafluorobicyclo[2.2.0]hex-1(4)-ene (**1b**) is much less reactive than **1a** toward dimerization.<sup>5</sup> Even upon prolonged heating, **1b** does not dimerize but, instead, undergoes electrocyclic ring opening.<sup>6</sup> The stability of **1b** toward dimerization has allowed its structure to be determined by electron diffrac-

Scheme 1



tion,<sup>7</sup> its Diels–Alder reactivity with aromatics to be explored,<sup>8</sup> and its reaction with alkenes to be used as an entry into the [2.2.2]propellane ring system.<sup>9</sup>

Why does perfluorination of **1a** render **1b** stable toward dimerization? To answer this question, we have performed density functional calculations. We find the much greater stability of **1b** is largely due to a much smaller release of strain

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(2) Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679. (b) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 197.

(3) For reviews of alkenes with pyramidalized equilibrium geometries, see: (a) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095. (b) Vázquez, S.; Camps, P. *Tetrahedron* **2005**, *61*, 55147.

(4) For a recent review, see: Lemal, D. M. *J. Org. Chem.* **2004**, *69*, 1.

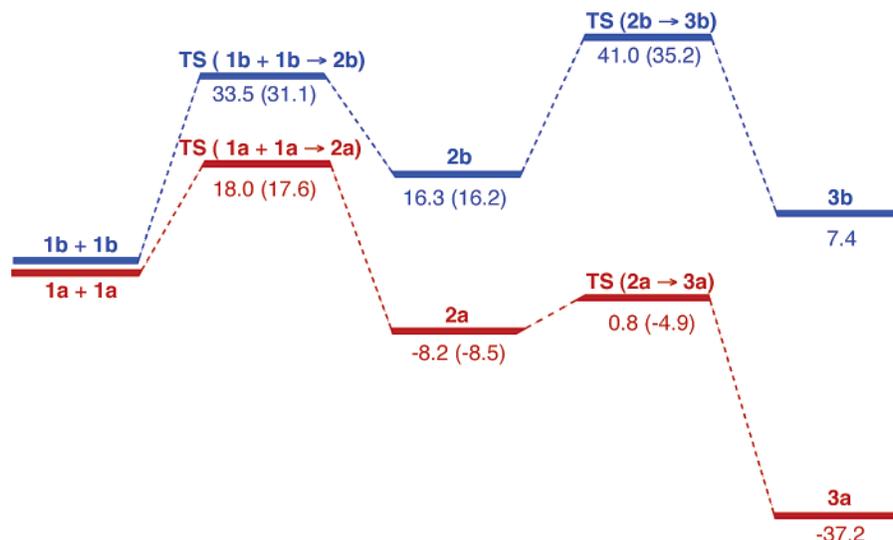
(5) Zhang, Y.; Smith, J.; Lemal, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 9454.

(6) Lemal, D. M. Dartmouth College, Private communication, 2005.

(7) Richardson, A. D.; Hedberg, K.; Junk, C. P.; Lemal, D. M. *J. Phys. Chem. A* **2003**, *107*, 3064.

(8) He, Y.; Junk, C. P.; Lemal, D. M. *Org. Lett.* **2003**, *5*, 2135.

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**Figure 1.** Enthalpy changes for dimerization of hydrocarbon **1a** and fluorocarbon **1b**. The enthalpies, relative to the reactants, are given in kcal/mol. The enthalpies, corrected for spin contamination,<sup>14</sup> are given in parentheses.

on breaking the  $\pi$  bond and pyramidalizing the doubly bonded carbons in fluorocarbon **1b** than in the hydrocarbon **1a**. We have investigated the origin of this difference between **1b** and **1a**, and our findings are discussed in this paper.

### Computational Methodology

DFT calculations were performed using Becke's three-parameter functional<sup>10</sup> and the correlation functional of Lee, Yang, and Parr.<sup>11</sup> B3LYP geometries were optimized, and transition structures were located with the 6-31G\* basis set.<sup>12</sup> Single-point energies were obtained with the 6-311+G (2df,2p) basis set.<sup>13</sup> Zero-point and thermal contributions to enthalpy differences at 298 K were obtained from B3LYP/6-31G\* vibrational analyses. For spin-contaminated "singlet" wave functions, the  $\langle S^2 \rangle$  values and (U)B3LYP triplet energies were used to estimate the energies of pure singlet wave functions.<sup>14</sup> All of the calculations were performed with the Gaussian 03 package of electronic structure programs.<sup>15</sup>

### Results and Discussion

**Dimerization of 1a and 1b.** The results of our (U)B3LYP calculations on the dimerization of **1a** and **1b** are shown graphically in Figure 1.

The enthalpy of the first transition structure (TS) in the dimerization of **1a** is calculated to be ca. 20 kcal/mol higher than that of the second. Although the entropy of the second TS is computed to be smaller than that of the first, at 300 K the difference of  $\Delta\Delta S = -5.1$  eu contributes only 1.5 kcal/mol to reducing the free-energy difference between the two TSs. Therefore, passage over the first TS in the dimerization of **1a** is predicted by our calculations to be rate determining.

The (U)B3LYP activation enthalpy of  $\Delta H^\ddagger = 18.0$  (17.6) kcal/mol for dimerization of **1a** is about 6 kcal/mol higher than the experimental value of  $\Delta H^\ddagger = 11.5$  kcal/mol, measured by

Wiberg and co-workers.<sup>1</sup> The change in the value of  $\langle S^2 \rangle$  for the (U)B3LYP wave function, from  $S^2 = 0$  for two molecules of **1a** to  $\langle S^2 \rangle = 1.00$  for diradical intermediate **2a**, may lead to the enthalpy of the transition structure in the dimerization reaction being overestimated by our calculations.

The value of  $\langle S^2 \rangle = 1.00$  for diradical intermediate **2a** means that its (U)B3LYP wave function is a 1:1 mixture of pure singlet and triplet states. At the geometry of **2a**, the triplet state is calculated to be 0.3 kcal/mol higher in energy than the spin-contaminated "singlet" wave function. Therefore, the enthalpy of the pure singlet wave function for singlet **2a**, uncontaminated by the triplet, is estimated<sup>14</sup> to be 8.5 kcal/mol lower than the enthalpy of **1a**. The computational finding that diradical intermediate **2a**, formed in the first step of the dimerization reaction, has a substantially lower enthalpy than two molecules of closed-shell alkene **1a** is indicative of the highly strained nature of **1a**.

Figure 1 shows that the first step in the dimerization of **1b** to **2b** not only has a 15.5 (13.5) kcal/mol higher activation enthalpy than that in the dimerization of **1a** to **2a** but is also endothermic by  $\Delta H = 16.3$  (16.2) kcal/mol, rather than being exothermic by  $\Delta H = -8.2$  (-8.5) kcal/mol. Thus, the calculated difference between the enthalpies for forming the diradical intermediates in the dimerization reactions amounts to  $\Delta\Delta H = 24.5$  (24.7) kcal/mol.

In addition, ring closure of **2b** to **3b** is calculated to be less exothermic than ring closure of **2a** to **3a** by  $\Delta\Delta H = 20.1$  (19.9) kcal/mol. Thus, whereas dimerization of bicyclo[2.2.0]hex-1(4)-ene (**1a**) to pentacyclododecane **3a** is computed to be overall exothermic by 37.2 kcal/mol, dimerization of octafluorobicyclo[2.2.0]hex-1(4)-ene (**1b**) to perfluoropentacyclododecane **3b** is actually computed to be endothermic by 7.4 kcal/mol.<sup>16</sup> Because dimerization of **1b** is not only enthalpically but also entropically unfavorable, our computational results are wholly consistent with the observation by Lemal and co-workers that **1b** does not undergo dimerization.<sup>6</sup>

(10) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(11) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

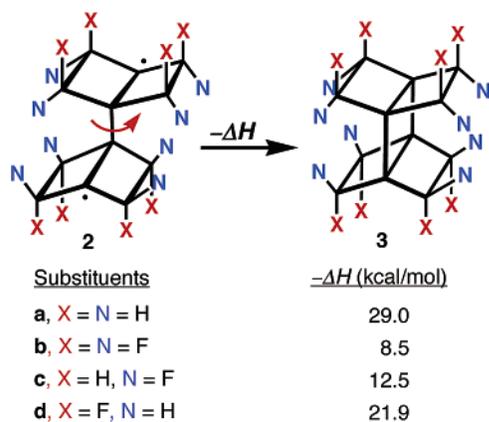
(12) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

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(14) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537.

(15) Frisch, M. J. et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford CT, 2004.

(16) Use of the Boys–Bernardi counterpoise correction for the basis set superposition error (Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.) decreases the exothermicity of the dimerization of **1a** to 36.0 kcal/mol but increases the endothermicity of the dimerization of **1b** to 11.7 kcal/mol.



**Figure 2.** Exothermicity of cyclization of diradicals **2a–d** to propellanes **3a–d**.

Of the 44.6 kcal/mol calculated difference between the overall enthalpies of dimerization of **1a** and **1b**, about 55% is due to the 24.5 (24.7) kcal/mol difference between the enthalpies of forming diradicals **2a** and **2b** and about 45% is due to the 20.1 (19.9) kcal/mol difference between the enthalpies of ring closure to, respectively, **3a** and **3b**. The difference between the calculated enthalpies of ring closure of **2a** and **2b** is easiest to understand, so we will begin by discussing its origin. For the sake of simplicity, the discussions in the next section and in the sections that follow it are based on enthalpy differences that are uncorrected for spin contamination.

**Difference between the Enthalpies of Ring Closure of 2a and 2b.** The simplest explanation of the 20.1 kcal/mol difference between the enthalpies of ring closure of diradicals **2a** and **2b** is that repulsions between the endo substituents in the cyclization products are much more severe for the fluorines in **3b** than for the hydrogens in **3a**. To test this hypothesis, we performed calculations on the enthalpies of cyclization of octafluoro diradical **2c**, in which all eight of the fluorines are endo, and octafluoro diradical **2d**, in which all eight of the fluorines are exo.

If the difference between the cyclization enthalpies of **2a** and **2b** is largely due to the *endo*-fluorines in cyclization product **3b**, then substituting fluorines for just the *endo*-hydrogens in **2a**, to form *endo*-octafluoro diradical **2c**, should have an effect on reducing the exothermicity of cyclization that is comparable to the effect of substituting fluorines for the *endo*-hydrogens in *exo*-octafluoro diradical **2d**, to give perfluoro diradical **2b**. The results provided in Figure 2 show that this is, in fact, the case. Cyclization of **2c** to **3c** is computed to be less exothermic than cyclization of **2a** to **3a** by 16.5 kcal/mol, and cyclization of **2b** to **3b** is computed to be less exothermic than cyclization of **2d** to **3d** by 13.4 kcal/mol.

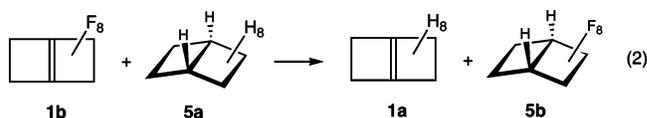
Substitution of fluorines for *exo*-hydrogens is computed to have a much smaller effect on reducing the exothermicity of cyclization of **2** to **3**. Substitution of the *exo*-hydrogens in **2a** by fluorines to give **2d** reduces the exothermicity of cyclization by 7.1 kcal/mol, and making the same substitution in **2c** to give **2b** also reduces the exothermicity, but by only 4.0 kcal/mol. Although the large effect of *endo*-fluorine substitution on reducing the exothermicity of cyclization almost certainly involves the destabilization of **3b** and **3c**, relative to **3a** and **3d**, it is less obvious whether the much smaller effect of *exo*-fluorine substitution is due to stabilization of the radical centers in **2b**

and **2d**, to destabilization of propellanes **3b** and **3d**, or to some combination of these two effects.<sup>17</sup>

**Difference between the Enthalpies for Forming Diradicals 2a and 2b.** As already noted, the difference between the enthalpies for forming diradicals **2a** and **2b** from, respectively, **1a** and **1b** is about 20% larger than the difference between the enthalpies for cyclizing **2a** and **2b** to, respectively, **3a** and **3b**. The difference,  $\Delta\Delta H = 24.5$  kcal/mol, between the enthalpies for forming diradicals **2a** and **2b** in the dimerization reactions of **1a** and **1b** can be divided into the difference between the dissociation enthalpies of the  $\pi$  bonds in **1a** and **1b** that are broken and the differences between the negatives of the dissociation enthalpies of the  $\sigma$  bonds in **2a** and **2b** that are made.

$$\Delta\Delta H = 2\Delta BDE^{\pi}(\mathbf{1b} - \mathbf{1a}) - BDE^{\sigma}(\mathbf{2b} - \mathbf{2a}) \quad (1)$$

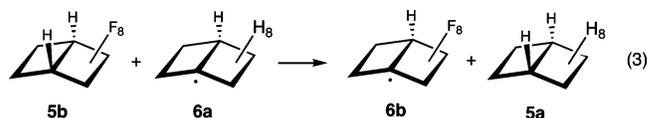
An experimental approach to obtaining the difference between the  $\pi$  BDEs of **1a** and **1b** might be to measure the difference between the heats of hydrogenation of the two alkenes. We have computed this difference, which is equal to the enthalpy of the isodesmic reaction in eq 2, for which we obtain  $\Delta\Delta H(\text{H}_2) = 1.0$  kcal/mol.



One might, therefore, conclude that **1b** has a  $\pi$  BDE that is greater than that of **1a** by only 1.0 kcal/mol. It would then follow that all but 2.0 kcal/mol of the 24.5 kcal/mol difference between the dimerization enthalpies of **1a** and **1b** must reside in a much weaker  $\sigma$  bond in **2b** than in **2a**. However, this conclusion would not only be surprising, but it would also be incorrect.

As we have pointed out for other hydrogenation reactions,<sup>18</sup> the difference between the heats of hydrogenation of two  $\pi$  bonds involves not only the difference between the strengths of the  $\pi$  bonds that are broken but also the difference between the strengths of the two pairs of C–H bonds that are formed. Consequently, to obtain the difference between the  $\pi$  BDEs of **1a** and **1b** from the difference between the heat of hydrogenation of these two alkenes, twice the difference between the C–H BDEs in **5b** and **5a** must be added to  $\Delta\Delta H(\text{H}_2)$ .

The difference between the C–H BDEs is given by the isodesmic reaction in eq 3. The enthalpy of this reaction is



computed to be  $\Delta BDE(\text{C–H}) = 6.8$  kcal/mol.

- (17) It is worth noting that the effects of *exo*- and *endo*-fluorines on reducing the exothermicity of cyclization of **2** to **3** deviate from being additive by  $-4.1$  kcal/mol. This deviation might indicate, for example, that X = F provides more stabilization to diradical **2** when N = H, as in **2d**, than when N = F, as in **2b**.
- (18) (a) Sun, H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1987**, *109*, 5275. (b) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750. (c) Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930. (d) Brown, E. C.; Borden, W. T. *Organometallics* **2000**, *19*, 2208.

Adding twice eq 3 to eq 2 gives eq 4 as the isodesmic reaction that defines the difference between the BDEs of the  $\pi$  bonds in **1b** and **1a**.



The same expression can be derived, starting from Benson's definition of the  $\pi$  BDEs of these two alkenes.<sup>19</sup>

The enthalpy computed for the reaction in eq 4 is  $\Delta\text{BDE}^\pi(\mathbf{1b} - \mathbf{1a}) = 14.6$  kcal/mol. Using this value and  $\Delta\Delta H = 24.5$  kcal/mol for the difference between the enthalpies of dimerization of **1b** to **2b** and **1a** to **2a** in eq 1 gives  $\Delta\text{BDE}^\sigma(\mathbf{2b} - \mathbf{2a}) = 4.7$  kcal/mol.<sup>20</sup> Thus, perfluorination is computed to strengthen not only the bridgehead C–H bond in **5b**, relative to that in **5a**, but also the newly formed C–C  $\sigma$  bond between the bridgehead carbons in **2b**, relative to the corresponding bond in **2a**.

Computing the difference between the adiabatic singlet–triplet splitting ( $\Delta E_{\text{ST}}$ ) in **1b** and in **1a** confirms the conclusion that perfluorination makes the  $\pi$  bond of **1b** ca. 15 kcal/mol stronger than that in **1a**. Although in a rigid alkene, such as **1**,  $\Delta E_{\text{ST}}$  is usually considerably larger than the  $\pi$  BDE,<sup>21</sup> one might expect that the difference between the  $\pi$  BDEs in **1a** and **1b** would be mirrored reasonably well by the difference between the adiabatic singlet–triplet splittings in the two alkenes.

The (U)B3LYP value for the adiabatic singlet–triplet splitting in **1b** is  $\Delta E_{\text{ST}} = 61.7$  kcal/mol, which is 16.6 kcal/mol larger than the value of  $\Delta E_{\text{ST}} = 45.1$  kcal/mol in **1a**. This value of  $\Delta\Delta E_{\text{ST}}(\mathbf{1b} - \mathbf{1a}) = 16.6$  kcal/mol is within 15% of the value of  $\Delta\text{BDE}^\pi = 14.6$  kcal/mol between these two alkenes, computed from the isodesmic reaction in eq 4.<sup>22</sup>

**Effect of Pyramidalization of the Radical Centers on  $\Delta\text{BDE}^\pi$ .** A possible contributor to the much larger  $\pi$  BDE in **1b** than in **1a** is that, on breaking the  $\pi$  bond in each alkene, pyramidalization of the doubly bonded carbons releases less strain in **1b** than in **1a**.<sup>23</sup> In fact, if eq 4 is used to define the difference between the  $\pi$  BDEs of these two alkenes and if the radical centers in **6a** and **6b** are constrained to be planar, our calculations find that lifting this geometry constraint releases 22.1 kcal/mol in **6a** but only 16.2 kcal/mol in **6b**. Thus, if eq 4 is used to define  $\Delta\text{BDE}^\pi(\mathbf{1})$ , this difference of 5.9 kcal/mol between the energies released on pyramidalization of the radical centers in **6a** and **6b** contributes  $2 \times 5.9 = 11.8$  kcal/mol (80%) of the 14.6 kcal/mol larger  $\pi$  BDE of **1b**, compared to **1a**.

**Table 1.** Relative Energies (kcal/mol) and C2–C1–C6 and C3–C4–C5 Bond Angles ( $\phi_a$ ,  $\phi_b$ ) at the Bridgehead Carbons of the Energy Minima, Transition Structures for Ring Inversion, and Planar Geometries of Triplet Alkenes **1a** and **1b** and of the Conformations of Triplet **7** with the Fluorines *endo*-(**7a**) and *exo*-(**7b**)

triplet	energy minimum	transition structure for ring inversion	planar geometry
<b>1a</b>	0 (120.4°)	36.6 (158.6°, 158.6°) <sup>a</sup>	43.2 (175.8°) <sup>b</sup>
<b>1b</b>	0 (122.6°)	30.0 (163.2°, 163.2°) <sup>a</sup>	30.8 (177.0°) <sup>b</sup>
<b>7a</b>	0 (122.9°)	34.4 (169.4°, 147.0°) <sup>c</sup>	<sup>d</sup>
<b>7b</b>	6.4 (119.5°)	34.4 (169.4°, 147.0°) <sup>c</sup>	<sup>d</sup>

<sup>a</sup>  $C_{2h}$  symmetry with the radical centers pyramidalized in opposite directions. <sup>b</sup> Second-order saddle point with  $D_{2h}$  symmetry. <sup>c</sup>  $C_s$  symmetry with the radical centers pyramidalized in opposite directions. The larger bond angle,  $\phi$ , in the TS is at the radical center that is syn to the hydrogens. <sup>d</sup> Nonstationary point, whose energy is actually 1.9 kcal/mol lower than that of the transition structure for ring inversion.

Similarly, if  $\Delta\Delta E_{\text{ST}}$  is used to define the difference between the  $\pi$  BDEs of these two alkenes, greater strain relief upon pyramidalization of the radical centers in triplet **1a** than in triplet **1b** is a major source of the 16.7 kcal/mol larger value of  $\Delta E_{\text{ST}}$  in **1b** than in **1a**. As shown in Table 1, on releasing the constraint of  $D_{2h}$  symmetry on the geometry of triplet **1a**, the energy decreases by 43.2 kcal/mol. Thus, as expected, allowing both radical centers in triplet **1a** to pyramidalize releases about twice as much strain energy as the 22.1 kcal/mol that is released when the single radical center in **6a** is allowed to pyramidalize.

Pyramidalization of both radical centers in planar triplet **1b** releases 30.8 kcal/mol, also about twice as much strain energy as the 16.2 kcal/mol that is released when the single radical center in **6b** is allowed to pyramidalize. However, the relief of strain on allowing pyramidalization of the two radical centers in triplet **1b** is 12.4 kcal/mol smaller than in triplet **1a**. Thus, 75% of the difference  $\Delta\Delta E_{\text{ST}} = 16.7$  kcal/mol between **1b** and **1a** comes from the fact that breaking the  $\pi$  bond in each alkene and allowing the radical centers to pyramidalize in the triplet diradicals formed releases less strain energy in **1b** than in **1a**.

As the foregoing discussion shows, it makes little difference whether the difference between the  $\pi$  BDEs of **1a** and **1b** are defined by  $\Delta\text{BDE}^\pi$  from eq 4 or by  $\Delta\Delta E_{\text{ST}}$ . Using either definition, the  $\pi$  BDE of **1b** is computed to be greater than that of **1a** by  $16 \pm 1$  kcal/mol, and about 75% of this difference comes from the ca. 12 kcal/mol larger amount of strain released when the  $\pi$  bond in **1a** is broken and the resulting radical centers are allowed to pyramidalize.

**Why Does Pyramidalization of the Radical Centers Release Less Strain Energy in Triplet **1b** than in Triplet **1a**?** A hypothesis to explain the reason pyramidalization releases less strain energy in triplet **1b** than in triplet **1a** is that nonbonded repulsions between the *endo*-fluorines at C2 and C6 and at C3 and C5 destabilize triplet **1b** more than the nonbonded repulsions between the *endo*-hydrogens at these carbons destabilize **1a**. Although this hypothesis is reasonable, we found that it is incorrect by performing B3LYP calculations on the two possible conformations of the triplet state of all-*cis*-2,3,5,6-tetrafluorobicyclo[2.2.0]hex-1(4)-ene (**7**). As shown in Table 1, the calculations revealed conformation **7a**, with the four fluorines *endo*, actually to be 6.4 kcal/mol lower in enthalpy than conformation **7b**, in which the four fluorines are *exo*.

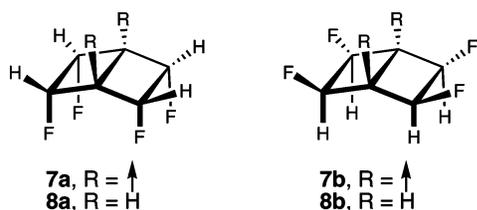
(19) Benson, S. E., Ed. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; pp 63–65.

(20) Consistent with this value for the difference between the  $\sigma$  C–C BDEs of **2b** and **2a**, the C–C  $\sigma$  bond, formed by dimerization of two molecules of radical **6b**, is computed to be 5.1 kcal/mol stronger than the C–C  $\sigma$  bond formed by dimerization of two molecules of radical **6a**.

(21) (a) Equal occupation of bonding and antibonding MOs results in net antibonding. For a brief discussion and leading references, see: (b) Jorgensen, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 6649.

(22) Because  $\Delta\Delta E_{\text{ST}}$  between **1b** and **1a** is 2.1 kcal/mol larger than  $\Delta\text{BDE}^\pi$ , the C–C  $\sigma$  bond that is made in forming singlet diradical **2b** from two molecules of triplet **1b** is computed to be  $2 \times 2.1 + 4.7 = 8.9$  kcal/mol stronger than the C–C  $\sigma$  bond that is made in forming singlet diradical **2a** from two molecules of triplet **1a**.

(23) (a) For example, the difference between the pyramidalization energies of the radical centers that are formed upon breaking the  $\pi$  bonds in ethylene and tetrafluoroethylene (TFE) is largely responsible for the  $\pi$  bond being considerably weaker in the fluorocarbon than in the hydrocarbon. The opposite effect of the fluorines in **1b** and in TFE is due to the fact that, unlike the eight fluorines in **1b**, the four fluorines in TFE are attached directly to the radical centers. Upon  $\pi$  bond breaking, pyramidalization of the  $\text{CF}_2$  radical centers in TFE releases much more, not much less, energy than pyramidalization of the  $\text{CH}_2$  radical centers in ethylene. (b) Wang, S. W.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. (c) Review: Borden, W. T. *Chem. Commun.* **1998**, 1919.



The rather surprising finding that **7a** is lower in energy than **7b** is presumably due to interactions between the radical centers and the adjacent C–F and C–H bonds being more favorable (or less unfavorable) in conformation **7a** than in conformation **7b**. To test this hypothesis that interactions involving the radical centers are responsible for conformation **7a** being preferred over **7b**, we replaced the radical centers in **7a** and **7b** with C–H bonds and computed the relative energies of the two stereoisomers (**8a** and **8b**) which result. As expected from the fact that **8a** contains two 1,3 interactions between pairs of *endo*-fluorines, **8a** was computed to be higher in enthalpy than **8b** by 2.6 kcal/mol.

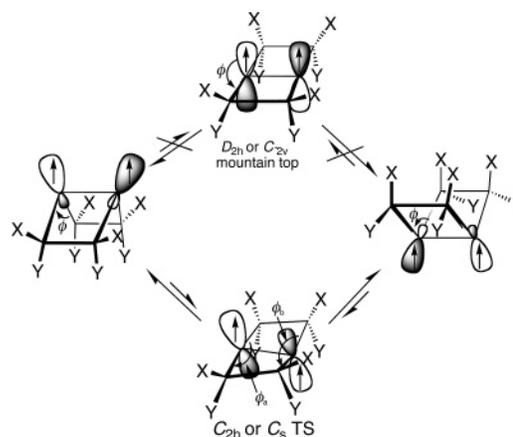
This finding indicates that the lower enthalpy of **7a**, relative to **7b**, must be due to interactions between the radical centers and the adjacent bonds being more favorable when the radical centers are pyramidalized syn to the C–H bonds as in **7a**, rather than syn to the C–F bonds as in **7b**. Despite the *endo*-fluorines in **7a**, which destabilize **8a** relative to **8b** by 2.6 kcal/mol, **7a** is nevertheless calculated to be 6.5 kcal/mol more stable than **7b**. These findings suggest that pyramidalization of the radical centers syn to the C–H bonds in conformation **7a** is actually a total of  $2.6 + 6.5 = 9.1$  kcal/mol more favorable than pyramidalization of the radical centers syn to the C–F bonds in conformation **7b**.<sup>24</sup>

The hypothesis that pyramidalization of radical centers syn to C–H bonds is more favorable than pyramidalization syn to C–F bonds also accounts for the larger amount of energy released upon pyramidalization of the bridgehead carbons in triplet **1a** than in triplet **1b**. In **1a**, pyramidalization of these carbons necessarily occurs syn to C–H bonds, whereas in **1b**, pyramidalization necessarily occurs syn to C–F bonds.<sup>25</sup>

However, another contributor to making pyramidalization of triplet **1a** 12.4 kcal/mol more exothermic than pyramidalization of triplet **1b** is the increase in repulsion between the *endo*-fluorines in the latter process. If the 2.6 kcal/mol enthalpy difference between **8a** and **8b** is taken as an estimate of the greater energetic cost of the *endo*-fluorines at the equilibrium geometry of **1b**, compared to the *endo*-hydrogens at the equilibrium geometry of **1a**, then pyramidalization of the radical centers syn to the C–H bonds in **1a** is found to be energetically more favorable by  $12.4 - 2.6 = 9.8$  kcal/mol than pyramidalization of the radical centers syn to the C–F bonds in **1b**. This

(24) This assumes, of course, that the 2.6 kcal/mol enthalpy difference between **8a** and **8b** is due entirely to interactions between the *endo*-fluorines in **8a** and that these interactions act to destabilize conformation **7a**, relative to conformation **7b**, by exactly this amount of energy. Although these assumptions are certainly not entirely correct, they do provide a useful way of approximating the contribution of repulsions between the *endo*-fluorines to the 6.5 kcal/mol enthalpy difference between **7a** and **7b**.

(25) The greater favorability of radical pyramidalization in the hydrocarbons than in the fluorocarbons argues against an alternative explanation of the lower energy of **7a** than **7b**—that pyramidalization of radical centers anti to C–F bonds is more stabilizing than pyramidalization anti to C–H bonds. If this hypothesis was correct, one would expect larger amounts of energy to be released upon pyramidalization of the radical centers in triplet **1b** and radical **6b** than in triplet **1a** and radical **6a**. Our calculations find the reverse to be true.



**Figure 3.** Depiction of ring inversion in the triplet states of alkenes **1a** ( $X = Y = H$ ) and **1b** ( $X = Y = F$ ) and interconversion of conformations **7a** (on the left) and **7b** (on the right) of the triplet state of all-*cis*-tetrafluorobicyclo[2.2.0]hex-1(4)-ene ( $X = H$ ,  $Y = F$ ).

value, based on the difference between the pyramidalization energies of triplet **1a** and **1b**, is in good agreement with the value of 9.1 kcal/mol, based on the enthalpy difference between conformations **7a** and **7b**.<sup>26</sup>

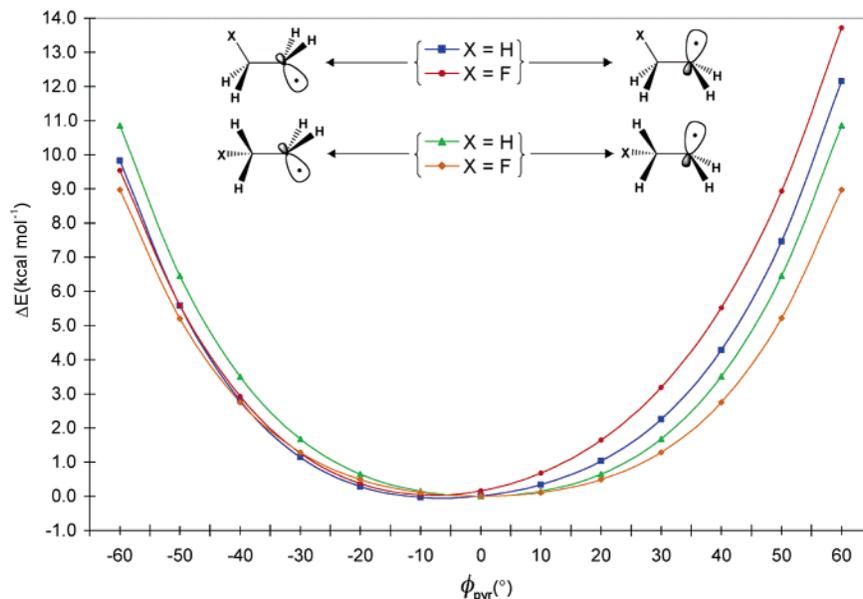
The greater favorability of pyramidalization of a radical center syn to a C–H bond, rather than to a C–F bond, is also evident in the difference between triplet **1a** and triplet **1b** in the energy released by allowing the  $D_{2h}$  planar geometries, which are both second-order saddle points (mountain tops), to relax to the  $C_{2h}$  geometries of the transition structures (TSs) for ring inversion. As illustrated in Figure 3, in the TSs, the radical centers are pyramidalized anti to each other, which relieves ring strain and also decreases the antibonding interaction<sup>21</sup> between the radical centers in the planar triplets.

As shown in Table 1, the  $C_{2h}$  TS is lower in energy than the  $D_{2h}$  mountain top by 6.6 kcal/mol in triplet hydrocarbon **1a** but by only 0.8 kcal/mol in triplet fluorocarbon **1b**. In addition, in the TSs for ring inversion, the smaller bond angles at the bridgehead carbons in triplet **1a** than in triplet **1b** mean that radical centers are more highly pyramidalized in the hydrocarbon TS than in the fluorocarbon TS. We attribute both the larger amount of pyramidalization and the larger amount of energy lowering on pyramidalization in the TS for ring inversion of triplet **1a** to the fact that pyramidalization at each radical center occurs syn to two C–H bonds in triplet **1a** but syn to two C–F bonds in triplet **1b**.<sup>27</sup>

Independent evidence that the interaction between a pyramidal radical center and a bond syn to it is more favorable for C–H than for C–F comes from calculations on ethyl radical and 2-fluoroethyl radical. As shown in Figure 4, at the

(26) Calculations on 1,2-difluorocyclopropane also support a value of about 2.5 kcal/mol as the energy difference between pyramidalization of a radical center syn to a C–H bond rather than to a C–F bond. The radical center created by removal of an H atom from C3 of *cis*-1,2-difluorocyclopropane prefers to be pyramidalized anti to the fluorines. Although there is no energy minimum for syn pyramidalization, constraining the radical center to have the same geometry in the syn-pyramidalized stereoisomer as in the anti results in the former stereoisomer being calculated to be 5.0 kcal/mol higher than the latter. In addition, the C3–H BDE is 2.5 kcal/mol higher in *trans*-1,2-difluorocyclopropane than in the *cis* stereoisomer, presumably because the radical formed from the *trans* stereoisomer necessarily has the radical center pyramidalized syn to one C–F bond.

(27) The slightly larger angles at the bridgehead carbons in the equilibrium geometries of triplets **1b** and **7b** than of triplets **1a** and **7a** almost surely reflect the fact that the former pair of triplets both have *endo*-fluorines, which are sterically more demanding than the *endo*-hydrogens in the latter pair of triplets.



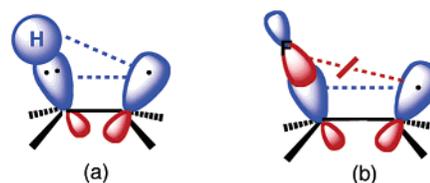
**Figure 4.** Effect of pyramidalization of the radical center on the energies of  $C_1$  and  $C_s$  conformations of ethyl radical (green and blue curves) and 2-fluoroethyl radical (orange and red curves). The differences in energy between the  $C_1$  and  $C_s$  conformers of each radical are reflected in the plots.

(U)B3LYP/6-31G\* level of theory, both radicals have  $C_s$  equilibrium geometries in which the radical center is pyramidalized anti, rather than syn, to the bond that is periplanar to it. However, at the equilibrium geometries, the radical center is pyramidalized by  $2.3^\circ$  more in the fluorocarbon than in the hydrocarbon.

In the  $C_1$  conformations of the radicals, pyramidalization is less energetically demanding in the 2-fluoroethyl radical (orange curve) than in the ethyl radical (green curve). The effect of the fluorine in these conformations of the 2-fluoroethyl radical should be largely steric and inductive rather than hyperconjugative. Therefore, the comparative ease of pyramidalization of the radical center in these conformations is most likely due to relief of torsional strain between one of the C(1)–H bonds and the C(2)–F bond that eclipses it at the planar  $C_s$  geometry. However, the greater ability of the electronegative fluoromethyl substituent to facilitate pyramidalization of the radical center to which it is attached<sup>28</sup> probably also contributes.

In the  $C_s$  conformations of the pyramidalized ethyl and fluoroethyl radicals, pyramidalization of the radical center anti to the C–F bond in the fluorocarbon radical (red curve) is slightly less energetically costly than pyramidalization anti to the unique C–H bond in the hydrocarbon radical (blue curve). Of course, syn pyramidalization, which leads to H–H eclipsing, is considerably more costly than anti pyramidalization in both radicals. However, in contrast to the case for anti pyramidalization of the radical centers, radical pyramidalization syn to the C–F bond is substantially more difficult than radical pyramidalization syn to the C–H bond.

**Why is Radical Pyramidalization Syn to a C–F Bond Disfavored?** We believe that the explanation of why syn pyramidalization of a radical center that eclipses a bond is more energetically costly when the bond is C–F, rather than C–H, is implicit in Figure 5. This figure depicts schematically the dominant orbital interaction between a syn pyramidalized radical center and (a) the C–H bond that eclipses it in the  $C_s$  ethyl



**Figure 5.** Schematic depiction of the dominant orbital interactions in (a) ethyl and (b) 2-fluoroethyl radicals at  $C_s$  geometries that are pyramidalized syn to the unique C–H bond in (a) and syn to the unique C–F bond in (b).

radical and (b) the C–F bond that eclipses it in the  $C_s$  2-fluoroethyl radical.

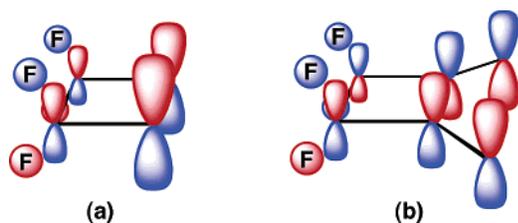
The C–H bond acts as a net hyperconjugative electron donor to a carbon radical center, so the singly occupied orbital in the  $C_s$  ethyl radical interacts more strongly with the filled C–H bonding orbital than with the unfilled C–H antibonding orbital. In the bonding C–H orbital, the hybrid orbital on carbon and the 1s AO of the hydrogen atom of course have the same phase, so interaction of both of these AOs with the singly occupied AO provides net stabilization for the hydrocarbon radical.

In contrast, in the fluorocarbon radical, the C–F bond is a net electron acceptor, so the singly occupied orbital interacts more strongly with the unfilled C–F antibonding orbital than with the filled C–F bonding orbital. In the antibonding C–F orbital, the hybrid orbital on carbon and the AO on fluorine have the opposite phase; therefore, the bonding interaction of the AO on carbon with the singly occupied AO is partially canceled by the antibonding interaction between the singly occupied AO and the AO on fluorine.<sup>29</sup>

We believe it is for this reason that, as shown in Figure 4, syn pyramidalization of the radical center in the 2-fluoroethyl radical is more destabilizing when the radical center eclipses a C–F bond, rather than a C–H bond. We ascribe to the same effect the result in Table 1 that conformation **7a** is more favored

(29) This is, of course, the reason that not only unshared pairs of electrons but also C–H bonds prefer to be oriented anti, rather than syn, to C–F bonds. For a brief discussion, see: Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Books: Sausalito, CA, 2006; pp 120–124.

(28) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

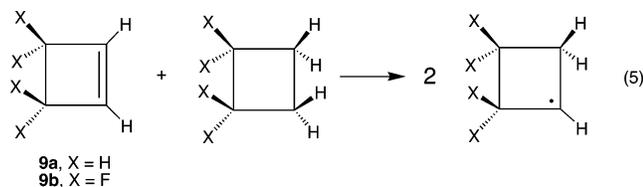


**Figure 6.** Schematic depiction of (a) the  $b_1$  combination of C–F  $\sigma^*$  orbitals that interact with the  $\pi$  orbital of the endocyclic double bond in **9b** and (b) the  $a_2$  combination of C–F  $\sigma^*$  orbitals that interact with the HOMO of the exocyclic diene in **10b**.

for the triplet state of all-*cis*-2,3,5,6-tetrafluorobicyclo[2.2.0]hex-1(4)-ene than conformation **7b** by 6.5 kcal/mol. Finally, we attribute the findings that pyramidalization of the radical centers provides (a) 12.4 kcal/mol less stabilization for triplet fluorocarbon **1b** than for triplet hydrocarbon **1a** and (b) 5.9 kcal/mol less stabilization for radical **6b** than for radical **6a** to the fact that radical-center pyramidalization places a total of four C–F bonds syn to the radical centers in the triplet state of **1b** and two C–F bonds syn to the radical center in radical **6b**.

**Hyperconjugative Interactions in Planar 1a and 1b.** As discussed above, the difference between the amount of strain released on breaking the  $\pi$  bonds in **1a** and **1b** accounts for about 75% of the greater  $\pi$  bond dissociation enthalpy of **1b**, as assessed from  $\Delta\Delta E_{ST} = 16.7$  kcal/mol, and about 80% as assessed from the Benson definition of  $\Delta BDE^{\pi} = 14.6$  kcal/mol. Thus, even when the radical centers formed by breaking the  $\pi$  bonds in **1a** and **1b** are constrained to remain planar, the  $\pi$  bond in **1b** is 3–4 kcal/mol stronger than the  $\pi$  bond in **1a**.

Substitution of C–F for the C–H bonds adjacent to the  $\pi$  bond in a single four-membered ring is calculated to result in a higher  $\pi$  BDE for 3,3,4,4-tetrafluorocyclobutene (**9b**) than for cyclobutene (**9a**). Using the Benson definition<sup>19</sup> of the  $\pi$  BDEs of **9a** and **9b** in eq 5, the difference between these  $\pi$  BDEs is computed to be 2.6 kcal/mol. In both cyclobutyl and

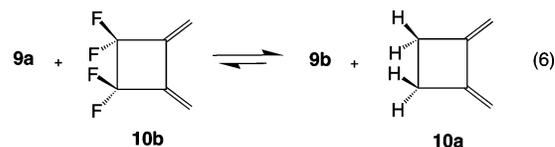


2,2,3,3-tetrafluorocyclobutyl radicals, the radical centers are calculated to be planar, so pyramidalization plays no role in the difference between the  $\pi$  BDEs of **9a** and **9b**.

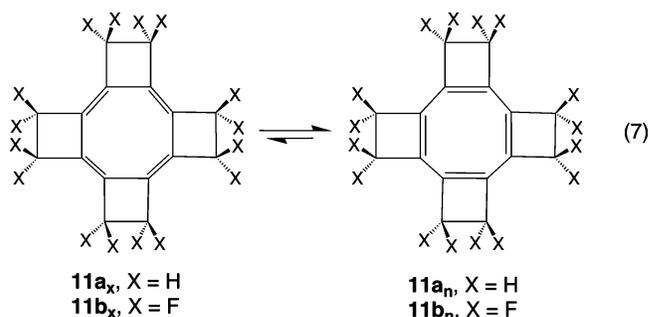
It is tempting to ascribe the strengthening of the  $\pi$  bonds in **1b** and **9b**, relative to those in, respectively, **1a** and **9a**, to electron donation from the filled  $\pi$  orbital into the combination of C–F  $\sigma^*$  antibonding orbitals of the same symmetry.<sup>23c,30</sup> This type of orbital interaction might prove to be less stabilizing if the endocyclic double bond in **9b** was replaced by a pair of exocyclic double bonds in **10b** because, as shown in Figure 6, the highest occupied (HOMO) of the diene in **10b** interacts with the  $a_2$  combination of C–F  $\sigma^*$  orbitals. Unlike the  $b_1$  combination of C–F  $\sigma^*$  orbitals, which interacts with the  $\pi$  orbital in **9b**, the  $a_2$  combination of C–F  $\sigma^*$  orbitals is C–C antibonding, so it is higher in energy than the  $b_1$  combination.

(30) Review: Getty, S. J.; Hrovat, D. A.; Dong Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689.

To test the hypothesis that  $\pi$  donation into C–F  $\sigma^*$  orbitals is more favorable in **9b** than in **10b**, we calculated the enthalpy of the isodesmic reaction in eq 6. Our calculations did, indeed, find this reaction to be exothermic by 5.3 kcal/mol.



There is already evidence, both experimental and computational, in the literature that four fluorines provide more stabilization for 3,3,4,4-tetrafluorocyclobutenes than for 3,3,4,4-tetrafluoro-1,2-dimethylenecyclobutenes. The experimental evidence comes from the X-ray structure of cyclooctatetraene **11b**, which shows that, at least in the crystal, endocyclic (**11b<sub>n</sub>**) rather than exocyclic (**11b<sub>x</sub>**) double bond fixation is preferred.<sup>31</sup> In fact, Baldrige and Siegel have calculated that **11b<sub>n</sub>** is favored over **11b<sub>x</sub>** by 17.2 kcal/mol or 4.3 kcal/mol for each four-membered ring in **11b**.<sup>32</sup>



Baldrige and Siegel also found that in cyclooctatetraenes, which are tetrakis-annulated with four-membered rings, the preference for exocyclic or endocyclic double bonds is dependent on the substituents attached to the four-membered rings.<sup>32,33</sup> For example, when the fluorines in **11b** are replaced by the hydrogens in **11a**, the 17.2 kcal/mol preference for **11b<sub>n</sub>** becomes a 2.3 kcal/mol preference for **11a<sub>x</sub>**. Therefore, the fluorines in **11b** actually result in a net change of 19.5 kcal/mol in the preference for exocyclic double bonds in **11a** to the preference for endocyclic double bonds in **11b**.<sup>34</sup> The change of 4.9 kcal/mol for each four-membered ring in eq 7 is very close to the enthalpy of 5.3 kcal/mol computed for the isodesmic reaction in eq 6.

(31) Einstein, F. W. B.; Willis, A. C.; Cullen, W. R.; Soulen, R. L. *Chem. Commun.* **1981**, 526.

(32) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 1755.

(33) Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 5514.

(34) Conversely, it was shown over 30 years ago that the filled  $\sigma$  orbitals of 1,3-bridged cyclobutane rings interact more favorably with the  $\pi$  orbitals of butadiene than with the  $\pi$  orbitals of ethylene.<sup>21b</sup> Indeed, our B3LYP/6-31G\* calculations find that the isodesmic reaction, bicyclo[2.1.1]hex-2-ene + *cisoid*-butadiene  $\rightarrow$  ethylene + 2,3-dimethylenebicyclo[2.1.1]hexane, is exothermic by 14.5 kcal/mol. The same preference for butadiene over ethylene as the 1,3-bridging group for cyclobutane rings is presumably responsible for the finding, both computational and experimental, that 1,3-bridged cyclobutane substituents result in exocyclic localization of the double bonds in both benzene<sup>35</sup> and cyclooctatetraene.<sup>32,36</sup>

(35) (a) Frank, N. L.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 2102. (b) Burgi, H. B.; Baldrige, K. K.; Hardcastle, K.; Frank, N. L.; Gantzel, P.; Siegel, J. S.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454.

(36) Komatsu, K. *J. Am. Chem. Soc.* **2001**, *123*, 1768.

## Conclusions

Our calculations find that the major factor in making dimerization of perfluorobicyclo[2.2.0]hex-1(4)-ene (**1b**) 44.6 kcal/mol less exothermic than dimerization of bicyclo[2.2.0]hex-1(4)-ene (**1a**) is the  $16 \pm 1$  kcal/mol stronger  $\pi$  bond in **1b** than in **1a**. About 25% of the greater strength of the  $\pi$  bond in **1b** can be attributed to electron donation from the bonding  $\pi$  MO into the  $\sigma^*$  orbitals of the eight C–F bonds that surround it. This type of stabilizing interaction is also responsible for the localization of the  $\pi$  bonds in cyclooctatetraene **11b**, so that they are endocyclic in the four-membered rings.

However, the major contributor to the stronger  $\pi$  bond in **1b** than in **1a** is found to be the unfavorable orbital interaction that results when a pyramidalized radical center is syn to a C–F bond. This effect not only strengthens the  $\pi$  bond in **1b**, relative to that in **1a**, but also is responsible for the rather surprising prediction that the more sterically congested endo conformation (**7a**) of the triplet state of all-*cis*-2,3,5,6-tetrafluorobicyclo[2.2.0]hex-1(4)-ene is favored over conformation **7b**, which places the fluorines exo but syn to the pyramidalized radical centers at C1 and C4.

The two different effects that serve to make the  $\pi$  bond in **1b** much stronger than the  $\pi$  bond in **1a** certainly must play roles elsewhere in fluorocarbon chemistry, and the roles that they do play are the subject of ongoing research.

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**Supporting Information Available:** Optimized geometries, energies, thermal corrections, and vibrational frequencies for all the minima and TSs discussed in the text and references and the complete list of authors for ref 15 (53 pages, print/PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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