

## Ab Initio Calculations of the Potential Surface for Rearrangement of 2,2,3,3-Tetrafluoromethylenecyclopropane to 1-(Difluoromethylene)-2,2-difluorocyclopropane

Haiyan Wei, David A. Hrovat, and Weston Thatcher Borden\*

Contribution from the Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, Texas 76203-5070

Received August 16, 2006; E-mail: borden@unt.edu

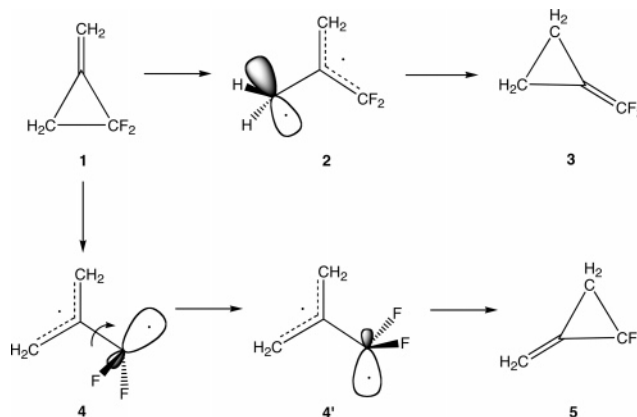
**Abstract:** (4/4)CASSCF and CASPT2 calculations have been performed to understand the reason that addition of a second pair of geminal fluorines to methylenecyclopropane lowers the barrier to rearrangement by 6.7 kcal/mol more than addition of the first pair. Our calculations duplicate this experimental finding by Dolbier and co-workers. Our computational results confirm Dolbier's conjecture, that the non-additive lowering of  $E_a$  for the rearrangement of 2,2,3,3-tetrafluoromethylenecyclopropane (**9**) to 1-(difluoromethylene)-2,2-difluorocyclopropane (**11**) is due to destabilization of **9** by the presence of the vicinal  $\text{CF}_2$  groups in this fluorocarbon. In the course of exploring the potential energy surface for the rearrangement of **9**, we have located a bond-stretch isomer (**20**) that differs from **9** by inversion of both  $\text{CF}_2$  groups. The enthalpy of **20** is computed to be 21.9 kcal/mol higher than that of **9**, but direct interconversion of these two "bond-stretch invertomers" requires passage over a TS whose enthalpy is calculated to be 11.7 kcal/mol higher than that of **20**.

### Introduction

Geminal fluorine substitution profoundly affects the reactivity of cyclopropane.<sup>1</sup> For example, the activation energy of  $E_a = 59.4$  kcal/mol for *cis*-*trans* isomerization of 1,2-dimethylcyclopropane<sup>2</sup> is reduced to  $E_a = 49.7$  kcal/mol in 1,1-difluoro-2,3-dimethylcyclopropane.<sup>3</sup> Moreover, as predicted by ab initio calculations,<sup>4</sup> the activation energy for racemization of optically active *cis*-1,1-difluoro-2-ethyl-3-methylcyclopropane is only  $E_a = 41.3$  kcal/mol,<sup>5</sup> 16.5 kcal/mol lower than the activation energy for racemization of optically active *cis*-2-ethyl-3-methylcyclopropane.<sup>6</sup>

Given the very large effects of geminal fluorine substitution on ring opening of cyclopropane, the finding by Dolbier and Fielder that  $E_a = 38.3$  kcal/mol for the methylenecyclopropane rearrangement of 2,2-difluoromethylenecyclopropane (**1**) to (difluoromethylene)cyclopropane (**3**) is lower by only about 2 kcal/mol<sup>7</sup> than the  $E_a$  for the rearrangement of the methyl-labeled hydrocarbon<sup>8</sup> was quite surprising. Ab initio calculations revealed that this experimental finding is a consequence of the

### Scheme 1



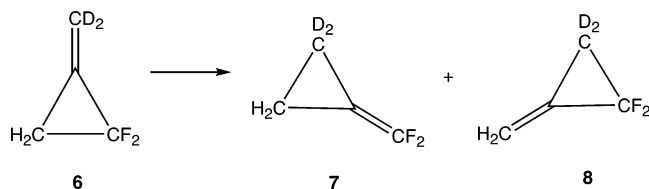
weakening of the  $\pi$  bond to the  $\text{CF}_2$  group in the transition structure (TS), connecting **1** to diradical intermediate **2** (Scheme 1),<sup>9</sup> by the strong preference of difluorinated radical centers for pyramidal geometries.<sup>10</sup>

On the other hand, in the *crypto* methylenecyclopropane rearrangement of **1** to **5**, via diradical intermediate **4**, a  $\pi$  bond is not formed to the  $\text{CF}_2$  group. Therefore, one would expect diradical intermediate **4** to be considerably lower in enthalpy than diradical **2**. Our ab initio calculations found this expectation to be borne out, with **4** computed to be lower in enthalpy than **2** by 6.3 kcal/mol.<sup>9</sup>

- (1) Reviews: (a) Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195. (b) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield, FL, 1986; Vol. 3, p 141. (c) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689.
- (2) Flowers, M. D.; Frey, H. M. *J. Chem. Soc. A* **1960**, 257, 121.
- (3) Dolbier, W. R., Jr.; Enoch, H. O. *J. Am. Chem. Soc.* **1977**, *99*, 4532.
- (4) Getty, S. J.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1521.
- (5) Tian, F.; Lewis, S. B.; Bartberger, M. D.; Dolbier, W. R.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 6187.
- (6) (a) Carter, W. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 7344. (b) Bergman, R. G.; Carter, W. L. *J. Am. Chem. Soc.* **1969**, *91*, 7411.
- (7) Dolbier, W. R., Jr.; Fielder, T. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 5577.
- (8) Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720.

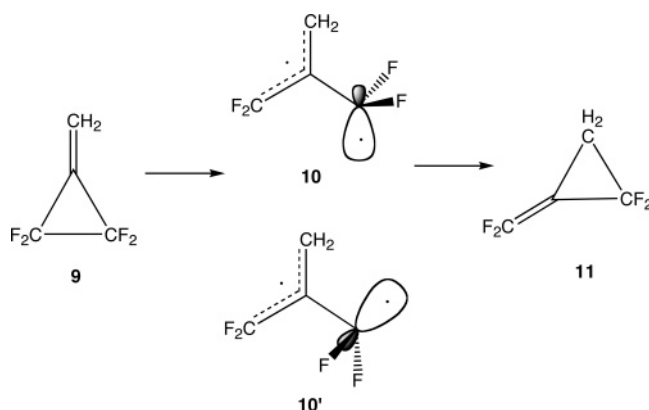
- (9) Lewis, S. B.; Hrovat, D. A.; Getty, S. J.; Borden, W. T. *J. Chem. Soc., Perkin Trans.* **1999**, 2339.
- (10) Review: Borden, W. T. *Chem. Commun.* **1998**, 1919.

However, a second expectation, that the TS connecting **1** to **4** should also be considerably lower in enthalpy than the TS connecting **1** to **2**, was proven to be incorrect by our calculations. The two TSs were computed to differ in enthalpy by only 1.1 kcal/mol.<sup>9</sup> Subsequent kinetic studies by Dolbier and co-workers on the competing rearrangements of **6** to **7** and **8** found the free energy difference between the TSs leading to these two products to be 0.7 kcal/mol at 453 °C,<sup>11</sup> in excellent agreement with the computational results.



The calculations revealed that the highly pyramidalized CF<sub>2</sub> group in diradical intermediate **4** is responsible for the higher than expected enthalpy of the TS connecting **1** to **4**.<sup>9</sup> The preferred pathway for the rearrangement of **1** to **5** is depicted in Scheme 1, which shows that ring opening of **1** occurs with inversion of the CF<sub>2</sub> group, giving diradical **4**. Microscopic reversibility is preserved in the closure of **4** to **5** by facile rotation about the bond to the CF<sub>2</sub> group in **4**, to form diradical **4'**, which closes to **5**, again with inversion of the configuration of the CF<sub>2</sub> group.

Dolbier and co-workers have also found that introduction of a second CF<sub>2</sub> group into the methylenecyclopropane ring results in the experimentally determined value of  $E_a = 29.6$  kcal/mol for rearrangement of 2,2,3,3-tetrafluoromethylenecyclopropane (**9**) to 1-(difluoromethylene)-2,2-difluoromethylenecyclopropane (**11**)<sup>12</sup> being 8.7 kcal/mol lower than  $E_a = 38.3$  kcal/mol for rearrangement of **1** to **3**.<sup>7</sup> To try to understand why the introduction of a second CF<sub>2</sub> group into the cyclopropane ring lowers  $E_a$  for methylenecyclopropane rearrangement by 6.7 kcal/mol more than introduction of the first CF<sub>2</sub> group, we have performed ab initio calculations on the rearrangement of **9** to **11**.



Herein, we report the results of our study. We find that the presence of two CF<sub>2</sub> groups destabilizes the cyclopropane ring of **9**, not only relative to the TS for ring opening, but also relative to the diradical intermediate (**10**) in the rearrangement and to

the product formed (**11**). Consequently, as conjectured by Dolbier and co-workers,<sup>12</sup> the low  $E_a$  for rearrangement of **9** is due to destabilizing interactions between the vicinal CF<sub>2</sub> groups in **9**, rather than to stabilization of the TS by the presence of two CF<sub>2</sub> groups.

In addition to establishing the reason for the surprisingly low barrier to rearrangement of **9**, our calculations also make the very interesting prediction of the existence of a C<sub>2v</sub> intermediate, which may be regarded as a bond-stretch isomer of **9**.<sup>13</sup> Unlike the case in methylenecyclopropane **9**, where the AOs that form the bond between the CF<sub>2</sub> groups have their large lobes pointed toward each other, in the bond-stretch isomer of **9** the CF<sub>2</sub> groups are inverted, so that the large lobes of these AOs are pointed away from each other. Consequently, direct closure of the bond-stretch isomer to **9** is calculated to have a high barrier, because this reaction requires simultaneous inversion of both of the highly pyramidalized CF<sub>2</sub> groups in the bond-stretch isomer.

### Computational Methodology

Stationary points on the potential surface for the rearrangement of **9** to **11** were located by carrying out (4/4)CASSCF calculations with the 6-31G\* basis set.<sup>14</sup> For **9**, the orbitals in the active space were comprised of the bonding and antibonding orbitals of the scissile  $\sigma$  bond, as well as the  $\pi$  and  $\pi^*$  MOs. For other stationary points on the potential energy surface, the orbitals in the active space consisted of the four MOs, formed by the mixing of the  $\sigma$ ,  $\sigma^*$ ,  $\pi$ , and  $\pi^*$  orbitals of **9** upon ring opening.

The geometries of the stationary points located are available as Supporting Information.<sup>15</sup> At each stationary point, a (4/4)CASSCF vibrational analysis was performed to identify it as an energy minimum, a transition structure (TS), or a hill top, and to obtain the vibrational frequencies necessary to compute the enthalpy at 298 K. In addition, for each TS, the transition vector, found by the vibrational analysis, was used to follow the reaction pathway from the TS in both directions, to determine which pair of energy minima is connected by that TS. These calculations were performed with the Gaussian 03 suite of programs.<sup>16</sup>

To include the effects of dynamic electron correlation,<sup>17</sup> single-point CASPT2 calculations<sup>18</sup> were carried out at each (4/4)CASSCF stationary point. The CASPT2 calculations were not only performed with the 6-31G\* basis set, but also with the larger 6-311+G(2df,2p) basis set.<sup>19</sup> The CASPT2 calculations were carried out with the MOLCAS package of ab initio programs.<sup>20</sup>

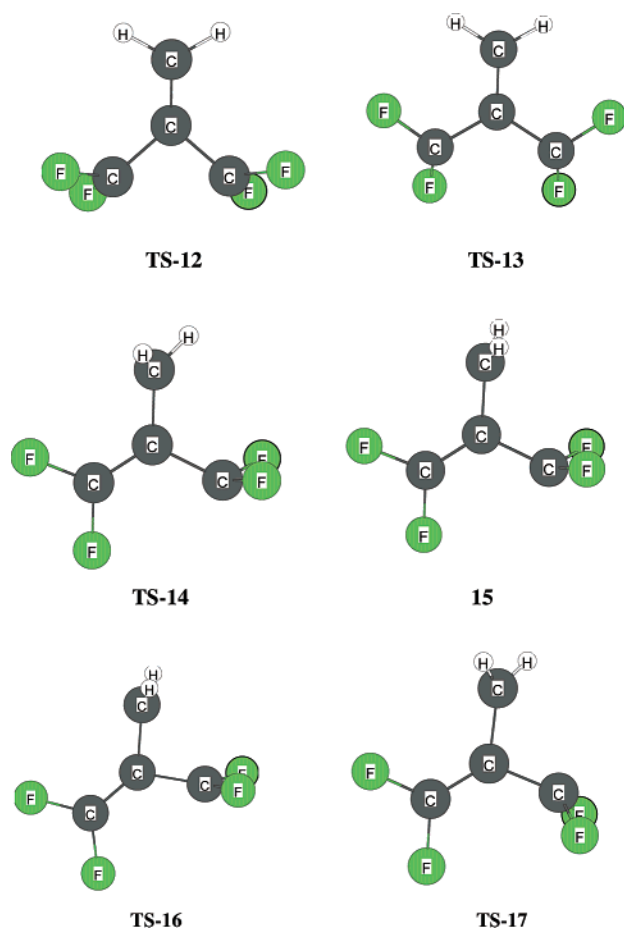
### Results and Discussion

#### Pathways for Ring Opening of 2,2,3,3-Tetrafluoromethylenecyclopropane (**9**) to Diradical Intermediates **10** and **10'**

- (13) (a) Review: Rohmer, M.-M.; Bénard, M. *Chem. Soc. Rev.* **2001**, *30*, 340. For more recent examples of this phenomenon, see: (b) Rodriguez, A.; Olsen, R. A.; Ghaderi, N.; Schedchkevit, D.; Tham, F. S.; Mueller, L. J.; Bertrand, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 4880. (c) Kárpáti, T.; Veszprémi, T.; Thirupathi, N.; Liu, X.; Wang, Z.; Ellem, A.; Nyulászi, L.; Verkade, J. G. *J. Am. Chem. Soc.* **2006**, *128*, 1500. (d) Kosa, M.; Karni, M.; Apeloig, Y. *J. Chem. Theory Comput.* **2006**, *2*, 956.
- (14) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- (15) This material is available free of charge via the Internet at <http://pubs.acs.org>.
- (16) Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (17) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 87.
- (18) (a) Anderson, K.; Malmqvist, P. A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218. (b) Andersson, K.; Malmqvist, P. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Chem. Phys.* **1990**, *94*, 5483.
- (19) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.
- (20) Molcas Version 6.2: Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrady, P.; Seijo, L. *Comput. Mater. Sci.* **2003**, *28*, 222.

(11) Dolbier, W. R., Jr.; Gautriad, E.; Cai, X. *J. Fluorine Chem.* **2005**, *126*, 339.

(12) Dolbier, W. R., Jr.; Seller, S. F.; Alsader, B. H.; Smart, B. E. *J. Am. Chem. Soc.* **1980**, *102*, 5398.



**Figure 1.** Some of the (4/4)CASSCF/6-31G\* stationary points on the potential surface for rearrangement of 2,2,3,3-tetrafluoro-methylenecyclopropane (**9**) to 1-(difluoromethylene)-2,2-difluorocyclopropane (**11**).

In analogy to the rearrangement of 2,2-difluoromethylenecyclopropane (**1**) to (difluoromethylene)cyclopropane (**3**) via the intermediacy of diradical (**2**) and to the *crypto* rearrangement of **1** to **5** via diradical **4**,<sup>9</sup> the rearrangement of **9** to **11** is expected to occur via the intermediacy of diradical **10** and/or **10'**. We began our calculations by searching for the lowest energy pathway for the ring opening of **9** to **10**.

Ring opening of **9** can occur, at least in principle, by three different pathways, involving disrotation, conrotation, or monorotation of the CF<sub>2</sub> groups. We found that the disrotatory path leads to a transition structure (TS) in which the CF<sub>2</sub> groups have rotated by 42.6° and the C2–C3 bond has lengthened by 0.69 Å from the equilibrium geometry of **9**. This TS (**TS-12**) is depicted in Figure 1, and Table 1 shows that **TS-12** is computed to be 30.0 kcal/mol higher in enthalpy than **9** at the CASPT2/6-311+G(2df,2p) level of theory.<sup>21</sup>

From **TS-12**, continued disrotation of the CF<sub>2</sub> groups by an additional 30.0° leads to another TS (**TS-13** in Figure 1), which is 4.3 kcal/mol lower than **TS-12**. In **TS-13**, the vibration with the imaginary frequency is no longer the *a'* disrotatory vibration of **TS-12** but, instead, an *a''* vibration for symmetry-breaking conrotation of the CF<sub>2</sub> groups. The point along the reaction coordinate at which the force constant for the *a''* vibration

(21) Unless otherwise noted, all of the enthalpies cited in the text were computed at the (4/4)CASPT2/6-311+G(2df,2p)/(4/4)CASSCF/6-31G\* level of theory.

**Table 1.** Relative Electronic Energies and Enthalpies (kcal/mol) of the Stationary Points on the Potential Surface for Rearrangement of 2,2,3,3-Tetrafluoromethylenecyclopropane (**9**) to 1-(Difluoromethylene)-2,2-difluorocyclopropane (**11**)<sup>a</sup>

	6-31G*		6-311+G(2df,2p)	
	CASSCF	CASPT2	CASSCF	CASPT2
<b>9</b>	0	0	0	0
<b>10</b>	21.7 (19.8)	21.8 (20.0)	21.4 (19.6)	21.4 (19.5)
<b>10'</b>	21.4 (20.4)	22.8 (21.7)	21.9 (20.8)	24.0 (22.8) <sup>b</sup>
<b>TS (10/10')</b>	25.7 (23.3)	25.1 (22.7)	26.0 (23.5)	25.1 (22.6)
<b>11</b>	−4.8 (−4.4)	−8.6 (−8.3)	−4.9 (−4.6)	−9.2 (−8.8)
<b>TS-12</b>	30.7 (29.3)	31.9 (30.5)	29.4 (28.1)	31.3 (30.0)
<b>TS-13</b>	23.7 (22.4)	25.4 (24.1)	24.1 (22.8)	27.0 (25.7)
<b>TS-14</b>	25.5 (23.2)	28.0 (25.6)	25.6 (23.3)	28.4 (26.1)
<b>15</b>	25.4 (23.6) <sup>c</sup>	28.3 (26.6)	25.4 (23.7) <sup>c</sup>	28.8 (27.1)
<b>TS-16</b>	31.6 (29.2)	28.6 (26.2)	30.5 (28.2)	26.4 (24.1)
<b>TS-17</b>	31.4 (29.0)	33.0 (30.6)	30.6 (28.2)	32.0 (29.6)
<b>18</b>	28.8 (27.4)	33.4 (32.0)	28.6 (27.3)	34.4 (33.1)
<b>18-triplet</b>	27.6 (26.4)	32.0 (30.8)	27.5 (26.3)	33.1 (31.9)
<b>19</b>	30.4 (28.5)	35.1 (33.2)	30.1 (28.2)	36.1 (34.1)
<b>19-triplet</b>	29.7 (27.8)	34.4 (32.5)	29.6 (27.7)	35.4 (33.5)
<b>20</b>	20.1 (19.4)	21.6 (21.0)	20.2 (19.6)	22.6 (21.9)
<b>20-triplet</b>	28.3 (27.2)	32.7 (31.5)	28.5 (27.4)	34.2 (33.1)
<b>TS (20/9)</b>	44.8 (41.6)	39.9 (36.7)	42.5 (39.3)	36.8 (33.6)

<sup>a</sup> Calculations were performed at (4/4)CASSCF/6-31G\* optimized geometries, and single-point CASSCF and CASPT2 energies were computed with both the 6-31G\* and the 6-311+G(2df,2p) basis sets. <sup>b</sup> Although the CASPT2 energy of **10'** is lower than that of **TS(10/10')**, the zero-point energy, associated with the one additional vibration that has a real frequency in **10'**, makes the CASPT2 enthalpy of **10'** slightly higher than that of **TS(10/10')**, which connects **10'** to **10**. <sup>c</sup> Although the CASSCF energy of **15** is slightly lower than that of **TS-14**, the zero-point energy, associated with the one additional vibration that has a real frequency in **15**, makes the CASSCF enthalpy of **15** higher than that of **TS-14**.

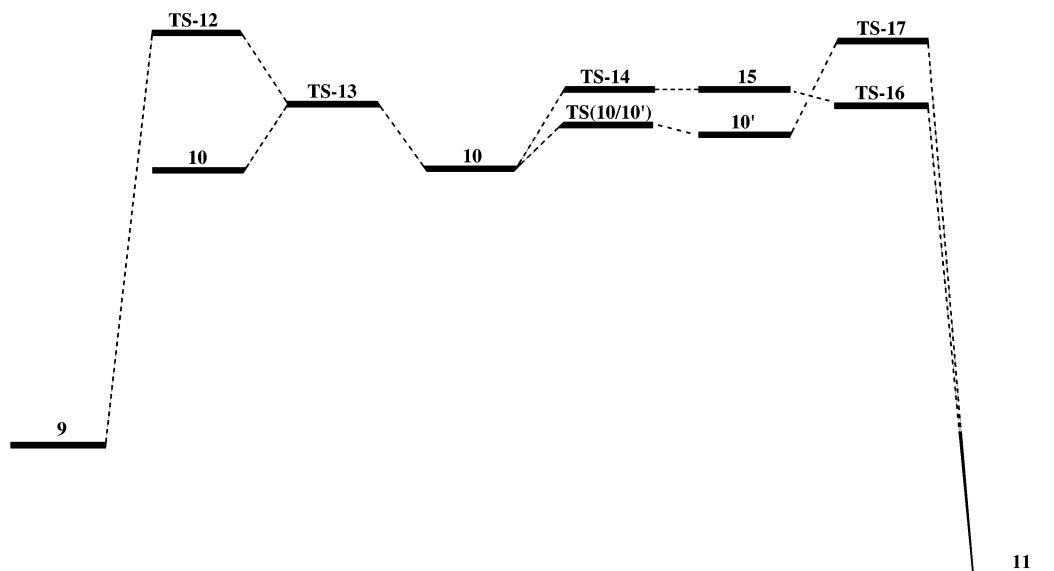
changes sign from positive at **TS-12** to negative at **TS-13** is called a valley-ridge inflection point.<sup>22</sup>

At the equivalent minima (**10**) that are connected by **TS-13**, one of the CF<sub>2</sub> groups in **TS 13** has become conjugated with the exocyclic double bond, and the other has rotated so that its singly occupied 2p AO lies in the plane of the four carbon atoms. Thus, **13** is the C<sub>s</sub> TS for interchange of the pair of nonequivalent CF<sub>2</sub> groups in intermediate **10**.<sup>23</sup>

Table 1 shows that **10** is lower in enthalpy than **TS-13** by 6.2 kcal/mol, and the enthalpic barrier to reclosure of **10** to **9** via **TS-12** is 10.5 kcal/mol. The relative enthalpies of these and other important stationary points on the potential energy surface connecting **9** and **11** are indicated graphically in Figure 2.

We were unable to locate a true TS for conrotatory opening of **9** to **10**. Following a C<sub>2</sub> reaction path from **9** did, indeed, lead to a CASSCF energy maximum. This stationary point is higher in energy than **TS-12** by 1.0 and 3.4 kcal/mol at,

- (22) (a) Metiu, H.; Ross, J.; Silbey, R.; George, T. F. *J. Chem. Phys.* **1974**, *61*, 3200. (b) Valatazanos, P.; Ruedenberg, K. *Theor. Chim. Acta* **1986**, *69*, 281. For recent discussions of valley-ridge inflection points in connection with the ene reaction of singlet oxygen, see: (c) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 1319. (d) Gonzalez-Lafont, A.; Moreno, M.; Lluch, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 13089.
- (23) We also located a C<sub>2</sub> intermediate that is connected by a pair of mirror-image C<sub>1</sub> TSs to the two equivalent minima, corresponding to **10**. The C<sub>2</sub> structure has (4/4)CASSCF energy that is only 0.1 kcal/mol lower than that for the pair of mirror-image C<sub>1</sub> structures, and, at the CASPT2/6-31G\* level of theory, the C<sub>2</sub> structure is actually 0.2 kcal/mol above the pair of mirror-image C<sub>1</sub> structures. Therefore, it is probably correct to call the C<sub>2</sub> structure a TS for exchange of non-equivalent CF<sub>2</sub> groups in **10**. The CASPT2/6-31G\* energy of this C<sub>2</sub> TS is actually 0.8 kcal/mol lower than that of the C<sub>s</sub> TS (**TS-13**) for CF<sub>2</sub> exchange in **10**. However, because the C<sub>2</sub> TS does not lie on the reaction coordinate for ring opening of **9**, it does not appear in Figure 1 or Table 1. Nevertheless, its geometry and CASSCF and CASPT2 energies are given in the Supporting Information.<sup>15</sup>



**Figure 2.** Schematic depiction of the relative CASPT2/6-311+G(2df,2p) enthalpies of the stationary points along the pathway for the ring opening of **9** to diradical **10** and for the closure of **10** to **11** with inversion (via **15**) or retention (via **10'**) of the configuration of the pyramidalized CF<sub>2</sub> group in **10**.

respectively, the (4/4)CASSCF/6-31G\* and CASPT2/6-31G\* levels of theory. However, a vibrational analysis found this C<sub>2</sub> energy maximum to have imaginary frequencies for both a<sub>1</sub> and a<sub>2</sub> vibrations. Thus, this C<sub>2</sub> geometry is a mountain top on the global (4/4)CASSCF/6-31G\* potential energy surface for rearrangement of **9**.

The fact that the C<sub>2</sub> conrotatory energy maximum is a mountain top suggests that there might be a true TS with no symmetry, in which ring opening of **9** to **10** occurs largely by rotation of just one CF<sub>2</sub> group. However, all attempts to locate such a monorotatory TS led back to **TS-12**. Therefore, it appears that the preferred pathway for ring opening of **9** involves initial disrotation of both CF<sub>2</sub> groups, passage over **TS-12**, followed by symmetry-breaking conrotation to form diradical intermediate **10**.<sup>24</sup>

Ring opening of **9** to diradical **10** occurs with retention of configuration of the pyramidalized CF<sub>2</sub> group that remains unconjugated with the double bond in **10**. However, ring opening of **9** could, at least in principle, also lead to diradical **10'**, which differs from **9** and **10** by inversion of the configuration of the pyramidalized CF<sub>2</sub> group.

At the CASSCF level, diradical **10'** was found to have a C<sub>1</sub> equilibrium geometry, with the conjugated CF<sub>2</sub> group pyramidalized by 43.2°. The CASSCF/6-31G\* energy of this C<sub>1</sub> geometry is 0.9 kcal/mol lower than that of the C<sub>s</sub> TS, connecting **10'** to its mirror image, which has the conjugated CF<sub>2</sub> group pyramidalized in the opposite direction. However, CASPT2/6-311+G(2df,2p) calculations found the energies of the C<sub>1</sub> and C<sub>s</sub> geometries of **10'** to be essentially the same. Presumably, the proximity of the fluorines on the non-conjugated CF<sub>2</sub> group to one of the vinylic fluorines in **10'** is responsible for **10'** being computed to be 2.6 kcal/mol higher in energy than **10**.

We were unable to find a low-energy TS for ring opening of **9** directly to **10'** with inversion of configuration of the non-

conjugated CF<sub>2</sub> group (vide infra). However, following ring opening of **9** to **10**, there are several possible pathways for interconversion of **10** and **10'**. The pathway of lowest energy was calculated to be the one that involves rotation about the C–C bond to the non-conjugated CF<sub>2</sub> group. The CASPT2 energy of the TS [**TS(10/10')** along this pathway] is computed to be 1.1 kcal/mol greater than that of **10'**. However, because **10'** has one more vibration with a real frequency than does **TS(10/10')**, the CASPT2 enthalpy of **10'** is actually computed to be 0.2 kcal/mol greater than that of **TS(10/10')**.

A higher energy pathway for interconversion of **10** and **10'** involves inversion of the non-conjugated CF<sub>2</sub> group. The CASPT2 barrier to transformation of **10** to **10'** by CF<sub>2</sub> inversion is calculated to be 8.2 kcal/mol, which is 5.1 kcal/mol greater than the barrier for formation of **10'** from **10** by rotation of the non-conjugated CF<sub>2</sub> group.

**Ring Closure of 10 and 10' to 1-(Difluoromethylene)-2,2-difluorocyclopropane (11).** Although diradical **10'** is computed to be higher in enthalpy than diradical **10** by 3.3 kcal/mol at the CASPT2 level of theory, if the TS for ring closure of **10'** were lower in energy than the TS for ring closure of **10**, **10'** could still lie on the lowest energy reaction pathway for rearrangement of **9** to **11**.

Ring closure of **10** to **11** inverts the configuration of the non-conjugated CF<sub>2</sub> group, whereas ring closure of **10'** to **11** occurs with retention of CF<sub>2</sub> configuration. Given the 8.2 kcal/mol CASPT2 energy barrier computed for inversion of the CF<sub>2</sub> group in forming **10'** from **10**, it might have been imagined that ring closure of **10'** with retention of CF<sub>2</sub> configuration would have a lower barrier than ring closure of **10** with inversion. However, this was not found to be the case. Instead, as in the *crypto* methylenecyclopropane rearrangement of **1** to **5**, where inversion of the CF<sub>2</sub> group was calculated to be the preferred pathway for ring opening of **1** and ring closure to **5**,<sup>9</sup> the TS for closure of **10** to **11** was computed to be lower than the TS for closure of **10'** to **11**.

As in the ring closure of **4'** to **5** with inversion of CF<sub>2</sub> configuration, CASSCF calculations find ring closure of **10** to **11** to involve passage over a TS (**TS-14**) to form a second

(24) **TS-12** for ring opening of **9** is similar to the TS for the ring opening of **1** to **4'** with retention of CF<sub>2</sub> configuration.<sup>9</sup> To reach the latter TS, the CH<sub>2</sub> and CF<sub>2</sub> groups in **1**, like the CF<sub>2</sub> groups in the ring opening of **9**, initially rotate in opposite directions.

diradical intermediate (**15**), which has nearly the same CASSCF energy as **TS-14**. As shown in Figure 1, in **15** the CH<sub>2</sub> and CF<sub>2</sub> groups are aligned for  $\sigma$  bond formation. Nevertheless, ring closure of **15** to **11** requires inversion of the CF<sub>2</sub> group, and, at the CASSCF/6-311+G(2df,2p) level of theory, ring closure is prevented by a 4.5 kcal/mol barrier to passage over **TS-16**.

However, inclusion of dynamic electron correlation has a large effect on lowering the barrier to CF<sub>2</sub> group inversion.<sup>9,25</sup> Consequently, at the CASPT2 level of theory, the energy of **TS-16** is actually 2.4 kcal/mol lower than that of **15** (Table 1).

The CASPT2 enthalpy of **TS-14** for ring closure of **10** to **11** with inversion of CF<sub>2</sub> configuration is calculated to be 3.5 kcal/mol lower than the CASPT2 enthalpy of **TS-17** for ring closure of **10'** to **11** with retention of the CF<sub>2</sub> group configuration. This enthalpy difference between the TSs for ring closure with, respectively, inversion and retention of configuration is about the same size as the CASPT2/6-31G\* energy difference between these two types of TSs in the *crypto* methylenecyclopropane rearrangement of **1** to **5**. As discussed previously for the latter rearrangement,<sup>9</sup> in the rearrangement of **9** to **11** ring closure with inversion of the configuration of the highly pyramidalized CF<sub>2</sub> group is favored over ring closure with retention by better overlap between the singly occupied AOs on the CF<sub>2</sub> and CH<sub>2</sub> groups in the TS for ring closure.

**Reaction Thermochemistry.** As shown graphically in Figure 2, our calculations find that the highest energy TS along the lowest energy pathway for the rearrangement of **9** to **11** is **TS-12**, which connects **9** to diradical intermediate **10**. The CASPT2 activation enthalpy of  $E_a = \Delta H^\ddagger + RT = 30.0 + 0.8 = 30.8$  kcal/mol for passage over this TS is in very good agreement with the value of  $E_a = 29.6 \pm 1$  kcal/mol measured by Dolbier and co-workers in the temperature range 150–160 °C.<sup>12</sup>

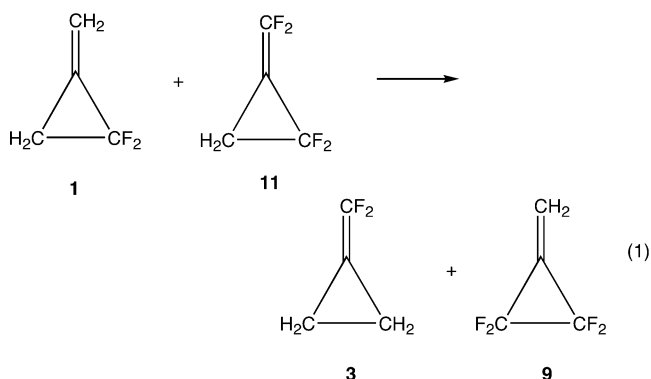
As noted in the introduction,  $E_a = 29.6$  kcal/mol for the rearrangement of **9** to **11** is much smaller than expected. Based on the effect of the CF<sub>2</sub> group in **1** on making  $E_a = 38.3$  kcal/mol for rearrangement of **1** to **3'** only 2 kcal/mol smaller than the  $E_a$  for rearrangement of the methyl-labeled hydrocarbon,<sup>8</sup> substituent-effect additivity would have predicted  $E_a \approx 36$  kcal/mol for the rearrangement of **9** to **11**. Thus, the effect of the pair of CF<sub>2</sub> groups in **9** on lowering the barrier to rearrangement to **11** is ca. 6–7 kcal/mol larger than that expected from additivity.

Dolbier and co-workers conjectured that this additional reduction in the lowering of  $E_a$  for the rearrangement of **9** to **11** is due to destabilization of **9** by unfavorable interactions between the CF<sub>2</sub> groups.<sup>12</sup> If this were the case, the rearrangement of **9** to **11** should be more exothermic by 6–7 kcal/mol than the value of  $\Delta H = -1.9$  kcal/mol that was both measured<sup>7</sup> and calculated<sup>9</sup> for the rearrangement of **1** to **3**.

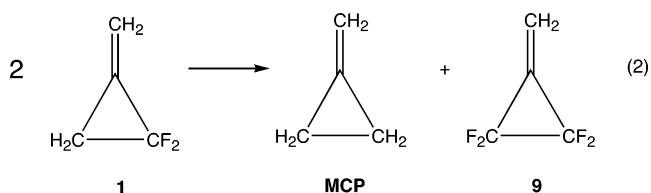
Unfortunately, so little **9** was present at equilibrium that Dolbier and co-workers were unable to measure  $\Delta H$  for the transformation of **9** into **11**.<sup>12</sup> However, we have calculated this enthalpy change, to see how it compares with the value of  $\Delta H \approx 8$ –9 kcal/mol that is expected, if repulsions between the CF<sub>2</sub> groups in **9** are wholly responsible for making the  $E_a$  for rearrangement of **9** to **11** 6–7 kcal/mol lower than predicted by substituent additivity. As shown in Table 1, our CASPT2

calculations do indeed find  $\Delta H = -8.3$  with the 6-31G\* basis set and  $\Delta H = -8.8$  kcal/mol with the 6-311+G(2df,2p) basis set for the transformation of **9** into **11**.

The difference between the enthalpies of the rearrangements of **1** to **3** and **9** to **11** is given by the isodesmic reaction in eq 1. We have confirmed that the CASPT2/6-31G\* value of  $\Delta H$

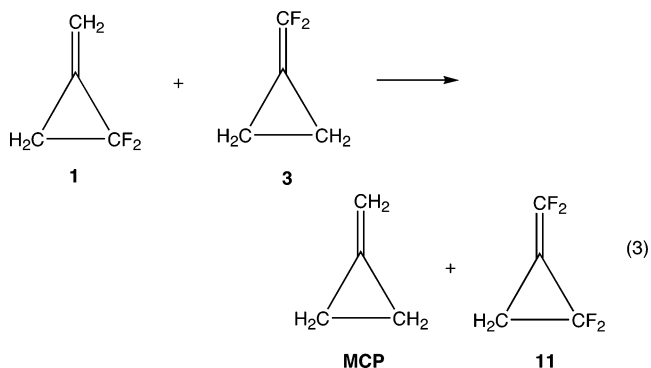


= 6.4 kcal/mol for the reaction in eq 1<sup>26</sup> is, indeed, due to repulsions between the CF<sub>2</sub> groups in **9**. To do so, we computed the enthalpy of the disproportionation reaction in eq 2, which gives the enthalpy difference between having a pair of CF<sub>2</sub> groups in the same methylenecyclopropane ring, as in **9**, or in



two different methylenecyclopropane rings, as in two molecules of **1**. The calculated CASPT2/6-31G\* enthalpy of the reaction in eq 2 is  $\Delta H = 7.0$  kcal/mol,<sup>26</sup> thus confirming the hypothesis of Dolbier and co-workers that the presence of two CF<sub>2</sub> groups in the same methylenecyclopropane ring destabilizes **9**.<sup>12</sup>

Subtracting eq 1 from eq 2 gives eq 3. The value of  $\Delta H = 0.6$  kcal/mol for eq 3 shows that having both CF<sub>2</sub> groups in the

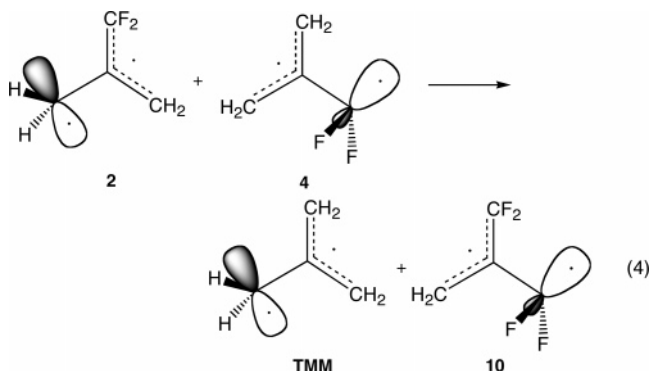


same molecule is also destabilizing for rearrangement product **11**, but by much less than for reactant **9**.

(25) For examples, see: (a) Hrovat, D. A.; Sun, H.; Borden, W. T. *THEOCHEM* **1988**, *163*, 51. (b) Johnson, W. T. G.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 5930. (c) Skancke, P. N.; Hrovat, D. A.; Borden, W. T. *J. Phys. Chem. A* **1999**, *103*, 4043.

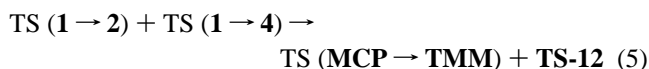
(26) CASPT2/6-31G\* enthalpies for **9**–**12** were used, so that they could be compared with the CASPT2/6-31G\* enthalpies for **1**–**5** that we had previously computed.<sup>9</sup> However, we have confirmed that the CASPT2/6-31G\* enthalpy changes, given in the text, for the reactions in eqs 1–3 differ by, at most, only a few tenths of a kcal/mol from the CASPT2/6-311+G(2df,2p) values of, respectively, 6.6, 7.2, and 0.6 kcal/mol for these three reactions.

Disproportionation reactions, similar to those in eqs 2 and 3, can be used to assess the effect of having a pair of CF<sub>2</sub> groups in diradical intermediate **10** and in the TS for ring opening of **9** to **10**. Using the CASPT2/6-31G\* results from ref 9 and from Table 1,<sup>26</sup> the enthalpy of  $\Delta H = 0.3$  kcal/mol for the reaction in eq 4 shows that, as in rearrangement product **11**, having both



CF<sub>2</sub> groups in diradical intermediate **10** results in an almost negligible amount of destabilization.

In contrast, if the four diradical intermediates in eq 4 are replaced by the four TSs that connect the diradicals to the reactants, then CASPT2/6-31G\* calculation of the enthalpy of the reaction in eq 5 finds that the presence of both CF<sub>2</sub> groups in **TS-12** destabilizes this TS to the extent of 3.7 kcal/mol.<sup>27</sup>



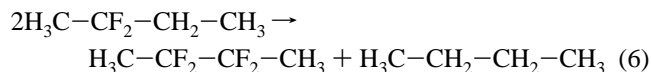
It is tempting to attribute this destabilization to a residuum of the interaction between the CF<sub>2</sub> groups, which destabilizes reactant **9** by  $\Delta H = 7.0$  kcal/mol at the CASPT2/6-31G\* level of theory.<sup>26</sup> However, the lengthening of the bond between the CF<sub>2</sub> groups, from 1.529 Å in **9** to 2.154 Å in **TS-12**, makes it not unreasonable to suppose that most of the repulsive interactions between the CF<sub>2</sub> groups in **9** are absent from **TS-12** or at least significantly reduced.

There is computational evidence that it is the stereochemistry, imposed on **TS-12** by the presence of two CF<sub>2</sub> groups, which is largely responsible for the destabilization of this TS. As already noted, **TS-12** for the ring opening of **9** retains the configuration of both CF<sub>2</sub> groups, because the TS for inverting one of them is quite high in energy (vide infra). In contrast, the TS that connects **1** to **4** maximizes overlap between the AOs of the CH<sub>2</sub> and CF<sub>2</sub> groups by inverting the configuration of the CF<sub>2</sub> group. The CASPT2/6-31G\* enthalpy of the TS that connects **1** to **4**, with retention of the configuration of the CF<sub>2</sub> group, is 3.1 kcal/mol higher than the TS that connects **1** to **4** by inverting the CF<sub>2</sub> group.<sup>9</sup> Therefore, it can be argued that the major factor in the destabilization of **TS-12** is the necessity

(27) This means that the expected value of  $\Delta H^\ddagger$  for the rearrangement of **9** to **11** is only  $7.0 - 3.7 = 3.3$  kcal/mol higher than the CASPT2/6-31G\* value of  $\Delta H^\ddagger = 30.5$  kcal/mol that is actually calculated. Using the experimental  $E_a$  values,<sup>8</sup> including an estimate of  $\Delta E_a = 0.7$  kcal/mol between the formation of **7** and **8** from **6**,<sup>11</sup>  $E_a = 38.3 - 1.9 - 0.7 = 35.7$  kcal/mol is expected for **9**  $\rightarrow$  **11**, which is 6.1 kcal/mol higher than the value of  $E_a = 29.6 \pm 1.0$  kcal/mol actually measured.<sup>10</sup> The major contributor to the  $6.1 - 3.3 = 2.8$  kcal/mol difference between the measured and calculated deviations from substituent-effect additivity in the rearrangement of **9**  $\rightarrow$  **11** is the fact that the value of  $E_a = 29.6 \pm 1.0$  kcal/mol, measured by Dolbier and co-workers for this reaction, is 1.7 kcal/mol lower than the CASPT2/6-31G\* value of  $E_a = 30.5 + 0.8 = 31.3$  kcal/mol.

for **9** to undergo ring opening with retention of configuration of both CF<sub>2</sub> groups.

**Why Is 9 Destabilized?** The near-zero enthalpies computed for the reactions in eqs 3 and 4 indicate that the CASPT2/6-31G\* value of  $\Delta H = 7.0$  kcal/mol that is computed for the reaction in eq 2<sup>26</sup> must have its origin either in the proximity of the CF<sub>2</sub> groups in **9** or in their cooperative destabilization of the three-membered ring of **9**. To test which of these two hypotheses is correct, we carried out MP2 calculations on the disproportionation reaction for the acyclic compounds in eq 6.



With the 6-31G\* basis set, this reaction was computed to be endothermic by 5.9 kcal/mol.<sup>28a,30</sup> Because this value is only 1.1 kcal/mol less than that computed for the disproportionation reaction in eq 2, it would appear that the proximity of the CF<sub>2</sub> groups in **9**, rather than their presence in the same three-membered ring, is largely responsible for the endothermicity of the reaction in eq 2.

However, the C–H and C–F bonds at C2 and C3 of **MCP**, **3**, and **9** in eq 2 are eclipsed, whereas those of the butanes in eq 6 are staggered.<sup>33</sup> Therefore, we repeated the calculation of the enthalpy of the reaction in eq 6, but with the butanes each constrained to an eclipsed conformation with the methyl groups syn to each other. With the C–H and C–F bonds at C2 and C3 of the butanes forced to be eclipsed, the reaction in eq 6 is computed to be endothermic by 11.2 kcal/mol at the MP2/6-31G\* level of theory.<sup>28b</sup>

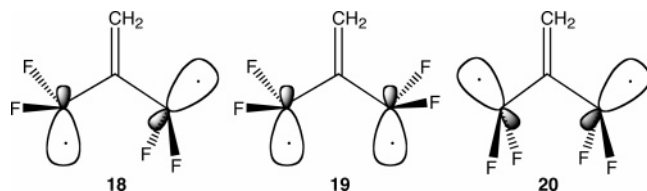
By computing the enthalpy change for anti to syn isomerization of each of the molecules in eq 6, it is easy to show that, when the butanes are constrained to the syn conformation, the 5.3 kcal/mol larger endothermicity of eq 6 is due to the large increase in destabilizing interactions in 2,2,3,3-tetrafluorobutane. The MP2/6-31G\* enthalpy increases for anti to syn isomeriza-

- (28) The following results were obtained at the MP2/6-311+G(2df,2p) level: (a) The reaction in eq 6 was computed to be endothermic by 6.5 kcal/mol, and by 6.4 kcal/mol at the G3 level of theory.<sup>29</sup> (b) With the butanes each constrained to have a syn geometry, the enthalpy of the reaction in eq 6 was computed to be 12.7 kcal/mol. (c) The enthalpy changes for anti  $\rightarrow$  syn in butane, 2,2-difluorobutane, and 2,2,3,3-tetrafluorobutane were calculated to be, respectively, 5.5, 4.3, and 9.3 kcal/mol.
- (29) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.
- (30) Unfortunately, experimental heats of formation have not been published for 2,2-difluorobutane or 2,2,3,3-tetrafluorobutane, so the accuracy of the predicted value for the endothermicity of eq 6 cannot be verified by comparison with experiment. However, the heats of formation of 1,1,1-trifluoroethane and hexafluoroethane, as well as that of ethane, are available,<sup>31</sup> and they can be used to provide an experimental value of  $\Delta H = 16.4$  kcal/mol for the enthalpy of another disproportionation reaction,  $2\text{H}_3\text{C}-\text{CF}_3 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{F}_6$ . The MP2/6-31G\* value is  $\Delta H = 17.2$  kcal/mol, and G2(MP2)<sup>32</sup> and G3 calculations<sup>29</sup> both give  $\Delta H = 17.8$  kcal/mol for this reaction.
- (31) NIST Chemistry WebBook, NIST Standard Reference Database Number 69, June 2005 Release.
- (32) Khursan, S. L. *Russ. J. Phys. Chem.* **2004**, *78 Suppl. 1*, S34.
- (33) In its lowest energy, staggered conformation, 2,2-difluorobutane is stabilized by hyperconjugative electron donation from two filled, C–H bonding orbitals at C3 into the unfilled, antibonding orbital of the C–F bond at C2 that is anti to each C–H bond. The same type of stabilizing interaction between the bonds at C2 and C3 is obviously unavailable to butane or to 2,2,3,3-tetrafluorobutane in the anti conformation. For discussions of hyperconjugation involving donation from C–H and C–C bonding orbitals into anti C–F antibonding orbitals (the “gauche effect”), see: (a) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 103. (b) Epiotis, N. D.; Yates, R. L.; Larson, C. R.; Kirmaier, C. R.; Bernardi, F. *J. Am. Chem. Soc.* **1977**, *99*, 8379. (c) Brunk, K.; Weinhold, F. *J. Am. Chem. Soc.* **1979**, *101*, 1700. (d) Rablen, P. R.; Hoffmann, R. W.; Hrovat, D. A.; Borden, W. T. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1719. (e) Goodman, L.; Sauer, R. L. *J. Chem. Theory Comput.* **2005**, *1*, 1185.

tion are 5.8 kcal/mol for butane, 5.3 kcal/mol for 2,2-difluorobutane, and 10.1 kcal/mol for 2,2,3,3-tetrafluorobutane.<sup>28c</sup> The increase in the enthalpy of 2,2,3,3-tetrafluorobutane is nearly twice as large as the increases for butane and 2,2-difluorobutane, presumably due to the much higher energetic cost of eclipsing between the pairs of C–F bonds in 2,2,3,3-tetrafluorobutane.

In **9**, as in *syn*-2,2,3,3-tetrafluorobutane, there are two pairs of eclipsed C–F bonds. Nevertheless, the enthalpy of the disproportionation reaction in eq 2 is 4.2 kcal/mol smaller than that of the disproportionation reaction in eq 6 for the *syn* conformers of the butanes. The probable reason for the smaller endothermicity of the reaction in eq 2 is that the small internal angles at C2 and C3 of the three-membered ring in **9** result in a calculated distance of 2.837 Å between eclipsed pairs of fluorines. This F–F distance in **9** is 0.434 Å larger than that in the *syn* conformation of 2,2,3,3-tetrafluorobutane. Therefore, the repulsions between the eclipsed C–F bonds are smaller in **9** than in *syn*-2,2,3,3-tetrafluorobutane.

**Ring Opening of **9** without CF<sub>2</sub> Rotations.** As already noted, we were unable to locate a low-energy TS for ring opening of **9** with inversion of configuration of just one CF<sub>2</sub> group. In C<sub>s</sub> symmetry, we were able to find a TS connecting **9** to a C<sub>s</sub> intermediate with one inverted CF<sub>2</sub> group (**18**), but on the global potential surface both this C<sub>s</sub> TS and **18** had an imaginary frequency for rotating the inverted CF<sub>2</sub> group into conjugation with the π bond to form **10**. Thus, this C<sub>s</sub> TS is actually a mountain top on the global potential energy surface, and its energy is 6.2 kcal/mol higher in energy than **TS-12** for ring opening of **9** with retention of configuration in both CF<sub>2</sub> groups.



Nevertheless, our finding that **18** has a 3.1 kcal/mol barrier to ring closure to **9** led us to investigate whether **19** and **20** are also separated from **9** by barriers. At the (4/4)CASSCF/6-31G\* level, we were, in fact, able to locate a shallow C<sub>2v</sub> minimum, corresponding to **19**, but **19** has imaginary frequencies for con- and disrotation of the CF<sub>2</sub> groups into conjugation with the double bond. The CASSCF barrier to ring closure of **19** directly to **9** is only 0.3 kcal/mol, and at the CASPT2 level ring closure of **19** to **9** becomes barrierless.

The CF<sub>2</sub> groups in **19** are, unlike those in **18**, both pyramidalized in the same direction. However, as in **18**, the singly occupied AOs in **19** are not well oriented for overlap. A measure of the degree to which singly occupied AOs interact through space in **18** and **19** is provided by the adiabatic energy differences between the lowest singlet and triplet states in these two diradicals. As shown in Table 1, in both diradicals the CASPT2 calculations actually find the triplet to be lower in energy than the singlet, by 1.2 kcal/mol in **18** and by 0.6 kcal/mol in **19**. Clearly, overlap between the singly occupied AOs in **18** and **19** is small.

Although the large lobes of the AOs on the CF<sub>2</sub> groups in **20** are directed away from each other, as in [1.1.1]propellane,<sup>34</sup> the favorable angular orientation of these AOs<sup>9</sup> was expected

to provide more bonding in **20** than in **18** or **19**. The fact that singlet **20** is calculated to be 11.2 kcal/mol lower in enthalpy than triplet **20** confirms this supposition. Table 1 shows that the CASPT2 enthalpy of **20** is also 11.2 and 12.2 kcal/mol lower than those of, respectively, **18** and **19** and only 2.4 kcal/mol higher than that of **10**.

A vibrational analysis finds that, like **9**, **20** is a true energy minimum on the global (4/4)CASSCF/6-31G\* potential energy surface. The σ bonding between the CF<sub>2</sub> groups in **20** makes their rotation unfavorable, and the large barrier to CF<sub>2</sub> group inversion makes ring closure of **20** directly to **9** energetically costly. In fact, the barrier to direct ring closure of **20** to **9** by simultaneous inversion of the configurations of both CF<sub>2</sub> groups via **TS(20/9)** is calculated to be 11.7 kcal/mol.<sup>35</sup>

Although simultaneous inversion of two isolated CF<sub>2</sub> groups would require twice as much energy as their sequential inversion, inversion of just one CF<sub>2</sub> group in **20**, to form **18**, sacrifices most of the bonding between the CF<sub>2</sub> groups in **20**. As a result, the enthalpy of the TS for ring closure of **20** to **9** via sequential inversion of the CF<sub>2</sub> groups is calculated to be 2.6 kcal/mol higher than that of **TS(20/9)** for ring closure of **20** directly to **9**, by simultaneous inversion of both CF<sub>2</sub> groups.

However, the lowest energy pathway connecting **20** to **9** involves CF<sub>2</sub> rotation, rather than inversion. Rotation of one CF<sub>2</sub> group in **20** into conjugation with the double bond has a barrier of only 1.6 kcal/mol and leads to intermediate **10'**. Rotation of the non-conjugated CF<sub>2</sub> group in **10'** requires passage over a TS that is 1.1 kcal/mol higher in energy than **10'**, and leads to **10**. From **10**, closure to **9** can occur via passage over **TS-12**. This TS is 3.6 kcal/mol lower in enthalpy than **TS(20/9)** for closure of **20** directly to **9** with simultaneous inversion of both CF<sub>2</sub> groups.

The existence of two energy minima, **9** and **20**, both with C<sub>2v</sub> symmetry and differing in the length of the C–C bonds between the two CF<sub>2</sub> groups (1.529 Å in **9** and 2.490 Å in **20**), may be regarded as a rare example of bond-stretch isomerism.<sup>13</sup> However, the relationship between **9** and **20** is unlike that between any of the other pairs of bond-stretch isomers that have been identified, experimentally or computationally. Bond-stretch isomers **9** and **20** differ in the direction of pyramidalization of the CF<sub>2</sub> groups, toward each other in **9** and away from each other in **20**. Direct interconversion of **9** and **20** is thus prevented by the large barrier to inversion of the configurations of two CF<sub>2</sub> radical centers.<sup>35</sup>

We propose the name “bond-stretch invertomers” to describe the relationship between **9** and **20** and between other bond-stretch isomers that are similarly related. Bond-stretch invertomers differ in the direction of pyramidalization of the two atoms that form a bond, so the members of a pair of bond-stretch invertomers can be distinguished by whether the large lobes or the small lobes of the AOs on these atoms point toward each other. The existence of a pair of bond-stretch invertomers

(34) Review: Wiberg, K. B. *Chem. Rev.* **1989**, *89*, 975.

(35) It should be noted that in the ring closure of **10** to **11** (and of **4'** to **5**),<sup>9</sup> the existence of an intermediate (**15**), which is analogous to **20**, is predicted at the CASSCF level of theory. However, ring closure of **15** to **11** via **TS-16** requires inversion of only one CF<sub>2</sub> group, whereas ring closure of **20** to **9** via **TS(20/9)** requires inversion of both CF<sub>2</sub> groups. Consequently, the CASSCF barrier to ring closure of 4.5 kcal/mol for passage over **TS-16** is much smaller than that of 19.7 kcal/mol for passage over **TS(20/9)**. In addition, with inclusion of dynamic electron correlation, the CASPT2 barrier to passage over **TS-16** vanishes, but the CASPT2 barrier of 11.7 kcal/mol for passage over **TS(20/9)** remains substantial.

requires that the overlap between the AOs in both geometries is strong enough and that the barrier to inversion of the pyramidalized atoms is high enough to make both geometries true energy minima.

### Conclusions

Our CASPT2 calculations give an energy of activation for the rearrangement of **9** to **11** that is in very good agreement with the value of  $E_a = 29.6$  kcal/mol measured by Dolbier and co-workers.<sup>12</sup> Our calculations confirm Dolbier's conjecture,<sup>12</sup> that the reason the  $E_a$  for rearrangement of **9** to **11** is 8.7 kcal/mol lower than  $E_a = 38.3$  kcal/mol for rearrangement of **1** to **3**<sup>7</sup> is destabilization of **9** by the pairs of eclipsed CF<sub>2</sub> bonds at C2 and C3 of its cyclopropane ring, rather than stabilization of the TS for forming **11** from **9**.

Our calculations reveal that eclipsing is much more destabilizing for vicinal pairs of C–F bonds than either for vicinal pairs of C–H bonds or for C–F bonds that are vicinal to C–H bonds. However, the calculated enthalpy of the disproportionation reaction in eq 6 shows that, even in the lowest energy, staggered conformations, the interactions between the vicinal pairs of C–H bonds in butane and the vicinal pairs of C–F bonds 2,2,3,3-tetrafluorobutane are less favorable than the interactions between the vicinal C–H and C–F bonds in 2,2-difluorobutane.<sup>30,33</sup>

Our CASPT2 calculations of the potential surface for rearrangement of **9** have identified **20**, a bond-stretch isomer of **9**, as a local minimum. These two isomers differ by inversion of both of the pyramidalized CF<sub>2</sub> groups that form the unique C–C bond in **9** and **20**. In **9**, bonding occurs between the large “front” lobes of the hybridized AOs on the CF<sub>2</sub> groups, whereas in **20** bonding involves the small “back” lobes of these AOs. We propose the name “bond-stretch invertomers” to describe the relationship between a pair of bond-stretch isomers that differ in this manner.

For a pair of bond-stretch invertomers both to be local minima, the overlap between the unique pair of AOs in both geometries must be strong enough to prevent rotation, and the barrier to inversion of the radicals that form the bond must be high enough to create a barrier to direct conversion of the higher to the lower energy bond-stretch invertomer. Molecules that contain pairs of atoms from the second row of the periodic table and beyond, where barriers to inversion of radical centers are higher than in the first row,<sup>36</sup> are therefore good candidates for having pairs of bond-stretch invertomers. Whether this is in fact the case and whether the existence of bond-stretch invertomers will prove to be of chemical significance, rather than of purely theoretical interest, are both the subject of computational studies that are currently in progress.

**Acknowledgment.** We thank the National Science Foundation and the Robert A. Welch Foundation for support of this research. Some of the results reported here were obtained on computers, purchased with funds provided by the National Science Foundation under grant CHE-0342824. We are grateful to Professor Bill Dolbier for his helpful comments on our manuscript and to Professor Roald Hoffmann for a stimulating exchange of e-mail messages about the possible effect of through-bond interactions on the singlet–triplet energy differences in bond-stretched invertomers.

**Supporting Information Available:** Optimized geometries, energies, thermal corrections, and vibrational frequencies for all of the minima and TSs discussed in the text and references, and the complete list of authors for ref 16. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA065963Y

(36) Review: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.