Ab Initio calculations of the potential surfaces for rearrangement of methylenecyclopropane and 2,2-difluoromethylenecyclopropane. Why do the geminal fluorines have little effect on lowering the activation energy? †

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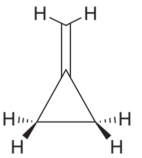
(4/4)CASSCF and CASPT2 calculations with the 6-31G* basis set have been performed in order to understand the experimental observation that the geminal fluorines in 2,2-difluoromethylenecyclopropane (**2**) have only a small effect on lowering the activation energies for its degenerate and non-degenerate methylenecyclopropane rearrangements, relative to the activation energy for the rearrangement of the hydrocarbon (**1**). As expected from previous experimental and computational studies, the geminal fluorines are calculated to destabilize the three-membered ring in **2** thermodynamically. The small amount of kinetic destabilization of **2** is shown to be due to a nearly equal destabilization of the transition structures for its rearrangements. The high energies of the transition structures are attributed to the strong preference of a CF_2 group for a pyramidal geometry. This preference is found to destabilize the transition structures both for forming a σ bond to the fluorinated carbon in the degenerate methylenecyclopropane rearrangement of **2** and for making a π bond to this carbon in the non-degenerate rearrangement of **2** to (difluoromethylene)cyclopropane (**4**).

It has been found experimentally that the presence of a pair of geminal fluorine substituents raises the strain energy of cyclopropane.[1] Heats of hydrogenation suggest a thermodynamic increment of 12–14 kcal mol^{-1}.[2] In good agreement with experiment, RHF calculations find that the hydrogenation energy of 1,1-difluorocyclopropane to give 2,2-difluoropropane exceeds the hydrogenation energy of cyclopropane by 11.7 kcal mol^{-1} with the 4-31G basis set,[3] by 12.5 kcal mol^{-1} with 6-31G*, and by 13.6 kcal mol^{-1} at the MP2/6-31G* level.[4] Kinetic studies by Dolbier and co-workers have found that geminal difluoro substitution at a ring carbon lowers E_a for *cis–trans* isomerization of 1,2-dimethylcyclopropane by 9.7 kcal mol^{-1} [5,7] and for the rearrangement of vinylcyclopropane to cyclopentene by 9.4 kcal mol^{-1}.[7]

However, Dolbier and Fielder[9] found that geminal difluoro substitution at a ring carbon in methylenecyclopropane (**1**) lowers E_a for the methylenecyclopropane rearrangement of **2** to **4** by only 2 kcal mol^{-1}, relative to the E_a for this rearrangement in the methyl derivative of the hydrocarbon. In subsequent studies on **3**, in which a methyl substituent also labels the methylene group of the ring, Dolbier and co-workers found that formation of the *E* and *Z* stereoisomers of **7** occurs at about 1.5 times the rate of formation of **5**.[10] Thus the CF_2 group in **2** appears to have little effect on accelerating either the degenerate methylenecyclopropane rearrangement of **2** to **6** or the non-degenerate rearrangement of **2** to **4**.

Unlike the case in either 1,1-difluorocyclopropane or in 1,1-difluoro-2-vinylcyclopropane, in **2** the only ring bond that can cleave is the one that is proximal to the fluorinated ring carbon. Therefore, Dolbier and Fielder drew the reasonable conclusion that geminal difluorination of a cyclopropane ring carbon exerts only a small effect on the energy required to cleave a C–C bond proximal to it but weakens the distal C–C bond by 9–10 kcal mol^{-1}.[9] This conclusion appears to have been generally accepted.[1]



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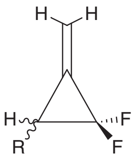
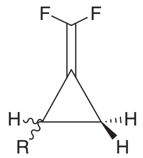
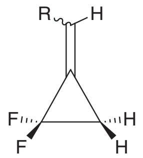


2, R = H
3, R = CH_3



4, R = H
5, R = CH_3



6, R = H
7, R = CH_3

Although reasonable, this conclusion is not supported by the results of *ab initio* calculations on the stereomutation of 1,1-difluorocyclopropane.[4a,6] At all levels of theory these calculations find that the transition structures for *cis–trans* isomerization by rotation of one methylene group have almost the same energy whether the ring bond broken is distal or proximal to the difluorinated carbon. This computational result explains why significant amounts of the products that arise from proximal C–C bond cleavage were found in the study of 1,1-difluoro-2-vinylcyclopropane rearrangements by Dolbier and Sellers.[8]

The enthalpies of activation for methylene monorotation in 1,1-difluorocyclopropane by cleavage of either distal or proximal ring bonds were calculated[4a,6] to be 7–8 kcal mol^{-1} lower than the enthalpy of activation for rotation of one methylene group in cyclopropane.[11] The calculated energy lowering is in good agreement with Dolbier and Enoch's experimental value of 9 kcal mol^{-1} for the effect of geminal fluorines on reducing the barrier to *cis–trans* isomerization in 1,2-dimethylcyclopropane.[5]

Since geminal fluorines are calculated to have a large effect on reducing the energy required for cleavage of a cyclopropane ring bond that is either proximal or distal to them, it is puzzling that the geminal fluorines in **2** have only a small effect on

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† Optimized geometries and energies for all the molecules for which calculations were performed are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/2339, otherwise available from BLDSC (SUPPL. NO. 57597) or the RSC library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

reducing the energy required for its methylenecyclopropane rearrangement, compared to that for rearrangement of unfluorinated **1**. In order to understand this experimental finding, we have performed *ab initio* calculations of the potential surfaces for the methylenecyclopropane rearrangements of **1** and **2**. In this paper we report the results of these calculations.

Computational methodology

Stationary points on the potential surfaces for the methylenecyclopropane rearrangements of **1** and **2** were located by performing (4/4)CASSCF calculations with the 6-31G* basis set.[12] Vibrational analyses were performed at these points, using analytical second derivatives of the (4/4)CASSCF/6-31G* energies. The vibrational analyses were used to identify stationary points as energy minima or transition structures; and, for the latter, the transition vectors were used to ascertain which pair of energy minima were connected by each transition structure. The zero-point and thermal corrections obtained from the vibrational analyses were used, without scaling, to calculate enthalpy differences at 500 K. The geometries of the stationary points are available as supplementary data.†

The (4/4)CASSCF wavefunctions consisted of all singlet configurations that can be formed by distributing four electrons among four active orbitals. In **1** and **2** these orbitals were the π and π^* orbitals and the σ and σ^* orbitals of the scissile C–C bond. The (4/4)CASSCF calculations were carried out using the Gaussian 94 suite of programs.[13]

The (4/4)CASSCF calculations do not include correlation between the active and inactive electrons. Dynamic correlation[14] between these two sets of electrons was included by performing CASPT2 calculations[15] at all the (4/4)CASSCF stationary points. The CASPT2 calculations were carried out with the MOLCAS package of *ab initio* programs.[16]

Results and discussion

The (4/4)CASSCF/6-31G* and CASPT2 calculations of the potential surface for rearrangement of the hydrocarbon **1** were carried out, so that the results could be compared with the results of our calculations on fluorocarbon **2**, performed at the same levels of theory. (4/4)CASSCF calculations on **1** were published in 1982.[17] However, the limitations of the computational hardware and software that were available eighteen years ago allowed geometry optimizations to be performed only with the minimal STO-3G basis set. In addition, at that time analytical second derivatives for characterizing stationary points and computing vibrational frequencies were unavailable. The results of our calculations on **1** are described in the next subsection.

The second subsection presents computational results which show that replacing two hydrogens in **1** by the geminal fluorines in **2** increases the ring strain by even more than introduction of geminal fluorines into cyclopropane. Consequently, the rather small effect of the fluorines in **2** on reducing the activation energies for its rearrangements to **4** and **6** must be due to the fact that the fluorines also raise the energies of the transition structures for these rearrangements, relative to the transition structure for the methylenencyclopropane rearrangement of **1**.

The subsequent subsections describe and discuss the results of calculations that were performed in order to understand why the fluorines in **2** apparently raise the energies of the transition structures for the methylenecyclopropane rearrangements of **2**. We find that the large energetic preference of a CF_2 radical center for a pyramidal geometry[18] is responsible for destabilizing the transition structures in both the degenerate methylenecyclopropane rearrangement of **2** to **6** and in the non-degenerate rearrangement of **2** to **4**.

Potential surface for the rearrangement of 1

The (4/4)CASSCF/6-31G* potential surface for methylenecyclopropane rearrangement of **1** has another energy minimum in addition to that for **1**. The second energy minimum corresponds to a ring-opened intermediate (**8**) in which one of the methylene groups in the cyclopropane ring of **1** has rotated by 90°, so that it is conjugated with the exocyclic double bond. These two minima are connected by the transition structure ($\mathbf{TS}_{1\rightarrow 8}$) shown in Fig. 1, which is encountered after this methylene group has rotated by about 60° from its geometry in **1**.

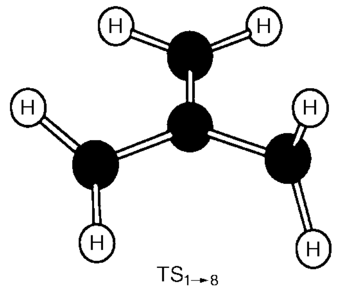
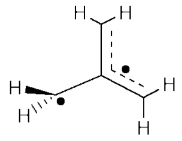


Fig. 1 Transition structure ($\mathbf{TS}_{1\rightarrow 8}$), connecting methylenecyclopropane (**1**) with the singlet trimethylenemethane diradical intermediate (**8**).

At the (4/4)CASSCF/6-31G* level of theory the methylene group that remains unrotated in **8** is slightly pyramidalized, so that the resulting geometry has C_s symmetry. Planarization of this methylene group gives a C_{2v} structure with one negative force constant, corresponding to the vibrational mode for inversion of this methylene group. At the CASSCF level this C_{2v} transition structure is calculated to be 0.1 kcal mol^{-1} higher in energy than the C_s structure, but at the CASPT2 level it is lower in energy than the C_s structure by 0.3 kcal mol^{-1}. The CASPT2 energy and enthalpy for **8** in Table 1 have been corrected for this 0.3 kcal mol^{-1} difference, so that they correspond to those of the C_{2v} geometry.

The reason for the energetic favorability of having one methylene group twisted out of conjugation in the singlet but not in the triplet state of the trimethylenemethane (TMM) diradical has been discussed previously.[17,19] The energetic preference for the "orthogonal" geometry of **8** over the planar geometry of **9** is responsible for the experimental finding that derivatives of **1** rearrange with predominant inversion of configuration at the migrating carbon.[20]



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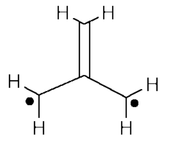


9

The planar diradical (**9**) can, in principle, be accessed from **1** by either conrotation or disrotation of both methylene groups or by 90° rotation of just one methylene group, to form **8**, followed by rotation of the second methylene group. However, on the (4/4)CASSCF potential surface conrotation and disrotation in **1** each lead to an energy maximum after coupled rotation of the methylene groups by about 50°. Vibrational analyses show that both of these stationary points are mountain tops on the global potential surface.[21] Each is an energy maximum with respect to both a symmetry-preserving and a symmetry-destroying vibration. In each case the latter type of vibration rotates one methylene group into conjugation with the double bond and the other methylene group out of conjugation with the double bond, thus leading toward the geometry of **8**.

The (4/4)CASSCF vibrational analysis finds that, unlike **8**, which is an energy minimum, **9** is a transition structure. The C_{2v} geometry of **9** means that it cannot be the transition structure for rotation of just one methylene group into planarity. This would require that both conrotation and disrotation have negative force constants; and, if **9** had two negative force

Table 1 Relative electronic and zero-point energies and enthalpies (kcal mol^{-1}) for the stationary points on the potential surface for the rearrangement of methylenecyclopropane (**1**). Calculated at (4/4)CASSCF optimized geometries with the 6-31G* basis set

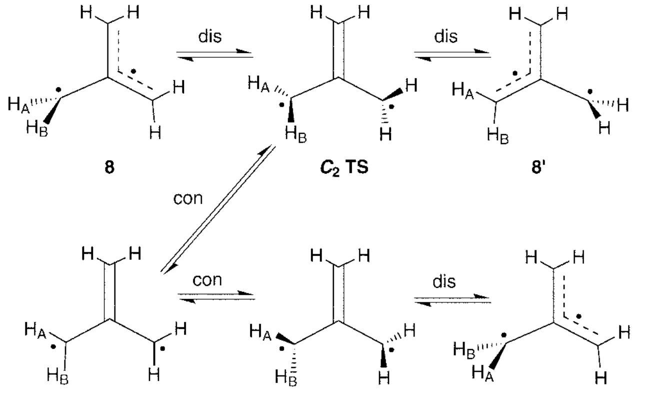
	CASSCF			CASPT2	
Structure	ΔE	ΔZPE	ΔH_{500}	ΔE	ΔH_{500}
1	−154.93227[a]	56.7[b]	−154.83002[a,c]	−155.41886[a]	−154.31661[a,c]
8	31.9[d]	−4.4[d]	29.0[d]	39.0[e]	36.2[e,f]
$\mathbf{TS_{1\rightarrow 8}}$	35.5	−4.4	31.9	42.5	38.9
$\boldsymbol{C_{2v}}$ **TS (9)**	37.1	−6.1	32.8	44.1	39.8
$\boldsymbol{C_2}$ **TS**	37.1	−6.0	32.8	44.2	39.9

[a] Energy in hartrees. [b] Energy in kcal mol^{-1}. [c] Sum of electronic energy and zero-point and thermal corrections, computed from CASSCF/6-31G* frequencies. [d] Value for the C_s geometry. [e] Value for the C_{2v} geometry, which is 0.3 kcal mol^{-1} lower in energy than the C_s geometry at the CASPT2 level. [f] Taken to be equal to the enthalpy of the C_s geometry, minus the 0.3 kcal mol^{-1} difference between the CASPT2 energies of C_s and C_{2v}.

constants, it would be a mountain top, not a transition structure. The single imaginary force constant in **9** corresponds to conrotation.

Following a conrotatory pathway from **9** leads to another transition structure after both methylene groups have been rotated about 8° from coplanarity. The lessening of steric interactions between the methylene hydrogens in the planar geometry of **9** is apparently almost exactly balanced by loss of conjugation of the methylene p-π orbitals with the double bond, because, on going from **9** to this nearby C_2 transition structure ($\boldsymbol{C_2}$ **TS**), the CASSCF energy decreases by only 0.003 kcal mol^{-1}.

Since the negative force constant in **9** is for conrotation, **9** cannot lead directly to another transition structure with a negative force constant for conrotation. Indeed, the negative force constant in $\boldsymbol{C_2}$ **TS** corresponds to a symmetry-breaking, disrotatory vibration that moves one methylene toward planarity and the other away from it. Thus, as shown in Scheme 1, $\boldsymbol{C_2}$ **TS** interchanges the non-conjugated methylene and one of the conjugated methylene groups in **8**. The C_{2v} geometry of **9** is the transition state for rotating the non-conjugated methylene group in **8** through the molecular plane.



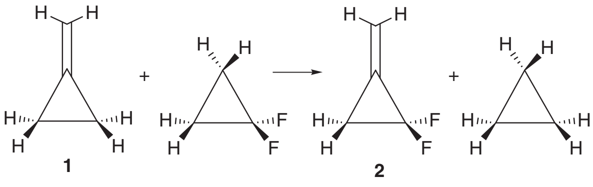
Scheme 1 Depiction of the interchange of conjugated and non-conjugated methylene groups in **8** to form **8′** *via* the $\boldsymbol{C_2}$ **TS** and the exchange of H_A and H_B in **8** to form **8″** *via* the $\boldsymbol{C_{2v}}$ **TS (9)**. The latter connects the $\boldsymbol{C_2}$ **TS** with its mirror image ($\boldsymbol{C_2}$ **TS′**), *via* a conrotatory reaction coordinate. The $\boldsymbol{C_2}$ **TS** connects **8** with **8′** *via* a disrotatory reaction coordinate, which destroys the C_2 symmetry of the transition structure.

As already noted, at the CASSCF level **9** and $\boldsymbol{C_2}$ **TS** have essentially the same energy; and this is also true at the CASPT2 level. The relative CASPT2 energies of **1**, **8**, $\mathbf{TS_{1\rightarrow 8}}$, **9**, and $\boldsymbol{C_2}$ **TS** are given in Table 1. Also given are the zero-point energies and enthalpy differences calculated using the unscaled thermal corrections from the CASSCF vibrational analyses.

The calculated value of $\Delta H^{\ddagger}_{500} = 38.9$ kcal mol^{-1} ($E_a = 39.9$ kcal mol^{-1} at 500 K) for the degenerate methylenecyclopropane rearrangement of **1**, *via* passage over $\mathbf{TS_{1\rightarrow 8}}$, is in excellent agreement with the experimental value of $E_a = 40.4$ kcal mol^{-1} measured for the methyl derivative of **1**.[22] As shown in Table 1, although the CASPT2 energy of intermediate **8** is calculated to be 5.1 kcal mol^{-1} lower than that of **9**, $\mathbf{TS_{1\rightarrow 8}}$ is computed to be only 1.6 kcal mol^{-1} below **9**. The small size of the calculated difference between the activation enthalpies for degenerate rearrangement of **1** with inversion of configuration, *via* $\mathbf{TS_{1\rightarrow 8}}$, and with loss of stereochemistry at the migrating carbon, *via* transition structure **9**, is consistent with the experimental finding that in the methylenecyclopropane rearrangements of derivatives of **1** inversion of configuration at the migrating carbon is accompanied by some racemization.[20a,d]

Relative strain energies of 1 and 2

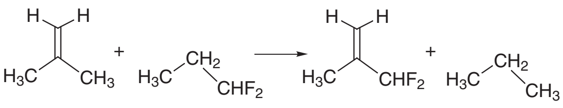
One possible explanation for the surprisingly small effect of the fluorines in **2** on reducing the activation energy for the rearrangement of **2** to **4**[9] and **6**[10] is that replacement of two geminal ring hydrogens in **1** by fluorines causes a smaller increase in strain energy than substitution of geminal fluorines in cyclopropane.[1–4] This possibility was checked computationally by calculating the energy of the isodesmic reaction (1). This



(1)

reaction is computed to be unfavorable, resulting in energy increases of 3.3 and 3.1 kcal mol^{-1} at, respectively, the RHF and MP2 levels of theory. Thus, introduction of geminal fluorines actually causes a larger increase in strain energy in **1** than in cyclopropane.[23]

The major part of this increase appears to come from introducing geminal fluorines at an allylic CH_2 group. The energetic unfavorability of this fluorine for hydrogen substitution reaction can be seen in the computational finding that the reaction (2) is unfavorable by, respectively, 2.5 and 2.6 kcal mol^{-1} at the RHF and MP2 levels of theory.



(2)

The energy computed for eqn. (1) shows that introduction of geminal fluorines into **1** to form **2** is actually >3 kcal mol^{-1} *more* thermodynamically destabilizing than introduction of geminal fluorines into cyclopropane. Therefore, the small size of the effect that geminal fluorination has on making the activation energy for rearrangement of **2** lower than that of **1**

Table 2 Relative electronic and zero-point energies and enthalpies (kcal mol^{-1}) for the stationary points on the potential surface for rearrangement of 1,1-difluoromethylenecyclopropane (**2**), calculated at (4/4)CASSCF optimized geometries with the 6-31G* basis set

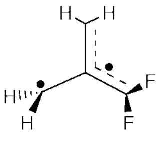
	CASSCF			CASPT2	
Structure	ΔE	ΔZPE	ΔH_{500}	ΔE	ΔH_{500}
2	−352.63499[a]	46.5[b]	−352.54608[a,c]	−353.45825[a]	−353.36934[a,c]
4	0.1	0.6	0.6	−2.4	−1.9
10	32.2	−3.2	30.3	37.5	35.6
11[d]	32.9	−4.3	29.6	36.5	34.6[e]
12[f]	24.9	−2.2	23.3	29.8	28.3
13[g]	36.0	−2.9	33.6	40.1	37.7
14	31.1	−2.8	28.7	37.1	34.6
15[h]	30.8	−2.5	29.4	37.2	35.8
16	36.6	−2.8	34.2	37.1	34.6
17[i]	27.3	−2.5	24.6	31.3	28.6
25[j]	33.3	−2.7	30.8	39.4	36.9
26[k]	35.1	−3.9	32.1	39.7	36.6

[a] Energy in hartrees. [b] Energy in kcal mol^{-1}. [c] Sum of electronic energy and zero-point and thermal corrections, computed from CASSCF/6-31G* frequencies. [d] CASPT2 intermediate in the rearrangement of **2** to **4**. [e] Taken to be equal to the enthalpy of **10**, minus the 1.0 kcal mol^{-1} difference between the CASPT2 energies of **10** and **11**. [f] Intermediate in the degenerate rearrangement of **2**. [g] Transition structure connecting **12** and $\mathbf{2}_A$. [h] Putative CASPT2 transition structure connecting **12** and $\mathbf{2}_B$ with inversion of the CF$_2$ group. [i] C_s transition structure for CF$_2$ rotation in **12**. [j] Transition structure connecting **11** and **2**. [k] Transition structure connecting **11** and **4**.

cannot be ascribed to a smaller destabilization of **2** than of 1,1-difluorocyclopropane. Thus, it must be the case that geminal fluorines destabilize the transition structures for the rearrangement reactions of **2**, relative to $\mathbf{TS}_{1\rightarrow 8}$ for the rearrangement of **1**, by almost as much as they thermodynamically destabilize **2**, relative to **1**.

Intermediates in the rearrangement of 2 to 4 and 6

In the rearrangement of **2** two different singlet diradicals, **10** and **12**, correspond to intermediate **8** in the rearrangement of **1**. CASSCF vibrational analyses show that **10** and **12** are, indeed,



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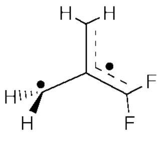

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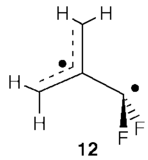

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intermediates on the singlet potential surface for rearrangement of **2**. Their CASSCF and CASPT2 energies are given in Table 2, relative to the energy of **2**. At all levels of theory, **10**, which is an intermediate in the rearrangement of **2** to **4**, is about 7 kcal mol^{-1} higher in energy than **12**, which is an intermediate in the degenerate rearrangement of **2** to **6**.

The lower energy of **12** can be attributed to the fact that it contains a highly pyramidalized CF$_2$ radical center; whereas, π bonding to the CF$_2$ group in **10** requires that it be much more nearly planar. We have previously shown that the preference of CF$_2$ radical centers for pyramidal geometries weakens π bonds,[18] for example, those in tetrafluoroethylene[24a] and in 1,1-difluoro- and 1,1,3,3-tetrafluoroallyl radicals.[24b,c] Upon ring opening of **2**, the same effect favors forming a π bond to CH$_2^{\bullet}$, to give **12**, in preference to forming a π bond to CF$_2^{\bullet}$, to give **10** or its C_s variant with a planar CF$_2$ group (**11**).[25a]

Not surprisingly, in the (4/4)CASSCF optimized geometries of **10** and **12** the pyramidalization angle, φ, at the CF$_2$ group[26] is smaller in the former ($\varphi = 32.7°$) than in the latter ($\varphi = 44.2°$). CF$_2$ pyramidalization in **10** sacrifices some allylic conjugation with the double bond; and the fact that in the CASSCF optimized geometry of **10**, the CF$_2$ group is pyramidalized at all gives some indication of how substantial the driving force for CF$_2$ pyramidalization must be.

Planarization of the CF$_2$ group in **12** requires 14.4 kcal mol^{-1} at the CASSCF level but only 10.9 kcal mol^{-1} at CASPT2.[25b] In previous studies we have also found that planarization of radical centers is less energetically costly when dynamic electron correlation is included.[27]

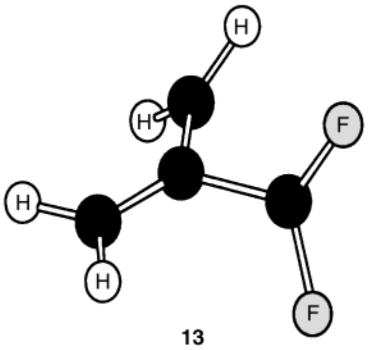
Planarization of **10** to form **11** requires only 0.7 kcal mol^{-1} at the CASSCF level; and at the CASPT2 level **11** is actually 1.0 kcal mol^{-1} lower in energy than **10**. Presumably, **11** is a true intermediate on the CASPT2 potential energy surface, and we assume that its CASPT2 enthalpy is equal to that of **10**, minus the 1.0 kcal mol^{-1} CASPT2 energy difference between them.

Comparison of the CASPT2 enthalpy difference of 36.2 kcal mol^{-1} between **8** and **1** in Table 1 with that of 28.3 kcal mol^{-1} between **12** and **2** in Table 2 shows that substitution of geminal fluorines on the ring of methylenecyclopropane reduces the calculated enthalpy difference between it and the diradical intermediate by 7.9 kcal mol^{-1}. Breaking a proximal bond in 1,1-difluorocyclopropane by rotating one methylene by 90° and forming a diradical with a pyramidalized CF$_2$ group is also calculated to require 7–8 kcal mol^{-1} less energy than the same process in cyclopropane.[4b,6]

However, the energetic cost of planarizing the CF$_2$ group in **12**, in order to form the π bond to this group in **11**, results in the enthalpy of **11** being computed to be 6.3 kcal mol^{-1} higher than that of **12** at the CASPT2 level. Consequently, the CASPT2 enthalpy difference between **11** and **2** is only 1.6 kcal mol^{-1} smaller than that between **8** and **1**. The experimental finding of Dolbier and Fielder,[9] that geminal fluorines have an effect of only about this size on lowering $\Delta H^{\ddagger}$ for the methylenecyclopropane rearrangement of **2** to **4**, can thus be understood on the basis of similar destabilizations by the geminal fluorines of **2** and the CASPT2 diradical intermediate (**11**) in this rearrangement.

Since the CASPT2 enthalpy of diradical **12** is 6.3 kcal mol^{-1} lower than that of diradical **11**, one might expect that the degenerate methylenecyclopropane rearrangement of **2** *via* **12** would be much faster than the non-degenerate rearrangement of **2** to **4** *via* **11**. However, this expectation is not supported by the experimental finding of Dolbier and coworkers that the rate of formation of **7** from **3** is only 1.5 times faster than the rate of formation of **5**.[10]

These experimental results are, of course, not necessarily inconsistent with the results of our calculations, since we find **11** and **12** to be intermediates, not transition structures, along the two different pathways by which **2** can rearrange. The experiments of Dolbier and coworkers indicate that the energy of the transition structure connecting **12** to **2** is comparable to that of the higher energy of the two transition structures connecting **11** to **2** and **4**. Therefore, the activation energy for ring closure of diradical intermediate **12** to **2** must be ~6 kcal mol^{-1}



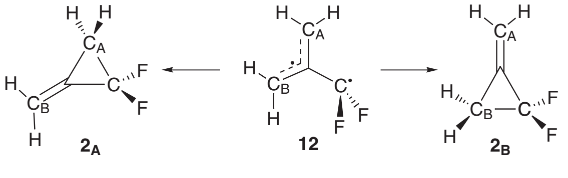
13

Fig. 2 Transition structure **13**, connecting 2,2-difluoromethylenecyclopropane (**2**) with the difluorotrimethylenemethane diradical intermediate (**12**) *via* a pathway that involves front-side bonding to the CF_2 group.

higher than the activation energy for closure of **11** to either **2** or **4**. In order to investigate why this apparently is the case, we performed additional calculations to locate the transition structures for closure of diradical intermediates **11** and **12**.

Transition structures connecting 2 and 12

Because the CF_2 group in diradical **12** is pyramidalized, there are two different modes of ring closure possible, depending upon which methylene group in **12** rotates to form a bond to the



CF_2 group. Rotation of C_A, leading to closure to 2_A, might be expected to be favored over rotation of C_B, leading to closure to 2_B, since the latter reaction pathway requires inversion of the pyramidal CF_2 group. However, our calculations find that the transition structure for the pathway that leads to 2_B is actually lower in energy by *ca.* 2 kcal mol^{-1} than the transition structure for the pathway that leads to 2_A.

The transition structure (**13**) connecting **12** to 2_A is shown in Fig. 2. Unlike the case in $TS_{1\rightarrow8}$, shown in Fig. 1, where only an allylic CH_2 group has rotated from its conformation in **8**, in **13** both the CF_2 and C_AH_2 group have rotated from their conformations in **12**. When the CF_2 group was constrained to be bisected by the plane containing the fluorinated carbon and the two carbons of the incipient double bond, as it is in **12**, the energy of **13** increased by 2.3 kcal mol^{-1}.

Because the CF_2 radical center in **12** must invert in order for closure to 2_B to occur, the pathway connecting **12** to 2_B is more complicated than the pathway that leads from **12** to 2_A. After rotation of C_BH_2 by 63.7° from its geometry in **12**, transition structure **14** (Fig. 3) is reached. As shown in Table 2, the CASPT2 enthalpy of **14** is 3.1 kcal mol^{-1} lower than that of transition structure **13**.

Surprisingly, following the reaction coordinate from **14** toward 2_B led, not to 2_B, but to another intermediate (**15**), lying 0.3 kcal mol^{-1} below **14** at the CASSCF level of theory. However, zero-point energy and thermal corrections result in **15** being slightly higher in enthalpy than **14** at both the CASSCF and CASPT2 levels of theory.

As shown in Fig. 3, the CF_2 and CH_2 groups in **15** are perfectly oriented for closure to 2_B; but, because C–C bond formation requires inversion of the CF_2 radical center, a barrier to ring closure is encountered at the CASSCF level of theory. This was found to be the case whether the 6-31G*, 6-311G*, or 6-31+G* basis set was used.

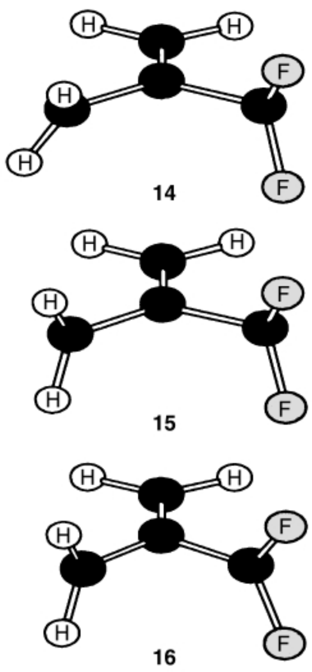


Fig. 3 (4/4)CASSCF stationary points (**14**–**16**), which lie on the pathway connecting 2,2-difluoromethylenecyclopropane (**2**) and difluorotrimethylenemethane diradical intermediate **12** with inversion of the CF_2 group. At (4/4)CASSCF **14** and **16** are transition structures, and **15** is an energy minimum with nearly the same energy as **14**, but at CASPT2 **15** is very slightly higher in energy than both **14** and **16**.

At the CASSCF/6-31G* level a transition structure (**16**) for closure of **15** to 2_B was located, 5.8 kcal mol^{-1} above **15**. Transition structure **16**, which is shown in Fig. 3 (bottom), has a C_B–C–CF_2 bond angle of 93.4° and a pyramidalization angle at the CF_2 group of 16.1°, which are, respectively, 17.8° and 25.0° smaller than the corresponding angles in **15**. These two angles are obviously strongly coupled in this region of the potential surface, showing that depyramidalization of the CF_2 group and ring closure to 2_B occur synchronously.

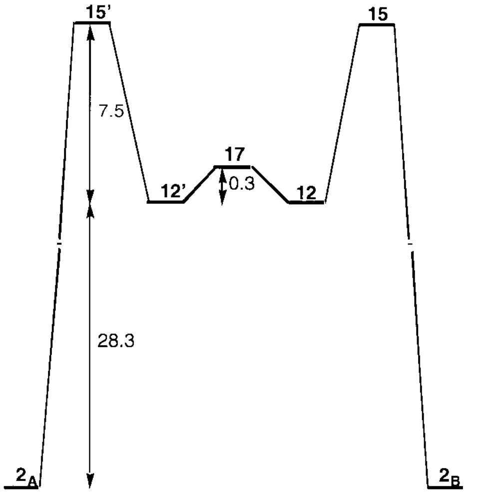
As discussed in connection with the energy required to planarize the CF_2 groups in diradicals **10** and **12**, inclusion of electron correlation has a substantial effect on reducing the energy required for planarization of a radical center.[27] Thus, it is perhaps not surprising that, as shown in Table 2, **16** is calculated to have essentially the same CASPT2 energy as **14** and **15**. In fact, **15**, which is an intermediate between transition structures **14** and **16** at the CASSCF level of theory is very slightly higher in energy than either **14** or **16** at the CASPT2 level. At this level of theory the substantial CASSCF energy barrier to closure of **14** has apparently almost disappeared, but the need to invert the geometry of the CF_2 radical center still keeps the CASPT2 energy from dropping rapidly on going from **14** to **16**. Consequently, this region of the CASPT2 potential energy surface for ring closure of **12** to 2_B is extremely flat.

The CASPT2 enthalpy of **15** is made higher than that of either **14** or **16** by the fact that at the CASSCF level **15** is an energy minimum and therefore has one more real vibrational frequency than both **14** and **16**. Nevertheless, because **15** has a slightly higher CASPT2 energy than either **14** or **16**, **15**, or a geometry close to it, is probably the transition structure for ring closure of **12** to 2_B on the CASPT2 energy surface. The CASPT2 enthalpy of **15** is, as shown in Table 2, 7.5 kcal mol^{-1} above that of **12** but 1.9 kcal mol^{-1} lower in enthalpy than the transition structure (**13**) that connects **12** and 2_A without inversion of the geometry of the CF_2 group. The reason for the rather surprising finding that the lowest energy pathway for ring closure of **12** is one in which bonding occurs at the "back side" of the CF_2 group is discussed in a subsequent section.

Without the labels at C_A and C_B, 2_A and 2_B are identical. Therefore, if **12** closes to 2_B with preferential inversion of the geometry of the CF_2 radical center, there must be a pathway that allows **12** also to close to $\mathbf{2}_A$ with CF_2 inversion. Clearly this pathway must involve a reversal in the direction of pyramidalization of **12**, so that the singly occupied orbital of the CF_2 group points toward C_BH_2, rather than towards C_AH_2.

One possible mechanism for reversal of the sense of pyramidalization of the CF_2 radical center would be for it to become planar. However, the 10.9 kcal mol^{-1} that is computed at the CASPT2 level to be required for planarization of the CF_2 group in **12** makes rotation of the CF_2 group a much lower energy pathway.

The transition structure for CF_2 rotation (**17**) has C_s, but not C_{2v} symmetry, because, as expected, the CF_2 group in **17** remains pyramidalized. Table 2 shows that at the CASPT2 level of theory, **17** is only 0.3 kcal mol^{-1} above **12** in enthalpy and 7.2 kcal mol^{-1} below **15**, the CASPT2 transition structure for ring closure of **12** to **2**. The enthalpy changes along the reaction path for the degenerate rearrangement of $\mathbf{2}_A$ to $\mathbf{2}_B$ are presented graphically in Scheme 2.



Scheme 2 Depiction of the surface (CASPT2 enthalpies in kcal mol^{-1}) for the degenerate methylenecyclopropane rearrangement of $\mathbf{2}_A$ to $\mathbf{2}_B$. Structures **12′** and **15′** are related to **12** and **15** by interchange of C_AH_2 and C_BH_2.

Effect of CF_2 pyramidalization on the ring closure of 12

As shown in both Scheme 2 and Table 2, the CASPT2 activation enthalpy for the degenerate methylenecyclopropane rearrangement of **2** *via* transition structure **15** is $\Delta H^{\ddagger} = 35.8$ kcal mol^{-1}. The activation enthalpy for this rearrangement of fluorocarbon **2** can be compared to the value of $\Delta H^{\ddagger} = 38.9$ kcal mol^{-1} for the analogous rearrangement of hydrocarbon **1** *via* $\mathbf{TS}_{1\rightarrow8}$. The difference of 3.1 kcal mol^{-1} between these activation enthalpies is less than half of the difference of 7.9 kcal mol^{-1} between the enthalpies of diradical intermediates, **8** and **12**, relative to the reactants, respectively, **1** and **2**. Presumably, the 4.8 kcal mol^{-1} larger barrier to closure for **12** than for **8** is due to the pyramidalized geometry of the CF_2 group in the former diradical.

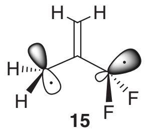
Comparison of the geometry in Fig. 1 of $\mathbf{TS}_{1\rightarrow8}$ for ring closure of **8** to **1** with that in Fig. 3 of transition structure **15** for ring closure of **12** to **2** is informative as to why the pyramidalized CF_2 group in the fluorocarbon diradical makes the barrier to ring closure nearly 5 kcal mol^{-1} higher in **12** than in **8**. In $\mathbf{TS}_{1\rightarrow8}$ the CH_2 radical center has rotated only about 30° from its geometry in **8**, where it benefits fully from the allylic stabilization energy of 13–15 kcal mol^{-1}.[28] The barrier to ring closure of 2.7 kcal mol^{-1} for **8** is slightly smaller than the *ca.* 3.5 kcal mol^{-1} that one would estimate for rotating a CH_2 group in the allyl radical by 30°, assuming that the resonance energy varies as the square of the cosine of this angle. This suggests that $\mathbf{TS}_{1\rightarrow8}$ already benefits from some σ bonding between the CH_2 group in **8** that rotates and the non-conjugated CH_2. Continued CH_2 rotation past the geometry of $\mathbf{TS}_{1\rightarrow8}$ lowers the energy, as σ bonding to the non-conjugated CH_2 group begins to more than compensate for the additional allylic π bonding that is lost.

In contrast to the "early" transition structure in the ring closure of **8** to **1**, transition structure **15** is quite "late", with the CH_2 group rotated completely out of conjugation. Therefore, all of the allylic π resonance energy has been lost before σ bonding to the "back side" of the highly pyramidalized ($\varphi = 41.1°$)[26] CF_2 group finally becomes strong enough to result in net lowering of the energy as **15** closes to **2**. Some bonding between the CH_2 and CF_2 radical centers obviously does occur before the geometry of **15** is reached; since, if this were not the case, rotating the CH_2 group in **12** to form **15** would require about twice the 7.5 kcal mol^{-1} energy increase that we compute for this process at the CASPT2 level of theory. Nevertheless, long-range bonding to the rotating CH_2 group is clearly weaker for the highly pyramidalized CF_2 radical center in **12** than for the planar CH_2 group in **8**; and it is for this reason that $\Delta H^{\ddagger}$ for ring closure is 4.8 kcal mol^{-1} higher for the former diradical than for the latter.

Why is back-side bonding to CF_2 favored in ring closure of 12?

If, as one might have anticipated, long-range bonding of the rotating CH_2 group to the "back side" of the highly pyramidalized CF_2 radical center in **12** is weak, why is transition structure **15** lower in energy than transition structure **13**, where bonding to the rotating CH_2 group occurs at the "front-side" of the CF_2 group? In order to attempt to answer this question, calculations were performed at the geometry of **15**, but with the CF_2 group rotated by 180°. In the resulting structure (**18**) the CF_2 group is pyramidalized by the same amount but in the opposite sense from that in **15**. Although in **18** the direction in which the CF_2 radical center is pyramidalized would appear to allow a stronger bonding interaction with the CH_2 radical center than in **15**, the CASSCF energy of **18** was calculated to be 8.2 kcal mol^{-1} higher than that of **15**.

Unconstrained optimization of the geometry of **18** led to ring closure to **2**. However, when the C–C–C bond angle in **18** was constrained to be the same as that in **15**, geometry reoptimization led to an energy decrease of only 1.1 kcal mol^{-1}. Thus, ring closure of **12** to **2** (and, of course, the reverse reaction—ring opening of **2** to **12**) with CF_2 inversion *via* diradical **15** is obviously preferred, because ring closure with retention *via* diradical **18** would require considerably higher energy. But why?



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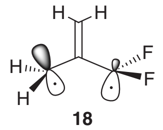
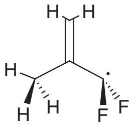


18

Part of the reason why **15** is preferred to **18** is that in **18** the C–F bonds interact more strongly in a destabilizing fashion with the terminal carbon of the C–C double bond. This can be shown by removing the interactions between the two radical centers in **15** and **18.** For example, when the CH_2 radical centers in **15** and in **18** are each either converted to a methyl group (as in **19** and **20**) or removed and replaced by a hydrogen atom (as in **21** and **22**), the conformation with the CF_2 group pyramidalized away from the double bond is still calculated to be preferred. The preference amounts to 2.6 kcal mol^{-1} for **19** over **20** and 2.2 kcal mol^{-1} for **21** over **22**.



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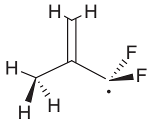

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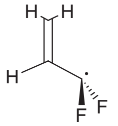

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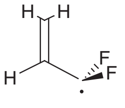
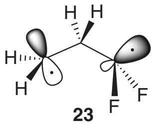


22

The energetic preference for the CF$_2$ conformation in **21** persists when a hydrogen is added to the CF$_2$ radical center in both **21** and **22** to form the two C_s conformations of 3,3-difluoropropene. The preference for having the C–F bonds pointed away from the terminal carbon of the double bond in 3,3-difluoropropene amounts to 3.4 kcal mol^{-1} at the RHF/6-31G* level of theory.

A similar, but smaller conformational preference has been found for the C–H bonds of the methyl group in propene and has been attributed to minimization of the destabilizing four-electron interaction between the π orbital of the double bond and the combination of C–H bonding orbitals of the same symmetry.[29] This effect may contribute to the surprisingly large pyramidalization ($\varphi = 25.1$) of the non-conjugated CH$_2$ group in $\mathbf{TS}_{1\rightarrow 8}$ to a geometry where, as can be seen in Fig. 1, the C–H bonds point away from the C–C double bond.

Since, even after partial geometry optimization of **18**, the preference for **15** still amounts to 7.1 kcal mol^{-1}, minimization of the interaction of the C–F bonds with the π orbital cannot be responsible for more than about half of the energy difference between these two conformational isomers. The only other possible contributor to this energy difference would appear to be interaction between the in-plane AOs at the CH$_2$ and CF$_2$ radical centers. One might have believed that such an interaction would favor **18**, which has the CF$_2$ radical center hybridized toward the radical center on the CH$_2$ group, rather than away from it, as in **15**. However, calculations on conformers **23** and **24** of 1,1-difluoropropane-1,3-diyl provided evidence that this is not at all the case.



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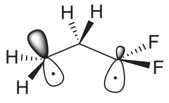


24

It was possible to optimize the geometry of **23** since, as in the case of the (4/4)CASSCF calculations on **15**, the inversion of the CF2 group that is required for ring closure of **23** creates a barrier to this process on the (2/2)CASSCF potential surface. As in the case of **18**, unconstrained optimization of the geometry of **24** led to ring closure. However, a geometry for conformation **24** was partially optimized with only the C–C–C bond angle fixed at the same value, 105.7°, as in **23**. The (2/2)CASSCF energy of the resulting geometry for **24** was 7.4 kcal mol^{-1} higher than that of **23**.

Some of the higher energy of **24** could come from H–F eclipsing interactions and other factors that are unrelated to the difference in bonding between the two radical centers in it and in **23**. In order to estimate the amount of the 7.4 kcal mol^{-1} energy difference between **23** and **24** that is due to factors unrelated to differences in C–C bonding, a hydrogen atom was added to the CF$_2$ radical center in **23** and in **24** and the C_s geometries of the resulting staggered and eclipsed 3,3-difluoroprop-1-yl radicals were optimized. The staggered geometry was calculated to be lower in energy than the eclipsed by 3.9 kcal mol^{-1}.

This finding suggests that a little less than half of the 7.4 kcal mol^{-1} of the energy difference between diradicals **23** and **24** comes from a stronger bonding interaction between the radical centers in the former than in the latter. A value of *ca.* 3.5 kcal mol^{-1} is consistent with the portion of the 7.1 kcal mol^{-1} energy difference between **15** and **18** that can reasonably be attributed to the same type of interaction, favoring the conformation of **15**, in which the CH$_2$ radical center interacts with the back side of the pyramidalized CF$_2$ radical center.

Both triplet ROHF orbital energies and singlet (2/2)CASSCF orbital occupation numbers indicate that long-range bonding between C-1 and C-3 is stronger when a CH$_2$ radical center interacts with the back side, rather than the front side of the pyramidal CF$_2$ radical center. For example, the HOMO of **15** is 7 kcal mol^{-1} lower and contains 0.13 more electrons than the HOMO of **18**, and the HOMO of **23** is 6 kcal mol^{-1} lower and contains 0.09 more electrons than the HOMO of **24**. Thus, a major factor in the preferential inversion of the CF$_2$ group found in the ring opening of **2** to **15** and of 1,1-difluorocyclopropane to **23**[30] is the greater long-range bonding in **15** than in **18** and in **23** than in **24**.

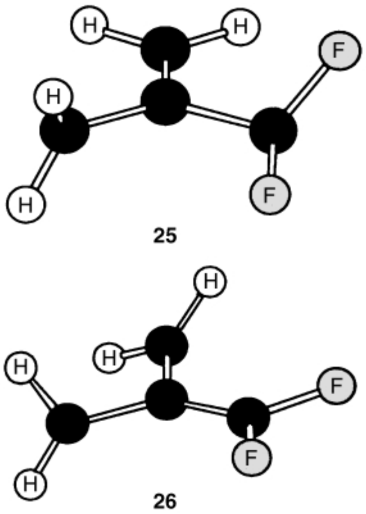


Fig. 4 Transition structures **25** and **26**, connecting difluorotrimethylenemethane diradical intermediate **11** with, respectively, 2,2-difluoromethylenecyclopropane (**2**) and (difluoromethylene)cyclopropane (**4**).

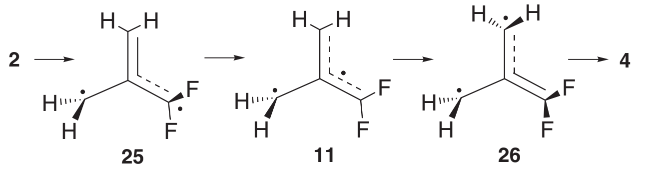
Why is long-range bonding to the back side of a pyramidal CF$_2$ group, as in **15** and **23**, stronger than to the front side, as in **18** and **24**? It is certainly the case that the larger lobe of the hybrid AO at the CF$_2$ radical center is directed toward the CH$_2$ radical center in **18** and **24** and away from it in **15** and **23**. This means that the singly occupied 2p AO at the CH$_2$ radical center is in phase with the 2s component of the singly-occupied, hybrid CF$_2$ AO in the former two conformations and out of phase with the 2s component in the latter two. This factor obviously favors the interactions between the CH$_2$ and CF$_2$ AOs in **18** and **24** over those in **15** and **23**. However, the angular orientations of the 2p AOs at the two radical centers cause them to overlap with more σ and less π character in **15** and **23** than in **18** and **24**. The better overlap between these AOs, coupled with the minimization of the destabilizing interaction between the C–F bonds and the π bond, causes the mode of CF$_2$ pyramidalization in **15** to be favored over that in **18**. This results in inversion of the CF$_2$ center being preferred to retention in the ring closure of **12** and, of course, in the reverse reaction, the ring opening of **2**.

Transition structures connecting 2 and 4 with 11

As already noted, on the CASPT2 potential energy surface diradical **11** is an intermediate; and the planar CF$_2$ group in **11** makes its enthalpy 6.3 kcal mol^{-1} higher than that of diradical **12**. However, our calculations find that the barriers to closure of **11**, both to **2** and to **4**, are much lower than the 7.5 kcal mol^{-1} barrier for closure of **12** to **2**.

Transition structure **25**, which connects **11** to **2**, is shown in Fig. 4. Its CASPT2 enthalpy is only 2.3 kcal mol^{-1} higher than that of **11**. Transition structure **26**, which connects **11** to **4** and is also shown in Fig. 4 has a CASPT2 enthalpy that is only 2.0 kcal mol^{-1} higher than that of **11**.

Despite the smaller barriers to closure of **11** than of **12**, the much lower energy of the latter diradical results in transition structures **25** and **26** for the non-degenerate rearrangement of **2** to **4** *via* diradical intermediate **11** each having a CASPT2 enthalpy that is about 1 kcal mol^{-1} higher than that of transition structure **15** for the degenerate rearrangement of **2** *via*



diradical intermediate **12**. Passage through transition structures **25** and **26** is rate determining in the rearrangement of **2** to **4**.

Comparison with experiment

The CASPT2 enthalpies shown in Table 2 are in excellent agreement with the enthalpies that have been measured in the experimental studies of the methylenecyclopropane rearrangements of **1** and **2**. For example, the rearrangement of **2** to **4** is calculated to be exothermic by 1.9 kcal mol^{-1}, which is exactly the value measured by Dolbier and Fielder.[9]

This rearrangement proceeds by opening of **2** to intermediate **11**, which then closes to **4**. The two highest energy transition structures, **25** and **26**, that lie along this reaction pathway have nearly the same CASPT2 enthalpies. The CASPT2 enthalpy of **25** is the higher of the two, and $\Delta H^{\ddagger}_{500} = 36.9$ kcal mol^{-1} is calculated for the rearrangement of **2** to **4**. The CASPT2 value of $E_a = 37.9$ kcal mol^{-1} at 500 K for the rearrangement of **2** to **4** is within experimental error of the value of $E_a = 38.3 \pm 0.4$ kcal mol^{-1}, reported by Dolbier and Fielder.[9]

We calculate $\Delta H^{\ddagger}_{500} = 35.8$ kcal mol^{-1} ($E_a = 36.8$ kcal mol^{-1} at 500 K) for passage through transition structure **15** in the degenerate rearrangement of **2**. This value is 1.1 kcal mol^{-1} lower than the enthalpy of activation for the non-degenerate rearrangement of **2** to **4**, which corresponds to a rate difference of 3.0 at 500 K.

Dolbier and co-workers have, in fact, found that the rearrangement of **3** to **7**, which is made non-degenerate by the presence of the methyl substituent, occurs 1.5 times faster than the non-degenerate rearrangement of **3** to **5**.[10] If, as seems likely, the methyl group selectively stabilizes the transition states, analogous to **25** and **26,** for the non-degenerate rearrangement of **3** to **5**, an experimental investigation of the degenerate and non-degenerate rearrangements in a ^{13}C- or deuterium-labelled variant of **2** could find that the ratio of the rates is even closer to the value of 3.0 suggested by the CASPT2 enthalpies in Table 2.

A final comparison that can be made between our calculations and experiments concerns the difference between the activation energies calculated for the degenerate rearrangement of hydrocarbon **1** and the non-degenerate rearrangement of fluorocarbon **2** to **4**. Our CASPT2 value of 2.0 kcal mol^{-1} is in perfect agreement with the experimental value,[9] which is based on Chesick's study of the methyl derivative of **1**.[22]

The essentially quantitative agreement between our calculated activation energies and those measured by Chesick and by Dolbier and co-workers[9,10] lends credibility to our computational results. This agreement provides evidence for the validity of the qualitative explanations, derived from our calculations, as to why the geminal fluorines in **2** have such a small effect on lowering the E_as for both its degenerate and non-degenerate methylenecyclopropane rearrangements, relative to the E_a for the methylenecyclopropane rearrangement of **1**.

Conclusions

Based on the calculated enthalpy differences between **8** and **1**, and **12** and **2**, the increase in strain, caused by the geminal fluorines in **2**, amounts to 7.9 kcal mol^{-1}. However, our calculations also find that the strong preference of a CF$_2$ radical center for a pyramidal geometry[18] raises the enthalpies of the transition structures for both the degenerate methylenecyclopropane rearrangement of **2** and for its non-degenerate rearrangement to **4** by a substantial fraction of the 7.9 kcal mol^{-1} by which the strain in **2** exceeds that in **1.** Consequently, in excellent agreement with the experimental results of Dolbier and co-workers,[9,10] the CASPT2 activation enthalpies for the degenerate and non-degenerate methylenecyclopropane rearrangements of **2** are, respectively, only 3.1 and 2.0 kcal mol^{-1} lower than the CASPT2 activation enthalpy for the degenerate rearrangement of **1**.

Acknowledgements

We thank the National Science Foundation for support of this research and for grants that allowed purchase of the IBM computers on which most of these calculations were performed.

W. T. B. dedicates this paper to the memory of Robert R. Squires, who made what is arguably the most important contribution of this decade to the experimental study of TMM. By devising a method for the generation of TMM radical anion in the gas-phase, Bob was able to measure the singlet–triplet energy difference in this diradical, the first such measurement made on any non-Kekulé hydrocarbon diradical. Bob grew to be as good at performing high-quality calculations as he was at doing experiments, and he made excellent use of both types of techniques in several of his most successful research projects.

I am happy that I had the opportunity to collaborate with Bob on the calculation of the doublet–quartet splitting in tridehydromesitylene, another non-Kekule hydrocarbon whose radical anion Bob succeeded in generating. I regret that several experimental collaborations in which we were engaged at the time of Bob's untimely death will no longer benefit from Bob's intelligence and expertise. However, even more than the loss of a scientific collaborator, I regret the loss of Bob as a personal friend. The number of chemists who have contributed manuscripts to this special issue of *Perkin Transactions 2* and to special issues of other journals, dedicated to Bob, is indicative of the fact that Bob was not only a highly respected scientist but also a good friend of many physical-organic and gas-phase ion chemists. For both reasons he will be very much missed.

References and notes

1 Reviews: (*a*) W. R. Dolbier, Jr. *Acc. Chem. Res.*, 1981, **14**, 195; (*b*) B. E. Smart, in *Molecular Structure and Energetics*, eds. J. F. Liebman and A. Greenberg, VCH, Deerfield Beach, FL, 1986; vol. 3, p. 141.

2 W. R. Roth, W. Kirmse, W. Hoffmann and H. W. Lennartz, *Chem. Ber.*, 1982, **115**, 2508.

3 A. Greenberg, J. Liebman, W. R. Dolbier Jr., K. S. Medinger and A. Skancke, *Tetrahedron*, 1983, **39**, 1533.

4 (*a*) S. J. Getty, D. A. Hrovat, J. D. Xu, S. A. Barker and W. T. Borden, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 1689; (*b*) 2,2-difluoropropane was computed to be 5.9 kcal mol^{-1} more stable than 1,1-difluoropropane at the RHF/6-31G* level and 7.3 kcal mol^{-1} more stable at the MP2/6-31G* level. Thus, the strain released upon formation of the latter from 1,1-difluorocyclopropane was calculated to exceed that released by formation of propane from cyclopropane by 6.6 kcal mol^{-1} at the RHF level and 6.3 kcal mol^{-1} at MP2.

5 (*a*) W. R. Dolbier, Jr. and H. O. Enoch, *J. Am. Chem. Soc.*, 1977, **99**, 4532; (*b*) However, as predicted by *ab initio* calculations,[4,6] the E_a for racemization of optically active *cis*-1,1-difluoro-2-ethyl-3-methylcyclopropane by coupled conrotation has subsequently been found to be 8.4 kcal mol^{-1} lower than the E_a for conversion of the *cis*-2,3-dimethyl fluorocarbon to the *trans* isomer.[7]

6 S. J. Getty, D. A. Hrovat and W. T. Borden, *J. Am. Chem. Soc.*, 1994, **116**, 1521.

7 F. Tian, S. B. Lewis, M. D. Bartberger, W. R. Dolbier Jr. and W. T. Borden, *J. Am. Chem. Soc.*, 1998, **120**, 6187.

8 W. R. Dolbier, Jr. and S. F. Sellers, *J. Am. Chem. Soc.*, 1982, **104**, 2494.

9 W. R. Dolbier, Jr. and T. H. Fielder, Jr., *J. Am. Chem. Soc.*, 1978, **100**, 5577.

10 W. R. Dolbier, Jr., C. R. Burkholder, A. L. Chaves and A. Green, *J. Fluorine Chem.*, 1996, **77**, 31.

11 (*a*) S. J. Getty, E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 2085; (*b*) J. E. Baldwin, Y. Yamaguchi and H. F. Schaefer III, *J. Phys. Chem.*, 1994, **98**, 7513.

12 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

13 Gaussian 94, Revision B.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.

14 Review: W. T. Borden and E. R. Davidson, *Acc. Chem. Res.*, 1996, **29**, 87.

15 K. Andersson, P.-Å. Malmqvist and B. O. Roos, *J. Chem. Phys.*, 1992, **96**, 1218.

16 MOLCAS version 3, K. Andersson, M. R. A. Blomberg, M. P. Fülscher, V. Kellö, R. Lindh, P.-Å. Malmqvist, J. Noga, J. Olsen, B. O. Roos, A. J. Sadlej, P. E. M. Siegbahn, M. Urban and P.-O. Widmark, University of Lund, Sweden, 1994.

17 D. Feller, K. Tanaka, E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 1982, **104**, 967.

18 Review: W. T. Borden, *Chem. Commun.*, 1998, 1919.

19 (*a*) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, 1973, **95**, 932; (*b*) W. T. Borden, *J. Am. Chem. Soc.*, 1975, **97**, 2906; (*c*) E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 1977, **99**, 2053.

20 (*a*) W. von E. Doering and H. D. Roth, *Tetrahedron*, 1970, **26**, 2825; (*b*) J. C. Gilbert and J. R. Butler, *J. Am. Chem. Soc.*, 1970, **92**, 2168; (*c*) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert and J. R. Butler, *Tetrahedron Lett.*, 1970, 845; (*d*) W. von E. Doering and L. Birladeanu, *Tetrahedron*, 1973, **29**, 449.

21 (*a*) In contrast to the (4/4)CASSCF results, (2/2)CASSCF calculations find that the disrotatory stationary point is a true transition structure, connecting **1** and **9**; B. Ma and H. F. Schaefer III, *Chem. Phys.*, 1996, **207**, 31; (*b*) for the results of other recent calculations on trimethylenemethane see C. J. Cramer and B. A. Smith, *J. Phys. Chem.* 1996, **100**, 9664.

22 J. P. Chesick, *J. Am. Chem. Soc.*, 1963, **85**, 2720.

23 Replacement of the remaining pair of ring hydrogens in **2** by fluorines has been computed to result in a 10 kcal mol^{-1} larger increase in strain than replacing a pair of geminal ring hydrogens in **1** by fluorines; A. Skancke and U. Wahlgren, *Acta Chem. Scand. A*, 1983, **37**, 771. It is generally the case in fluorocarbons that substitution of fluorine for hydrogen at carbons adjacent to CF$_2$ groups is destabilizing,[1] and this is probably the reason why the E_a for methylenecyclopropane rearrangement is 9 kcal mol^{-1} smaller in 1,1,2,2-tetrafluoromethylenecyclopropane than in **2**; W. R. Dolbier, Jr., S. F. Sellers, B. H. Al-Sader and B. E. Smart, *J. Am. Chem. Soc.*, 1980, **102**, 5398.

24 (*a*) S. Y. Wang and W. T. Borden, *J. Am. Chem. Soc.*, 1989, **111**, 7282; (*b*) J. H. Hammons, M. B. Coolidge and W. T. Borden, *J. Phys. Chem.*, 1990, **94**, 5468; (*c*) A. Nicolaides and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 8682.

25 (*a*) The calculated CISD difference of 5.7 kcal mol^{-1} between the energy required to twist a CH$_2$ group out of conjugation in allyl radical and the CF$_2$ group out of conjugation in 1,1-difluoroallyl radical[24b,c] is, in fact, similar to the CASPT2 differences of 7.7 and 6.7 kcal mol^{-1} between the energies of, respectively, **10** and **12** and **11** and **12**; (*b*) the CISD energy of 12.7 kcal mol^{-1} that is required to planarize the twisted CF$_2$ group in 1,1-difluoroallyl radical is also similar to the CASPT2 energy of 11.0 kcal mol^{-1} required to planarize the CF$_2$ group in **12**.

26 The pyramidalization angle, φ, is the angle between the plane of the CF$_2$ group and the extension of the C–C bond to it.

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

28 H.-G. Korth, H. Trill and R. Sustmann, *J. Am. Chem. Soc.*, 1981, **103**, 4483; (*b*) D. A. Hrovat and W. T. Borden, *J. Phys. Chem.*, 1994, **98**, 10460 and references cited therein.

29 W. J. Hehre, J. A. Pople and A. J. P. Devaquet, *J. Am. Chem. Soc.*, 1976, **98**, 664.

30 The transition structure for methylene rotation in 1,1-difluoropropane-1,3-diyl has the CH$_2$ group rotated 90° from its conformation in **23**. In the transition structure there is, therefore, no interaction between the CH$_2$ and CF$_2$ radical centers; and its (2/2)CASSCF energy is, consequently, 7.7 kcal mol^{-1} higher than that of **23**.[6]

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