

Ab Initio Calculations on Spiropentane Stereomutations Lead to a Reinterpretation of the Experimental Results

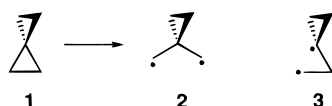
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Abstract: The potential energy surfaces for stereomutation of spiropentane (**1**) and *cis*- and *trans*-1,2-dimethylspiropentanes (**4** and **7**) have been explored, using ab initio methods. In diradicals **2**, **5**, and **6**, which are formed by cleavage of the peripheral bond between C-1 and C-2 in the spiropentanes, the weakly electron-donating cyclopropane ring results in the lowest energy pathway for stereomutation of all three being computed to be conrotatory. A larger preference for double over single rotation is computed in **4** than in **7**, in agreement with the experimental results reported in 1980 by Gajewski and Chang. However, in contrast to the assumption made by these authors, our calculations find that the *s-cis*-methyl conformation in diradical **6** is lower in energy than the *s-trans*-methyl conformation in diradical **5**, and moreover, **6** is statistically favored over **5** by a factor of 2. Thus, double rotation is both computed and found to be preferred by more in the stereomutation of **4** than of **7** because **4** undergoes *conrotatory* opening to **6**, the lower energy diradical. A long-range attraction between the *s-cis* methyl group at C-1 and the nonbonding p- π AO at C-3 in **6** is shown to contribute to stabilizing this diradical.

The first study of the stereomutation of spiropentane (**1**) was published 30 years ago.¹ Gilbert reported that, upon heating, *cis*-1,2-²H₂-spiropentane isomerizes to *trans*-1,2-²H₂-spiropentane, prior to undergoing structural rearrangement.² Subsequently, Gajewski and Burka pyrolyzed the proximal, medial, and distal stereoisomers of 1,4-dimethylspiropentanes,³ and from the kinetics of interconversion that they observed, they concluded that fission of a peripheral bond, to form diradical **2**, is preferred to cleavage of a radial bond, to form diradical **3**. Stereomutation of **1** by exclusive formation of 1,1-dimethylenecyclopropane (**2**) is supported by the results of additional experiments by Gajewski.⁴



Gajewski and Chang (G&C) investigated the pyrolyses of *syn*-4,4-²H₂-*cis*-1,2-dimethylspiropentane (**4**-²H₂) and of optically active *trans*-1,2-dimethylspiropentane (**7**) at 290 °C.^{5a} Coupled rotation was found to be slightly favored over monorotation in both spiropentanes.

G&C based their assignment of the mode of coupled rotation that is preferred on the experimental finding that double rotation is favored over monorotation by a factor of 3.6 in the pyrolysis of **4**-²H₂ and by a factor of only 1.4 in the pyrolysis of **7**. On the basis of the experimental results in the pyrolyses of other

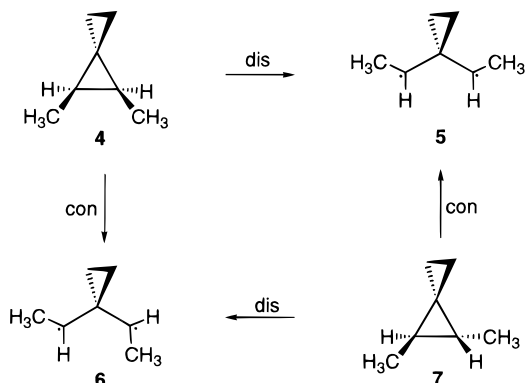


Figure 1. Diradicals formed by con- and disrotatory ring opening of *cis*- and *trans*-1,2-dimethylspiropentane.

hydrocarbons, G&C assumed that “outward” rotation of a methyl group in **4** and **7** is sterically less demanding than “inward” rotation. Therefore, they expected formation of diradical **5** to provide a lower energy pathway for double rotation than formation of diradical **6**. This assumption, together with the modes of coupled rotation that connect **4** and **7** to **5** and **6** (shown in Figure 1), resulted in G&C interpreting the experimental ratios of single to double rotation in **4** and **7** as indicating that disrotation is preferred to conrotation in the stereomutations of these spiropentanes.

The apparent preference for disrotation, rather than conrotation, in the pyrolyses of **4** and **7** was unexpected. In 1968 Hoffmann published the results of extended Hückel (EH) calculations on the ring opening of cyclopropane, which predicted a large preference for conrotation over both dis- and monorotation.⁶ Hoffmann showed that this preference arises from hyperconjugative electron donation from the C–H bonds

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Figure 2. Idealized (0,0) and (0,90) conformations of trimethylene. at C-2 into the in-phase (b_1) combination of p - π AOs at the terminal carbons in the (0,0) conformation of the trimethylene diradical (shown in Figure 2). Although subsequent ab initio calculations have found a much smaller preference than the EH calculations for conrotation [via the (0,0) geometry] over both disrotation and monorotation [via a (0,90) geometry], the qualitative preference for conrotation does persist at the highest levels of theory.⁷

At least in the stabilization of carbocations, the strained C—C bonds of cyclopropane rings are known to be better hyperconjugative electron donors than C—H bonds.⁸ Therefore, if a preference for coupled rotation were observed in the stereomutation reactions of derivatives of **1**, such as **4** and **7**, one would have expected that the preferred mode of coupling would have been found to be conrotatory.⁹ Thus, if correct, the conclusion that disrotation is preferred in the stereomutation reactions of **4** and **7** is surprising, especially in light of more recent calculations which show that disrotation is expected only when the bonds at C-2 that hyperconjugate with the p - π AOs at C-1 and C-3 are electron *acceptors*, not *donors*.¹⁰ The strong preference for disrotation, predicted in the stereomutation of 1,1-difluorocyclopropanes, has, in fact, been experimentally confirmed.¹¹

Nevertheless, when G&C reinvestigated the thermal isomerizations of the four 1,2,4-trimethylspiropentanes,^{5b} using optically active *trans* compounds,^{5a} they again found that, as in **4** and **7**, the ratio of double to single rotation is about a factor of 3 larger in each of the two *cis* stereoisomers than in each of the two *trans* compounds. This result was interpreted as additional evidence for the conclusion, drawn from the study of dimethylspiropentanes **4** and **7**, that disrotation is preferred to conrotation in spiropentane stereomutation reactions.

The trimethylspiropentane experiments also led to another unexpected observation. In each of the two *trans* compounds epimerization of the C-4 methyl group (by some combination of single rotation of C-4 and double rotation of C-4 in concert with C-5, the unsubstituted carbon) is roughly a factor of 5 faster than double rotation of C-1 and C-2. This result is surprising because epimerization at C-4 proceeds through a diradical that has one primary center (C-5), while coupled rotation of C-1 and C-2 produces a diradical with two secondary centers.

To try to understand why disrotation is apparently preferred to conrotation in the pyrolyses of both the 1,2-dimethyl- and

the 1,2,4-trimethylspiropentanes, we have undertaken ab initio calculations of the potential surfaces for the stereomutations of **1**, **4**, and **7**. We have also investigated why double rotation of C-1 and C-2 in the *trans*-1,2,4-trimethylspiropentanes is slower than epimerization at C-4. Herein we report the results of our calculations, which lead to a reinterpretation of the experimental results of G&C.^{5a}

Computational Methodology

All calculations were performed with the 6-31G* basis set.¹² Geometries of alkanes were optimized at the RHF level of theory, and geometries of monoradicals and triplet diradicals were optimized at the ROHF level. Singlet diradical geometries were optimized with (2/2)CASSCF wave functions. The geometries of stationary points were located and vibrational analyses were performed with Gaussian 94.¹³ The geometries of all the stationary points are available as Supporting Information.

The effects of including dynamic electron correlation¹⁴ were investigated by performing CASPT2 calculations,¹⁵ for which the RHF, ROHF, and (2/2)CASSCF wave functions were used as the references. A CASPT2 calculation with an RHF wave function as the reference is an MP2 calculation, and our MP2 calculations were carried out with Gaussian 94.¹³ All the other CASPT2 calculations and some ROMP2 calculations on monoradicals were performed with the MOLCAS suite of ab initio programs.¹⁶

Results and Discussion

Stereomutation of Spiropentane (1). The geometry of **1** was optimized in D_{2d} symmetry and was shown to be a minimum by vibrational analysis. The (0,0) geometry of 1,1-dimethylcyclopropane (**2**) was optimized in C_{2v} symmetry, but **2-(0,0)** was found to have three modes with imaginary frequencies. These modes involved syn and anti pyramidalization of the two radical centers and conrotation of both methylene groups.

Other stationary points located on the potential surface for the stereomutation of **1** were a C_2 transition state for conrotation in diradical **2 (2-con)**, a C_s transition state for disrotation in **2 (2-dis)**, and a diradical energy minimum (**2-min**), also with C_s symmetry. The last of these stationary points connects two conrotatory transition states. The lowest frequency vibration in **2-min** is computed to be only 5 cm^{-1} , so **2-min** exists in a very shallow energy well.¹⁷

As shown in Table 1, the (2/2)CASSCF energies of **2-con** and **2-(0,0)** are identical to within 0.1 kcal/mol. This is not too surprising since the geometry of **2-con** differs from that of

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(17) As is also the case on the (2/2)CASSCF reaction path of lowest energy for ring opening and closure of cyclopropane,⁷ the lowest frequency mode in this C_s intermediate corresponds to a symmetry-breaking rotation of the two methylene groups in the same direction. Formation of this intermediate by deviation from a purely conrotatory path allows the inward rotating hydrogens on the methylene groups to minimize their steric compression by avoiding the (0,0) geometry and passing sequentially through the plane of the carbon atoms.

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(9) (a) The C—Si bonds in 2,2-disilyltrimethylene, which are much better hyperconjugative electron donors than C—H bonds at C-2 in trimethylene, have been calculated to greatly enhance the preference for conrotatory ring opening of 1,1-disilylcyclopropane, relative to the hydrocarbon. (b) Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079.

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Table 1. Relative RHF,^a MP2,^a (2/2)CASSCF,^b and CASPT2,^b and Zero-Point Energies, Heat Capacity Corrections at 298 K, and Relative Enthalpies for the Stationary Points on the Singlet Potential Surfaces for Spiropentane (all in kcal/mol)

species	sym- metry	SCF	PT2	ZPE	$C_{v,298} \times$ 298 K	ΔH_{298} (SCF)	ΔH_{298} (PT2)
1 (¹ A ₁)	D _{2d}	-35.9	-52.8	5.8	-1.3	-31.4	-48.3
2-con (¹ A)	C ₂	0.0	0.0	0.0	0.0	0.0	0.0
2-dis (¹ A')	C _s	0.7	3.0	0.3	-0.2	0.8	3.1
2-mono (¹ A)	C ₁	0.8	2.8	0.4	-0.2	1.0	3.0
3 (¹ A)	C ₁	6.6	10.7	1.5	-0.6	7.4	11.6
2-min (¹ A')	C _s	-0.4	0.4	0.7	0.3	0.6	1.4
2-(0,0) (¹ A ₁)	C _{2v}	0.1	-0.2	-0.8 ^c	-1.0 ^c	-1.7	-2.0
2-(0,90) (¹ A')	C _s	1.0	2.6	-0.2 ^d	-0.6 ^d	0.1	1.8

^a For **1**. ^b For all diradicals. ^c A vibrational analysis showed this structure to have three modes with imaginary frequencies. ^d A vibrational analysis showed this structure to have two modes with imaginary frequencies.

2-(0,0) by a mere 9.1° of conrotation. As usual, upon including dynamic electron correlation, the more delocalized structure is selectively stabilized,¹⁴ and the CASPT2 energy of **2-(0,0)** is found to be slightly lower than those of both **2-con** and **2-min**. On the CASPT2 potential energy surface **2-(0,0)**, or a geometry very close to it, is probably the transition state for conrotatory opening and closure of **1**.

The geometry of the (0,90) conformer of **2** was optimized in C_s symmetry, but **2-(0,90)** was found to have two vibrational modes with imaginary frequencies, corresponding to pyramidalization and rotation of the methylene group that lies in the symmetry plane. Allowing this radical center to pyramidalize led to the monorotatory transition state (**2-mono**).

Using an optimized geometry for the radially cleaved triplet diradical as a starting point, searching for a singlet transition structure led to the (2/2)CASSCF geometry of **3**. The relative (2/2)CASSCF and CASPT2 energies of **2-(0,90)**, **2-mono**, and **3** are given in Table 1.

After corrections for the ZPE and heat capacity differences, given in Table 1, the enthalpy of activation that we calculate at the CASPT2 level of theory for isomerization of **1** via rate-determining passage through **2-mono** is $\Delta H^\ddagger_{298} = 51.3$ kcal/mol. This calculated value is in superb agreement with Gilbert's experimental value of $\Delta H^\ddagger_{298} = 50.9 \pm 1.0$ kcal/mol for isomerization of *cis*-1,2-²H₂-spiropentane to *trans*-1,2-²H₂-spiropentane. The (2/2)CASSCF value for ΔH^\ddagger is far too low, due to the absence from these calculations of correlation for the electrons in all three of the strained σ bonds of the three-membered ring that undergoes opening.⁷

Also in agreement with experiment,^{3,4} our calculations show that breaking a peripheral bond in **1** to form diradical **2** requires substantially less energy than cleaving a radial bond to form diradical **3**. The former diradical possesses one more bond to a cyclopropyl ring carbon than the latter, and the large amount of 2s character in this bond makes it stronger than the bond to the sp³ carbon that is absent in **2** but present in **3**.^{18,19}

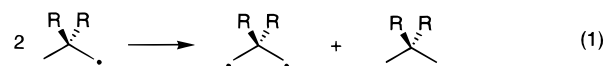
Whether the energies of **2-con** and **2-mono** or **2-(0,0)** and **2-(0,90)** are compared, conrotation is computed to be preferred over monorotation in the stereomutation of **1** by 2.8 kcal/mol at the CASPT2 level of theory. The CASPT2 energy of the transition state for conrotation is lower than that for disrotation by about the same amount. These preferences for conrotatory ring opening of **1** are a little more than 1 kcal/mol larger than

those computed for stereomutation of cyclopropane,²⁰ but they are much smaller than those calculated at the same level of theory for stereomutation of 1,1-disilylcyclopropane.^{9b,22}

Hyperconjugation in 2-(0,0). At least some of the energetic preference for the (0,0) over the (0,90) conformation in diradical **2** has the same origin as the preference for the bisected (0) over the staggered (90) CH₂ conformation in cyclopropylcarbinyl monoradical. The bisected conformation allows the singly occupied p AO on the CH₂ group to be stabilized by interacting with both the bonding and antibonding Walsh orbitals of the cyclopropane ring that also have a'' symmetry. The preference for the (0) over the (90) CH₂ conformation in cyclopropylcarbinyl radical is calculated to amount to 2.2 kcal/mol at the CASPT2 level of theory,¹⁸ a value which is in very good agreement with the experimental value of 2.4 ± 0.5 kcal/mol.²³

In contrast, the (0) and (90) conformations of the 1-propyl radical have the same energies to within 0.2 kcal/mol.^{10b} The energy difference between the (0) and (90) CH₂ conformations in cyclopropylcarbinyl radical is thus ca. 2 kcal/mol larger than in propyl radical, and this might have been expected to be the amount by which the energy difference between the (0,0) and (0,90) conformations is larger in diradical **2** than in trimethylene. However, as already noted, the CASPT2 energy difference between the (0,0) and (0,90) conformations in **2** is only about 1 kcal/mol larger than in trimethylene.²⁰

The somewhat smaller than expected energetic preference for (0,0) over (0,90) in **2** could be due to the hyperconjugative interaction of the two radical centers with the cyclopropane ring bonds in **2-(0,0)** being competitive, rather than cooperative. Whether the hyperconjugative interaction of radical centers at C-1 and C-3 with the exocyclic bonds to C-2 is competitive or cooperative in a 1,3-diradical can be assessed by computing the energy of the isodesmic reaction in eq 1.^{10b} If the reaction



is calculated to be energetically favorable, the interaction is cooperative, but if the reaction is calculated to be energetically unfavorable, the interaction is competitive. Strongly electron accepting bonds (e.g., R = F) or strongly electron donating bonds (e.g., R = SiR₃) at C-2 result in a cooperative interaction of the two radical centers. For example, for R = F the CASPT2 energy of the reaction in eq 1 is -3.8 kcal/mol,^{10b} and for R = SiH₃ the reaction in eq 1 is computed to be energetically favorable by -10.1 kcal/mol at this level of theory.^{9b} In contrast, for R = H, the reaction in eq 1 is computed to be unfavorable by 0.7 kcal/mol at the CASPT2 level, showing that the radical centers in (0,0)-trimethylene act competitively, rather than cooperatively.^{9b,10b}

For R-R = H₂C-CH₂ the reaction in eq 1 is also computed to be energetically unfavorable and actually by 0.4 kcal/mol more than in trimethylene. This result indicates that the cyclopropane ring in **2-(0,0)** is certainly not a significantly better hyperconjugative, two-electron donor than the C-H bonds at C-2 in (0,0)-trimethylene. This finding is quite surprising, since, as already noted, the strained C-C bonds of cyclopropane rings are known⁸ to be much better hyperconjugative, two-electron donors than C-H bonds in the stabilization of carbocations.²⁴

(20) The energy difference between the (0,0) and (0,90) conformations of trimethylene is 1.2 kcal/mol at the SD-CI level^{7a} and 1.7 kcal/mol at CASPT2.²¹

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Another indication of whether the C–R bonds at C-2 in a 1,3-diradical either accept electron pairs from or donate electron pairs to the two radical centers is the singlet–triplet energy separation. Both the electron-accepting C–F bonds in (0,0)-2,2-difluorotrimethylene and the electron-donating C–Si bonds in (0,0)-2,2-disilyltrimethylene strongly lift the near degeneracy of the b_1 and a_2 NBMOs in these diradicals and result in each diradical being computed to have a singlet ground state.^{9b,10b} At the CASPT2 level of theory, $\Delta E_{ST} = -4.8$ in the former^{21,25} and $\Delta E_{ST} = -11.9$ kcal/mol in the latter.^{9b}

In the (0,0) conformation of the parent trimethylene diradical the interaction of the p - π AOs at C-1 and C-3 with the weakly electron-donating C–H bonds at C-2 is not very effective in lifting the degeneracy between the b_1 and a_2 combinations of these AOs. In the triplet diradical ROHF the orbital energy difference between the b_1 and a_2 NBMOs is only 4.1 kcal/mol for R = H, which is only about 20% as large as the difference of 18.9 kcal/mol for R = SiH₃. As a result, the occupation numbers of the b_1 and a_2 NBMOs in the (2/2)CASSCF singlet wave function for R = H are, respectively, 0.91 and 1.09, compared to 0.49 and 1.51 for R = SiH₃. Consequently, in contrast to the singlet ground state with $\Delta E_{ST} = -11.9$ predicted for (0,0)-2,2-disilyltrimethylene,^{9b} a triplet ground state with $\Delta E_{ST} = 0.7$ kcal/mol is computed for (0,0)-trimethylene.^{10b}

In **2-(0,0)** the b_1 orbital of the cyclopropane ring is slightly more effective than the b_1 combination of C–H bonds in (0,0)-trimethylene at lifting the degeneracy of the b_1 and a_2 NBMOs. The ROHF orbital energies in **2-(0,0)** differ by 5.7 kcal/mol, about 40% more than in (0,0)-trimethylene, and the occupation numbers of the a_2 and b_1 NBMOs in **2-(0,0)** are, respectively, 1.12 and 0.88, compared to 1.09 and 0.91 in (0,0)-trimethylene. Nevertheless, not only is **2-(0,0)** predicted to have a triplet ground state, but the CASPT2 value of $\Delta E_{ST} = 2.0$ kcal/mol in **2-(0,0)** is nearly 3 times larger than ΔE_{ST} in (0,0)-trimethylene.^{10b}

The value of ΔE_{ST} in a diradical depends not only on the energy difference between the NBMOs but also on the degree to which the GVB orbitals derived from them are disjoint.²⁶ The b_1 combination of p - π AOs at C-1 and C-3 interact more strongly with *both* the bonding and the antibonding b_1 cyclopropane Walsh orbitals in **2-(0,0)** than with the bonding and antibonding C–H orbitals in (0,0)-trimethylene. The larger

(24) Our calculations do indeed find that two-electron, hyperconjugative donation from the C–C bonds of a cyclopropane ring into the empty p - π AO of a carbocation is highly stabilizing and to about the same extent as hyperconjugative donation from the C–Si bonds of two geminal silyl groups. Since our calculations also find that the cyclopropane ring bonds in **2-(0,0)** are much poorer hyperconjugative electron donors than the geminal C–Si bonds in the (0,0) conformation of 2,2-disilylpropane-1,3-diyl, this difference between the relative electron donating abilities of cyclopropane and geminal C–Si bonds in carbocations and in 1,3-diradicals presents an apparent paradox. We believe that the resolution of this paradox is that hyperconjugative electron donation in **2-(0,0)** necessitates charge separation, whereas, even in 2,2-disilylpropane, the C–Si bonds are highly polarized, with positive charges on silicon and a negative charge at the carbon to which they are attached. Consequently, hyperconjugative stabilization in 2,2-disilylpropane-1,3-diyl largely involves delocalization of negative charge, already at C-2 in 2,2-disilylpropane, to C-1 and C-3, rather than creation of charge separation, as required for hyperconjugative electron donation in **2-(0,0)**.

(25) As predicted,^{10c} the ground state of a cyclic derivative of 2,2-difluorotrimethylene has been shown experimentally to be a singlet: Adam, W.; Borden, W. T.; Burda, C.; Foster, H.; Heidenfelder, T.; Heubes, M.; Hrovat, D. A.; Kita, F.; Lewis, S. B.; Scheutnow, D.; Wirz, J. *J. Am. Chem. Soc.* **1998**, *120*, 593.

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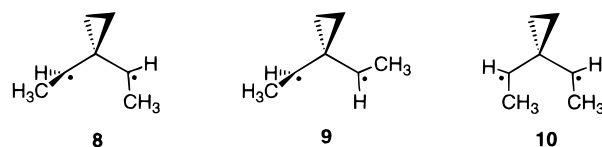
Table 2. Relative RHF,^a MP2,^a (2/2)CASSCF,^b and CASPT2,^b and Zero-Point Energies, Relative Heat Capacity Corrections at 560 K, and Relative Enthalpies of the Stationary Points on the Singlet Potential Surfaces for 1,2-Dimethylspiropentane, (all in kcal/mol)

species	symmetry	SCF	PT2	ZPE	$C_{v,560} \times 560$ K	ΔH_{560} (SCF)	ΔH_{560} (PT2)
4 (¹ A')	C_s	-35.0	-51.7	3.6	-0.3	-31.7	-48.4
7 (¹ A)	C_2	-36.4	-52.9	3.5	-0.3	-33.1	-49.6
6-con (¹ A)	C_1	0.0	0.0	0.0	0.0	0.0	0.0
5-dis (¹ A)	C_1	0.7	1.9	-0.2	0.1	0.5	1.7
8 (¹ A)	C_1	-0.1	1.3	-0.4	0.1	-0.4	1.0
9 (¹ A)	C_1	-0.3	1.5	-0.3	0.1	-0.5	1.2
5-con (¹ A)	C_2	0.5	0.6	-0.5	0.2	0.2	0.3
6-dis (¹ A)	C_1	0.4	2.5	-0.3	0.0	0.1	2.2
5-min (¹ A')	C_s	0.5	1.0	-0.1	1.2	1.5	2.0
5 (¹ A ₁)	C_{2v}	1.6	0.9	-1.6 ^c	-3.0 ^c	-3.0	-3.7
6 (¹ A')	C_s	0.9	-0.7	-1.4 ^d	-1.9 ^d	-2.4	-3.9
10 (¹ A ₁)	C_{2v}	3.9	2.4	-1.0 ^d	-2.0 ^d	0.9	-0.6

^a For **4** and **7**. ^b For all diradicals. ^c A vibrational analysis showed this structure to have four vibrational modes with imaginary frequencies. ^d A frequency analysis showed this structure to have three vibrational modes with imaginary frequencies.

amount of orbital mixing that results from this *pair* of interactions in **2-(0,0)** leads to its GVB orbitals being less disjoint than those in (0,0)-trimethylene.²⁷

Stereomutation of 1,2-Dimethylspiropentanes 4 and 7. We have previously found that, at the (2/2)CASSCF level of theory, terminal methyl groups reduce the energy difference of 0.7 kcal/mol between the (0,90) and (0,0) conformations of trimethylene to a difference of only 0.2 kcal/mol between (0,90) and the lowest energy *s-trans,s-trans*-(0,0) conformation of pentane-2,4-diyl.^{10b} A similar effect is seen on comparison of the (2/2)CASSCF energies in Tables 1 and 2. At this level of theory the *s-cis* (**8**) and *s-trans* (**9**) monorotatory transition states for interconversion of *cis*- and *trans*-1,2-dimethylspiropentane (**4** and **7**) are actually lower in energy than any of the other stationary points that we located on the potential surface for stereomutation of **4** and **7**. Presumably, hyperconjugation of the terminal methyl groups with the radical centers in diradicals **5**, **6**, **8**, and **9** reduces the importance of hyperconjugation of these centers with the strained C–C bonds of the cyclopropane ring.



However, in addition to this electronic effect, Table 2 shows there are apparently also some steric effects on the relative energies of these diradical conformers, due to the presence of the cyclopropane ring. These effects make the *s-cis*-methyl conformation relatively more favorable in **6** and **8** than in pentane-2,4-diyl. In the latter diradical the *s-trans,s-trans*-(0,0) conformation is favored over *s-cis,s-trans*-(0,0) by 1.2 kcal/mol at the (2/2)CASSCF level of theory.^{10b} In contrast, **8** is calculated to be within 0.2 kcal/mol of **9** at both the (2/2)-CASSCF and CASPT2 levels of theory, and **6** is actually calculated to be lower in energy than **5** by 0.7 kcal/mol at (2/2)CASSCF and by 1.6 kcal/mol at CASPT2. With inclusion of dynamic electron correlation at the latter level of theory, **6** becomes the lowest energy diradical stationary point that we located.²⁸

(27) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.

The rather surprising finding that the *s-cis,s-trans* conformation of diradical **6** is lower in energy than the *s-trans,s-trans* conformation of diradical **5** prompted us also to compute the energy of the *s-cis,s-cis* conformation of diradical **10**. In the latter conformation there is considerable steric crowding between the two "inward-rotated" methyl groups. Consequently, as shown in Table 2, **10** is computed to be higher in energy than either **5** or **6** at both the (2/2)CASSCF and CASPT2 levels of theory.

Our finding that the *s-cis,s-trans*-(0,0) diradical conformation (**6**) is lower in energy than the *s-trans,s-trans*-(0,0) conformation (**5**) has profound implications for interpreting the experiments of G&C.^{5a} As discussed above, these experiments found that the ratio of double to single rotation is higher in **4** than in **7**, and G&C correctly interpreted this finding as being due to **4** undergoing ring opening to the more stable (0,0) diradical conformation. However, G&C made the reasonable but erroneous assumption that diradical **5** is lower in energy than **6**. Since, as shown in Figure 1, **4** must open to **5** by disrotation, G&C concluded that disrotation is preferred to conrotation in the stereomutations of **4** and **7**.

Our calculations find, in contrast to what G&C assumed, not only that **6** is lower in energy than **5**, but, in addition, that the *s-cis,s-trans* conformation of **6** is favored by a statistical factor of 2 over the *s-trans,s-trans* conformation of **5**. Therefore, we reinterpret the results of G&C's experiments as having shown that the ratio of double to single rotation is higher in **4** than in **7**, because **4** preferentially undergoes ring opening *not* to **5** but to **6**.²⁹ Since, as illustrated in Figure 1, **4** opens to **6** by conrotation, we conclude that conrotation is preferred to disrotation in the stereomutations of **4** and **7**.

This conclusion is in accord with the expectation, based on qualitative theory and discussed above, that since the cyclopropane ring in **5** and **6** is a hyperconjugative electron donor, conrotatory ring opening of these spiropentanes should be preferred. Our reinterpretation of the experimental results of G&C is also consistent with the results of our calculations on the stereomutation reactions of **1**, **4**, and **7**. As shown in Tables 1 and 2, we find that at the CASPT2/(2/2)CASSCF level of theory the disrotatory transition states are 2–3 kcal/mol higher in energy than their conrotatory counterparts.

In agreement with the experimental results of G&C is our finding that at the CASPT2/(2/2)CASSCF level of theory transition states **8** and **9** for effecting the interconversion of **4** and **7** by monorotation are both higher in energy than the preferred transition states for ring opening of **4** and **7** by double rotation.³⁰ In addition, and also as found experimentally by

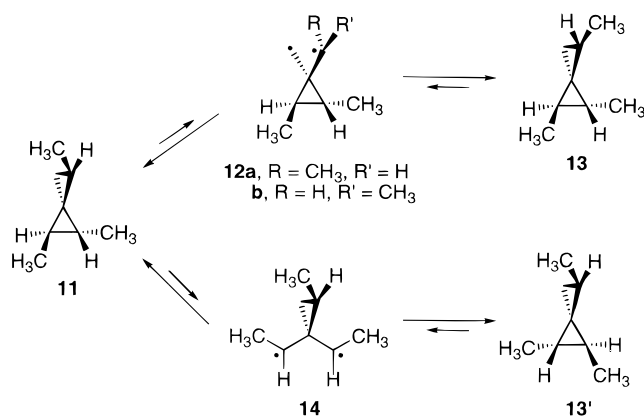


Figure 3. Pathway for stereomutation of *trans*-1,2,4-trimethylspiropropane (**11**) to **13** by cleavage of the bond between C-4 and C-5 and to **13'**, the enantiomer of **13**, by conrotatory cleavage of the bond between C-1 and C-2 in **11**.

G&C, our calculations predict that the ratio of double to single rotation should be larger in **4** than in **7**.

As shown in Table 2, at both the CASSCF and CASPT2 levels **6-con**, the preferred transition structure for double rotation in the ring opening of **4**, is computed to be slightly lower in energy than **5-con**, the preferred transition structure for double rotation in the ring opening of **7**.²⁹ Since monorotation transition structures **8** and **9** are each accessible from both **4** and **7**, the 0.3 kcal/mol lower enthalpy of **6-con**, relative to **5-con**, predicts that at 560 K the ratio of conrotation to monorotation should be a factor of just 1.3 larger in **4** than in **7**. However, **6-con** is also statistically favored over **5-con** by a factor of 2, so that our calculations predict that the ratio of conrotation to monorotation at 560 K should actually be a factor of 2.6 larger in **4** than in **7**. Probably fortuitously, this is *exactly* the factor by which the experiments of G&C^{5a} found the ratio of double to single rotations to be larger in the stereomutation of **4** than of **7**.³⁰

1,2,4-Trimethylspiropentanes. As discussed in the Introduction, the experiments of G&C also found that epimerization of C-4 in **11** and **13**, the two *trans* stereoisomers of 1,2,4-trimethylspiropentane, is about 5 times faster than the rate of double rotation of C-1 and C-2. Presumably, this unexpected finding that the less substituted peripheral bond preferentially cleaves is due to both **11** and **13** undergoing conrotatory ring opening to an *s-trans,s-trans*-(0,0) diradical geometry upon cleavage of the more substituted peripheral bond. In contrast, cleavage of the less substituted peripheral bond allows the C-4 methyl to epimerize via an *s-cis*-(0,0) geometry (**12a**). On the basis of the relative CASPT2 energies of **5** and **6** in Table 2, an *s-cis*-methyl group should be preferred to an *s-trans*-methyl group by 1.6 kcal/mol, and the two *s-trans*-methyl groups in diradical **14** might prove sufficient to favor conrotation of C-4 and C-5 over conrotation of C-1 and C-2 in the ring opening of **11**.

To test whether this is indeed the case, we carried out calculations on *s-cis* (**12a**) and *s-trans* (**12b**), the two (0,0) conformations of the diradical formed by cleavage of the bond between C-4 and C-5 in 1,2,4-trimethylspiropropane (**11**) and on **14**, the (0,0)-*s-trans,s-trans* conformation of the diradical formed by conrotatory cleavage of the bond between C-1 and C-2 in **11** (Figure 3). Diradicals **12a** and **12b** are the two idealized transition structures for interconversion of **11** and **13** by double rotations, and diradical **14** is the idealized transition structure for the preferred mode of double rotation by which **11** isomerizes to the enantiomer of **13** (**13'**).

(28) On the basis of the energies in Table 2, it seems likely that the (0,0) diradical geometries, **5** and **6**, would be found to be closer than the (2/2)CASSCF conrotatory transition structures, **5-con** and **6-con**, to the geometries of the CASPT2 conrotatory transition states. Unfortunately, analytical gradients have not yet been implemented in MOLCAS for CASPT2 wave functions, so currently, this conjecture cannot be easily verified.

(29) Even though the (2/2)CASSCF geometries of **5-con** and **6-con** are probably not the transition structures for conrotatory ring opening of, respectively, **7** and **4** on the CASPT2 surface,²⁸ comparison of the enthalpies of **5-con** and **6-con** is more meaningful than comparison of the enthalpies of diradicals **5** and **6**, since at the (2/2)CASSCF level the former diradical has one more imaginary vibrational mode than the latter.

(30) To compute the actual ratios of double to single rotations in the stereomutations of **4** and **7**, reaction dynamics calculations would be necessary. Dynamics calculations on the stereomutation of cyclopropane have found that molecules which undergo disrotatory ring opening do not, as predicted by transition state theory, contribute to net monorotation by undergoing preferential conrotatory closure.^{7c,d} Instead, dynamical effects favor molecules which undergo disrotatory ring opening contributing to double rotation by undergoing disrotatory closure.

Our calculations find that **12a** is favored over **12b**, by 3.0 kcal/mol at the (2/2)CASSCF level and by 4.0 at CASPT2. These energy differences are larger than those between **6** and **5** at these two levels of theory, which, as shown in Table 2, amount to only 0.7 and 1.6 kcal/mol, respectively. The larger energy differences between **12a** and **12b** can be ascribed in part to the presence in these two diradicals of the *trans*-methyl groups, one of which sterically destabilizes the *s-trans*-methyl group in **12b** more than the *s-cis*-methyl group in **12a**.

The same type of steric interaction is present in **14** too, and it also serves to destabilize **14**, relative to **12a**. The (2/2)-CASSCF energy of **12a** is computed to be lower than that of **14** by 2.7 kcal/mol, and CASPT2 calculations find this energy difference to increase to 3.8 kcal/mol. The size of the calculated energy difference between these two diradicals is large enough to account easily for the factor of 5 by which G&C found the rate of interconversion of **11** and **13** to be faster than the rate of interconversion of **11** and **13'** at 290 °C.

Why Is the *s-cis*-Methyl in **6 Preferred to the *s-trans*-Methyl in **5**?** Previous studies have provided evidence for a long-range electronic interaction between an *s-cis*-methyl at C-1 and the nonbonding p- π AO at C-3 in 1,3-diradicals.^{10b} With hyperconjugatively electron accepting C-F bonds at C-2, this interaction is computed to be destabilizing. This leads to a large preference for (0,0)-*s-trans,s-trans* over (0,0)-*s-cis,s-trans* transition structures being both predicted¹⁰ and found¹¹ in the stereomutations of 1,1-difluoro-2,3-dialkylcyclopropanes.

However, with hyperconjugatively electron donating bonds at C-2, the long-range electronic interaction between an *s-cis*-methyl at C-1 and the nonbonding p- π AO at C-3 is expected to be stabilizing.^{10b} Thus, the weakly electron donating C-H bonds at C-3 in pentane-2,4-diyl result in the energy difference between the *s-cis,s-trans*- and the *s-trans,s-trans*-(0,0) conformations being computed to be 3 times smaller in the hydrocarbon than in the fluorocarbon diradical.^{10b}

As shown by the relative energies of **5** and **6** in Table 2, the (0,0)-*s-cis,s-trans* conformation of the latter is actually lower in energy than the (0,0)-*s-trans,s-trans* conformation of the former. This reversal in conformational preference from that calculated for the (0,0) diradicals formed by conrotatory opening of *cis*- and *trans*-1,2-dimethylcyclopropane could be due either to steric destabilization of an *s-trans*-methyl group in **5** or to electronic stabilization of the *s-cis*-methyl group in **6** or to a combination of both these effects.

To assess the relative contributions of electronic and steric effects to the energetic preference for **6** over **5**, we compared the size of the energy difference between them to that between the *s-cis* (**15d**) and *s-trans* (**16d**) conformations of a closely related monoradical. In both **15d** and **16d** a C-H bond at C-3 was constrained to eclipse the bond between C-1 and C-2, so that the orientation of the inward hydrogen at C-3 in **15d** and **16d** was similar to that of the hydrogen at C-3 in **6** and **5**. We also compared the energy differences between the *s-cis*- and *s-trans*-methyl conformations of the analogous monoradicals and diradicals with geminal hydrogens, fluorines, and silyl substituents at C-2. The results of these calculations are given in Table 3.

The differences in energy between the *s-cis* (**15**) and *s-trans* (**16**) conformations of the monoradicals should largely reflect the differences in the diradicals between the steric interactions of the *s-cis*-methyl at C-1 in **6** and **17** with the in-plane hydrogen at C-3 and of the *s-trans*-methyl in **5** and **18** with the geminal substituents, R, at C-2 (Figure 4). The results in Table 3 for the monoradicals show that the *s-trans*-methyl conformation in **16**

Table 3. Relative ROHF, (2/2)CASSCF, ROMP2, and (2/2)CASPT2 Energies for the *s-cis* \rightarrow *s-trans* Isomerization of Radicals **15** and **16** and of Diradicals **5**, **6**, **17**, and **18**

reaction	ROHF, (2/2)CASSCF ^a	ROMP2, (2/2)CASPT2 ^b
18a \rightarrow 17a	1.2	0.3
16a \rightarrow 15a	2.2	2.0
18a + 15a \rightarrow 17a + 16a	-1.0	-1.7
18b \rightarrow 17b	3.5	4.1
16b \rightarrow 15b	2.1	2.2
18b + 15b \rightarrow 17b + 16b	1.4	1.9
18c \rightarrow 17c	-4.6 ^c	-6.4 ^c
16c \rightarrow 15c	-0.5 ^c	-0.5 ^c
18c + 15c \rightarrow 17c + 16c	-4.1 ^c	-5.9 ^c
5 \rightarrow 6	-0.7	-1.6
16d \rightarrow 15d	0.4	0.7
5 + 15d \rightarrow 6 + 16d	-1.1	-2.3

^a ROHF for radicals and (2/2)CASSCF for diradicals. ^b ROMP2 for radicals and (2/2)CASPT2 for diradicals. ^c For R = SiH₃ the lower energy conformation is the one in which a methyl C-H bond eclipses the C-C rather than the C-H bond at the radical center.

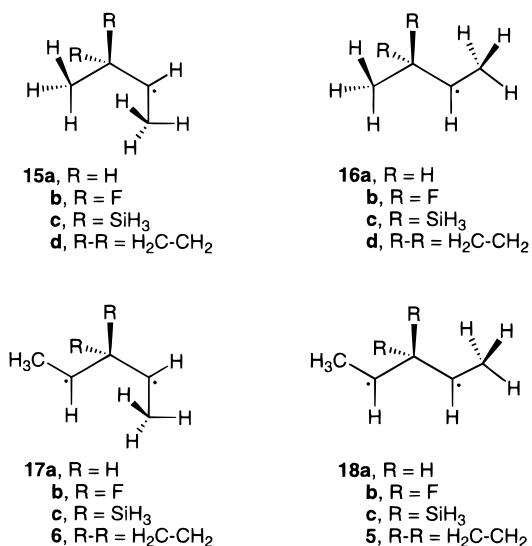


Figure 4. *s-cis* (**15**) and *s-trans* (**16**) monoradical and *s-cis,s-trans* (**17** and **6**) and *s-trans,s-trans* (**18** and **5**) diradical conformations.

is favored over the *s-cis* conformation in **15** by about the same amount for R = H and R = F. For R-R = H₂C-CH₂, the more sterically demanding ethano group at C-2 makes conformation **15d** only slightly higher in energy than **16d**. The larger still geminal silyl groups in **15c** and **16c** lead to the *s-cis*-methyl conformation of the former actually being favored. The energy differences between conformations **15** and **16** are nearly the same at both the ROHF and ROMP2 levels, as might be expected for energy differences that are largely steric in origin.

In diradicals **6** and **17** only for R = F is the preference for an *s-trans*-methyl conformation enhanced, relative to that in the corresponding monoradical. As already noted, with hyperconjugatively electron accepting C-F bonds at C-2, the long-range interaction between the *s-cis*-methyl at C-1 and the nonbonding p- π AO at C-3 is destabilizing.^{10b} This destabilizing electronic interaction in **17b** results in a 1.4–1.9 kcal/mol greater energetic preference for the *s-trans* conformation in diradical **18b** than in monoradical **16b**.

For electron donating C-R bonds at C-2 in the 1,3-diradicals the long-range interaction between the *s-cis*-methyl at C-1 and the nonbonding p- π AO at C-3 is stabilizing.^{10b} As already discussed in the comparison of diradical **2** with trimethylene, C-H bonds and cyclopropane C-C bonds at C-2 appear to

have nearly comparable electron donating abilities in 1,3-diradicals, and both of these types of bonds at C-2 are significantly less effective hyperconjugative electron donors than C–Si bonds. Therefore, it is not surprising that, for R = H and for R–R = H₂C–CH₂, the preferences for the *s-cis* conformation in diradicals **17a** and **6** are only slightly greater than in monoradicals **15a** and **15d**, amounting to ca. 1 kcal/mol at the (2/2)CASSCF,ROHF levels and 2 kcal/mol at (2/2)CASPT2,-ROMP2. However, for R = SiH₃, the preference for an *s-cis*-methyl conformation is much larger in diradical **17c** than in the monoradical, amounting to 5.9 kcal/mol at the (2/2)-CASPT2,ROMP2 levels.³¹

As shown in Table 3, the difference between the preferences for *s-cis*-methyl conformations in the diradicals and in the monoradicals increases on going from (2/2)CASSCF,ROHF to (2/2)CASPT2,ROMP2. This increase is 2–3 times larger for R = SiH₃ than for R = H and R–R = H₂C–CH₂. Inclusion of dynamic electron correlation generally enhances electron delocalization,¹⁴ and delocalization increases the attractive interaction between an *s-cis*-methyl at C-1 and the nonbonding p- π AO at C-3 in the diradicals. The enhancement of this attraction by inclusion of dynamic electron correlation is greatest for geminal silyl groups at C-2, because hyperconjugative donation of electrons from the C–R bonds at this carbon to the in-phase combination of p- π AOs at C-1 and C-3 is much larger for R = SiH₃ than for R = H or R–R = H₂C–CH₂.

Conclusions

Our calculations find that spiro-pentane (**1**) prefers conrotatory over monorotatory and disrotatory ring opening by only a slightly larger amount than cyclopropane. Moreover, at least part of this increased preference for conrotatory ring opening of **1** to the (0,0) conformation of diradical **2** resides in the preference for a bisected (0) conformation in cyclopropylcarbinyl monoradical. Despite the well-known ability of cyclopropane C–C bonds to stabilize carbocations hyperconjugatively,⁸

(31) The stabilization associated with the long-range attraction between an *s-cis*-methyl group at C-1 and the nonbonding p- π AO at C-3 in **17** can be reduced by rotating the *s-cis*-methyl group such that the π combination of C–H bonds points away from the C-3 radical center. For both R = H and R–R = H₂C–CH₂, rotating the *s-cis*-methyl group in this fashion costs ca. 1.5 kcal/mol, and for R = SiH₃, this rotation raises the energy by 2.6 kcal/mol. For R = F, rotating the *s-cis*-methyl group costs only 0.4 kcal/mol, because in **17b** the long-range interaction between the *s-cis*-methyl group at C-1 and the nonbonding p- π AO at C-3 is repulsive rather than attractive.^{10b}

neither the energies calculated for the isodesmic reaction in eq 1 for R = H and for R–R = H₂C–CH₂ nor the sizes of ΔE_{ST} computed in **2** and in (0,0)-trimethylene indicate that the cyclopropane ring in the former diradical is a significantly better hyperconjugative electron donor than the C–H bonds in the latter.²⁴

The weak electron donation from the cyclopropane ring in diradical **2** is further reduced by the presence of the methyl groups in diradicals **5** and **6**. Nevertheless, at the CASPT2 level of theory, conrotation is the preferred pathway for ring opening of *cis*-1,2-dimethylspiro-pentane (**4**) and of the *trans* isomer (**7**). The larger computed preference for double rotation over monorotatory ring opening in **4** than in **7** is in agreement with the experimental results of G&C.^{5a}

However, in contrast to the assumption made by these authors, our calculations find that diradical **6** is lower in energy than diradical **5**, and in addition, **6** is statistically favored over **5** by a factor of 2.²⁹ Consequently, the reason double rotation is both computed and found to be preferred by more in the stereomutation of **4** than of **7** is not that **4** undergoes disrotatory opening to **5**, as concluded by G&C. Quite the opposite, the larger preference for double rotation found in **4** is due to the fact that the transition structure (**6-con**) for conrotatory opening of **4** to diradical **6** has a lower free energy than the transition structure (**5-con**) for conrotatory opening of **7** to diradical **5**.

Contributing to the lower electronic energy of the *s-cis*-methyl conformation in **6**, relative to the *s-trans*-methyl conformation in **5**, is a weak long-range attraction between the *s-cis*-methyl group and the nonbonding p- π AO at C-3. Our calculations find that the much more strongly electron donating C–Si bonds at C-2 in **17c** make the long-range attraction between the *s-cis*-methyl and the p- π AO at C-3 much stronger in this diradical than in **6**, whereas the electron accepting C–F bonds at C-2 in **17b** make the interaction between the *s-cis* methyl and p- π AO at C-3 repulsive in this diradical.

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Supporting Information Available: Optimized geometries and energies for **1–18** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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