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Ab Initio Calculations of the Potential Surfaces for the Lowest Singlet and Triplet States of 2,2-Difluorocyclopentane-1,3-diyl. The Singlet Diradical Lies Below the Triplet

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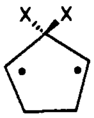
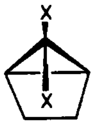
Abstract: *Ab initio* calculations on the lowest singlet and triplet states of 2,2-difluorocyclopentane-1,3-diyl (**2**) find that the singlet lies well below the triplet at all geometries. The planar singlet is the transition state for molecular inversion of 5,5-difluorobicyclo[2.1.0]pentane (**4**), for which ΔH^* is computed to be 18.3 kcal/mol at the CASPT2N/6-31G* level of theory. The small enthalpy difference between **2** and **4** suggests that the 1,3-diphenyl derivative of singlet diradical **2** should be thermodynamically stable toward ring closure.

In 1975 Buchwalter and Closs reported the EPR spectrum of cyclopentane-1,3-diyl (**1**), the first localized diradical to be observed directly.[1] In agreement with experiment, calculations by Conrad, Pitzer, and Schaefer on the planar diradical found the triplet to lie below the singlet by 0.9 kcal/mol.[2] More recent calculations by Sherrill, Seidl, and Schaefer have confirmed that the triplet diradical lies below the singlet, but the calculations found that a planar C_{2v} structure is not an energy minimum on the potential surface for either electronic state.[3]

The calculations found energy minima of C_2 symmetry for both states of **1**, with the triplet below the singlet by 1.2 kcal/mol at the CISD level of theory when the Davidson correction for quadruple excitations was included. The barrier to ring closure of singlet **1** to **3** was computed to be 1.3 kcal/mol at this level and only 0.7 kcal/mol after corrections for zero-point vibrational energies. The small energy barriers to ring closure, calculated for the triplet and singlet, are in good agreement with the experimental results of Buchwalter and Closs for the triplet and Herman and Goodman for the singlet diradical.[4]



1: X = H
2: X = F



3: X = H
4: X = F

The planar geometry of cyclopentane-1,3-diyl is obviously related to the (0,0) conformation of the trimethylene diradical, for which a triplet ground state has also been predicted.[5] However, our calculations on the 2,2-difluoro derivative of trimethylene found the singlet to lie well below the triplet.[6] Therefore, we undertook *ab initio* calculations on 2,2-difluorocyclopentane-1,3-diyl (**2**) in order to verify whether the singlet would also be found to lie below the triplet in this difluorinated diradical.

Extended Hückel calculations by Porter and co-workers predicted that, unlike the case in **1**,[3] the lowest singlet state of **2** should undergo ring closure without a barrier.[7] The finding that singlet **2** was a transition state, rather than an intermediate, would presage poorly for the observation of even a small amount of triplet **2** in thermal equilibrium with a lower singlet diradical, since intersystem crossing of the triplet would lead directly to closure of the singlet diradical to 2,2-difluorobicyclo[2.1.0]pentane (**4**). Therefore, we also investigated whether closure of singlet **2** to **4** is, in fact, barrierless; and we computed the energy required for molecular inversion (bridge flipping) in **4** *via* ring opening to **2**.

Theoretical Methodology

Calculations were performed with the 6-31G* basis set.[8] Geometries were optimized using ROHF wave functions for the triplet and TCSCF wave functions for the lowest singlet. The geometry optimizations[9] and the subsequent vibrational analyses were performed with Gaussian 92.[10] CISD calculations on **2** proved too large for us to carry out. Therefore, the effect of including additional electron correlation was investigated by performing CASPT2N calculations,[11] using ROHF and TCSCF reference wave functions. These calculations are the equivalent of RMP2 for the triplet and MP2 with two reference configurations for the singlet. The CASPT2N calculations were carried out with the MOLCAS suite of *ab initio* programs.[12]

Results and Discussion

The geometries of both the singlet and triplet states of **2** were optimized in C_{2v} symmetry. Vibrational analyses found the C_{2v} geometry of the singlet to have one imaginary frequency and that of the triplet two. Therefore, the optimized C_{2v} geometry on the

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Table 1. Calculated TCSCF,[a] ROHF,[b] and CASPT2N/6-31G* Energies (kcal/mol) of the Stationary Points on the Singlet and Triplet Potential Surfaces for 2,2-Difluorocyclopentane-1,3-diyl (**2**), Relative to the Energy of 5,5-Difluorobicyclo[2.1.0]pentane (**4**)[c,d]

state	geometry	TCSCF-ROHF	CASPT2N
singlet	C_{2v}	15.1	20.9
triplet	C_{2v}	21.8	30.7
triplet	C_s	21.8	30.9
triplet	C_2	21.2	30.6

[a] For singlet **2** and for **4**. [b] For triplet **2**. [c] *E*(TCSCF/6-31G*) = −391.6540 hartrees. [d] *E*(CASPT2N/6-31G*) = −392.6440 hartrees.

singlet surface is a transition state, and on the triplet surface it is a mountain top.

For the singlet the mode with the imaginary frequency preserves C_s symmetry. Following this mode led directly to **4**. Therefore, singlet **2** is the transition state for molecular inversion of **4**.

For the triplet, one of the modes with an imaginary frequency also preserves a plane of symmetry; the other preserves the C_2 axis. Both C_s and C_2 geometries were optimized, and vibrational analyses showed that the C_s geometry is a transition state that links two enantiomeric C_2 minima.

The TCSCF, ROHF, and CASPT2N energies of the stationary points on the singlet and triplet potential surfaces for **2** are given in Table 1. The triplet potential surface is so flat that at the ROHF level the C_{2v} geometry has essentially the same energy as C_s. However, at the CASPT2N level the C_{2v} geometry is slightly lower in energy than C_s. The change in the relative energies of these two triplet geometries on going from ROHF to CASPT2N is probably due to the fact that the planar C_{2v} geometry allows more hyperconjugative delocalization of one of the unpaired electrons by the C–F bonds.[6] Delocalization is generally favored by increasing the amount of electron correlation that is included in a calculation.[13]

The C_2 triplet geometry is 0.6 kcal/mol below C_{2v} at the ROHF level, but C_2 is only 0.1 kcal/mol lower than C_{2v} at CASPT2N. The C_2 geometry has the advantage over both C_{2v} and C_s of allowing partial deeclipsing of the hydrogens that are attached to C_4 and C_5. However, at the CASPT2N level the greater delocalization that is allowed by the planar geometries that the radical centers at C_1 and C_3 have in C_{2v} symmetry almost compensates for this advantage of the C_2 geometry.

The triplet C_2 energy minimum lies 6.1 kcal/mol above the singlet C_{2v} transition state at the ROHF-TCSCF level and 9.7 kcal/mol above it at CASPT2N. The C_{2v} singlet lies well below the triplet because in the singlet both, rather than just one, nonbonding electrons can occupy an MO that contains a hyperconjugative contribution from a low-lying antibonding orbital of the CF_2 group.[6] The increase in the size of the singlet–triplet energy difference with an increase in the amount of electron correlation provided is consistent with the hypothesis that the CF_2 group provides significantly more delocalization for the singlet than for the triplet.

The selective stabilization of the singlet by hyperconjugation with the CF_2 group is evident in comparison of the C_{2v} geometries of the two states. In the singlet the bond length of 1.475 Å between C_1 and C_2 is 0.015 Å shorter than that in the triplet, but the C–F bond length in the singlet of 1.361 Å is 0.006 Å longer than that in the triplet. In addition, because the orbital that is selectively occupied in the singlet has the p–π orbitals at C_1 and C_3 in phase,[6,7] the C_1–C_2–C_3 bond angle of 103.0° in the singlet is smaller by 1.8° than that in the triplet.

The five-membered ring in **2** causes the C_1–C_2–C_3 bond angle in the singlet to be smaller than that of 113.0° in the (0,0) geometry of singlet 2,2-difluorotrimethylene.[6] The smaller distance between C_1 and C_3, which allows a stronger bonding interaction between these two carbons in singlet **2** than in singlet 2,2-difluorotrimethylene, probably contributes to the finding that the singlet–triplet gap in the cyclic diradical is calculated to be a factor of 2 larger than that computed at a comparable level of theory for its acyclic counterpart.[6] The ethano bridge also makes a major electronic contribution to the increased singlet–triplet splitting in **2**, since calculations show that addition of alkyl groups to the terminal carbons of 2,2-difluorotrimethylene serves to stabilize the (0,0) singlet.[6]

The prediction that diradical **2** has a singlet ground state will be difficult to verify experimentally, since our *ab initio* calculations confirm Porter's extended Hückel finding[7] that singlet **2** is not a stable intermediate and should undergo barrierless ring closure to **4**. In contrast, a barrier to ring closure to **3** is calculated for the singlet state of hydrocarbon diradical **1**.[3]

The two diradicals differ, because in **1**, as in trimethylene,[14] interaction of the two radical centers with the central CH_2 group results in the out-of-phase combination of nonbonding p–π orbitals at C_1 and C_3 being selectively occupied. This orbital occupancy in **1** causes disrotatory closure to encounter a small energy barrier in trimethylene,[15,16] as well as in **1**. On the other hand, in **2**, as in 2,2-difluorotrimethylene,[6] the low-lying anti-bonding orbitals of the CF_2 group result in the in-phase combination of nonbonding p–π orbitals at C_1 and C_3 being stabilized.[7] The selective occupancy of this nonbonding MO allows disrotatory closure of **2** to **4** to proceed without encountering an energy barrier.

Since **2** is the transition state for molecular inversion of **4**, the energy required for this process is equal to the energy difference between these two species. As shown in Table 1, at the TCSCF level this energy difference is computed to be 15.1 kcal/mol, which increases to 20.9 kcal/mol at the CASPT2N level. A slightly larger increase, from 27.4 at the TCSCF level to 35.6 kcal/mol with inclusion of CI, was found in the calculations of the barrier to ring opening of **3** to **1**.[3] Both energy differences increase because provision of correlation beyond the TCSCF level has the greatest stabilizing effect on the strained ring bonds of **3** and **4**, for which no correlation is provided at the TCSCF level.[6,15]

At the CASPT2N level molecular inversion of **4** is predicted to require 14.7 kcal/mol less energy than that computed at the CI level for molecular inversion of **3**.[3] This predicted energy lowering is in qualitative agreement with the experimental finding that the presence of geminal fluorines generally lowers the barriers to cyclopropane ring openings,[17] with the results of calculations of the effect of fluorines on this reaction,[6] and with experimental data which show that electronegative substituents at C_5 of **3** lower the activation energy for molecular inversion.[18]

The geminal fluorines in **4** have a much greater effect on lowering the energy required to form the singlet than the triplet state of diradical **2**. In the hydrocarbon the C_s singlet and triplet states of diradical intermediate **1** are calculated at the CI level to be respectively 34.4 and 33.2 kcal/mol above **3**.[3] Using the CASPT2N energies in Table 1, the geminal fluorines are calculated to make the energy difference between singlet **2** and **4** smaller by 13.5 kcal/mol than the CI energy difference between singlet **1** and **3**.[3] In contrast, the geminal fluorines are calculated to make the CASPT2N energy difference between triplet **2** and **4** only 2.6 kcal/mol smaller than the CI energy difference between triplet **1** and **3**.

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However, with the 6-31G* basis set we calculate that the ring opening of **3** to both singlet and triplet **1** requires 1.7 kcal/mol more energy than the values obtained by Schaefer and co-workers with a DZP basis set.[3] Thus, if 6-31G* energies were used throughout, the CASPT2N values for the effect of the fluorines in **2** and **4** on lowering the energy differences between **1** and **3** would be 15.2 kcal/mol for the singlet diradicals and 4.3 kcal/mol for the triplets. For comparison, in the ring opening of 1,1-difluorocyclopropane to form 2,2-difluorotrimethylene, the presence of the fluorines is calculated to reduce the CI energy for ring opening of cyclopropane to (0,0) trimethylene by 11.6 kcal/mol for the singlet diradical and 6.3 kcal/mol for the triplet.[6,19]

As in the ring opening of hydrocarbon **3**,[3] inclusion of zero-point energy differences between the reactant and the transition state decreases the energy that is calculated to be required for ring opening of fluorocarbon **4** by about 3 kcal/mol, from 20.9 kcal/mol to 18.1 kcal/mol. Inclusion of calculated differences in heat capacities raises the predicted value of $\Delta H^{\ddagger}$ to 18.3 kcal/mol at 298 K.[20] At this temperature $\Delta S^{\ddagger}$ is calculated to be 1.3 cal/(mol·K), which gives a computed value of $\Delta G^{\ddagger} = 17.9$ kcal/mol at 298 K. If, as predicted, $\Delta G^{\ddagger}$ for molecular inversion of **4** is of about this size, it should be possible to employ dynamic ^{1}H or ^{19}F NMR to measure the free energy of activation for this process.

Since the enthalpy difference between singlet **2** and **4** is predicted to be only 18 kcal/mol, substituents at C_1 and C_3 might provide sufficient differential stabilization for singlet **2** to make the diradical lower in energy than the ring-closed form. For example, Coms and Dougherty have found that phenyl groups at C_1 and C_3 reduce the barrier to molecular inversion in **3** by nearly 25 kcal/mol.[22] Stabilization of singlet **2** by a similar amount, relative to **4**, is predicted to render the 1,3-diphenyl derivative of **2** thermodynamically stable toward ring closure.

Spectroscopic identification of 2,2-difluoro-1,3-diphenylcyclopentane-1,3-diyl should be facilitated by the presence of the phenyl chromophores. The absence of an EPR signal and/or obtaining a CPMAS solid-state NMR spectrum[23] would establish that, as expected from the calculations on **2**, the diradical has a singlet ground state. Efforts directed toward the preparation of both **4** and the diphenyl derivative of **2**[25] are in progress.

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Supplementary Material Available: Optimized geometries and energies for **4** and all the stationary points found on the singlet and triplet potential surfaces for **2** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(19) Calculations of the energies of isodesmic reactions show that introduction of the geminal fluorines stabilizes **3**, relative to cyclopropane, by 1.7 kcal/mol at the TCSCF level and by 1.5 kcal/mol at the CASPT2N level of theory. This selective stabilization of **3** accounts for most of the 2.0 kcal/mol greater effect of the geminal fluorines on cyclopropane than on **3** in reducing the energy required for ring opening to a triplet diradical. However, the selective stabilization of **3** by geminal fluorines, taken together with the 3.6 kcal/mol greater effect of geminal fluorines on reducing the energy difference between **3** and singlet **1**, implies that the fluorines furnish about 5 kcal/mol more stabilization for singlet **1** than for singlet trimethylene. An isodesmic reaction reveals that geminal fluorines at C-3 of pentane-2,4-diyl also provide substantially more stabilization for this singlet diradical than geminal fluorines at C-2 provide for singlet trimethylene.[6b] Therefore, hyperconjugative delocalization of electron density from the C–H bonds of the ethano bridge is the major contributor to the difference between the effect of fluorines on singlet **1** and on singlet trimethylene.

(20) $\Delta H^{\ddagger} = 32.3$ kcal/mol for molecular inversion of **3** was calculated at 0 K, but computed values of $\Delta H^{\ddagger}$ at higher temperatures were not given.[3] $\Delta H^{\ddagger} = 36.8$ kcal/mol was measured around 480 K.[21] Calculation of $\Delta H^{\ddagger}$ at this temperature would be expected to give a slightly higher value of $\Delta H^{\ddagger}$ than at 0 K and, thus, would provide a computed value in better agreement with experiment, as would use of the 6-31G* basis set.

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