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Cooperative and Competitive Effects of Substituents at C1 and C4 on the Barriers to Ring Inversion of 5,5-Difluorobicyclo[2.1.0]pentanes

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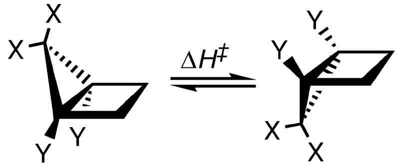


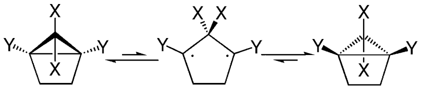
$$\Delta H^{\ddagger}_{X=F,Y=H} + \Delta H^{\ddagger}_{X=H,Y=F} > \Delta H^{\ddagger}_{X=Y=H} + \Delta H^{\ddagger}_{X=Y=F}$$

$$\Delta H^{\ddagger}_{X=F,Y=H} + \Delta H^{\ddagger}_{X=H,Y=CN} < \Delta H^{\ddagger}_{X=Y=H} + \Delta H^{\ddagger}_{X=F,Y=CN}$$

To identify the reasons for the very low barrier that has been measured for ring inversion of 1,4,5,5-tetrafluorobicyclo[2.1.0]pentane ($\Delta G^{\ddagger} = 6.8 \pm 0.2$ kcal/mol), CASSCF and CASPT2 calculations have been performed on ring inversion in this and other bicyclo[2.1.0]pentanes. The results of the calculations show that a cooperative interaction between the geminal fluorines at C2 and the fluorines at C1 and C3 in the singlet cyclopentane-1,3-diyl transition structure (TS) contributes 3.7 kcal/mol to lowering the barrier to ring inversion in the tetrafluoro compound. In contrast, a competitive substituent effect in the TS for ring inversion of 1,4-dicyano-5,5-difluorobicyclo[2.1.0]pentane is predicted to raise the barrier height by 6.1 kcal/mol. The origin of these cooperative and competitive substituent effects is discussed.

Introduction

Although cyclopentane-1,3-diyl (**2a**) has a triplet ground state,[1,2] ab initio calculations predicted 2,2-difluorocyclopentane-1,3-diyl (**2b**) would be found to have a singlet ground state.[3] This prediction was confirmed by subsequent experiments.[4,5]



1 **2** **1′**

a, X = Y = H; **b**, X = F, Y = H; **c**, X = H, Y = F
d, X = Y = F; **e**, X = H, Y = CN; **f**, X = F, Y = CN

Hyperconjugation with the C−F bonds,[6] which stabilizes singlet diradical **2b** relative to the triplet, was also predicted to make the energy difference between singlet **2b** and 5,5-difluorobicyclo[2.1.0]pentane (**1b**) 15.2 kcal/mol smaller than the energy difference between **2a** and **1a**.[3] If this energy lowering is equated with the lowering of the barrier to ring inversion of **1b**, relative to **1a**, the barrier of 36.8 kcal/mol measured for ring inversion of **1a**[7] leads to an expected barrier of about 22 kcal/mol for interconversion of **1b** and **1b′**.

Recently, Lemal and co-workers have measured the barrier to ring inversion of 1,4,5,5-tetrafluorobicyclo[2.1.0]pentane (**1d**) and found $\Delta G^{\ddagger} = 6.8$ kcal/mol at $-$ 55° C.[8] Because entropy

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TABLE 1. Calculated Effects of Substituents on Lowering the Enthalpy Differences[a] (kcal/mol) between Substituted Bicyclo[2.1.0]pentanes (1) and the Singlet Cyclopentane-1,3-diyl Transition Structures for Ring Inversion (TS 2) and Also between 1 and the Corresponding Triplet Cyclopentane-1,3-diyls (Triplet 2)[b]

	CASSCF/6-31G*		CASPT2/6-31G*		CASPT2/6-311G**	
bicyclopentane (**1**)	TS **2**	triplet **2**	TS **2**	triplet **2**	TS **2**	triplet **2**
a (X = Y = H)[c]	*25.9*	*23.3*	*33.7*	*32.5*	*32.0*	*31.2*
b (X = F, Y = H)	13.4	4.3	15.5	4.1	17.0	5.3
c (X = H, Y = F)	3.2	4.7	6.1	6.8	5.5	6.6
d (X = Y = F)	15.6	7.8	24.8	10.9	26.2	11.2
e (X = H, Y = CN)	10.3	10.8	14.4	15.0	14.8	15.4
f (X = F, Y = CN)	20.6	13.4	25.9	18.9	25.7	18.8

[a] All calculations were performed at CASSCF/6-31G* optimized geometries. Energies were converted to enthalpies at 298 K, using the results of CASSCF/6-31G* vibrational analyses. [b] Calculated values of $\Delta H^{\ddagger}$ for ring inversion of **1a** and of the enthalpy difference between **1a** and the triplet state of cyclopentane-1,3-diyl (**2a**) are given in the first row of the table in italics. Subsequent rows provide the amount by which each set of substituents is computed to reduce the enthalpy differences given in the first row. [c] The amount by which the enthalpy difference between **1a** and TS **2a** is lowered by substituents is $\Delta\Delta H^{\ddagger}$.

is not expected to make a large contribution to $\Delta G^{\ddagger}$ for interconversion of **1d** and **1d′** at this temperature, it appears that the four fluorines in **1d** lower the barrier to ring inversion by ca. 30 kcal/mol, relative to the barrier in **1a**. If it is assumed that the geminal fluorines at C5 in **1d** contribute 15 kcal/mol of this energy lowering (the amount predicted for the geminal fluorines at C5 in **1b**), then it also appears that the fluorines at C1 and C4 lower the barrier to ring inversion of **1d** by about as much as the geminal fluorines at C5.

There are several possible contributors to the large effect of the fluoro substituents at C1 and C4 of **1d**. A fluorine substituent does provide a small amount of stabilization for a radical center at the carbon to which the fluorine is attached, and fluorine substituents are also known to increase the strain in cyclopropane rings.[9] Both of these effects should reduce the energy difference between not only the singlet but also the triplet state of diradical **2d**, relative to **1d**. However, fluorine is also a π electron donor,[9] and there is both experimental[5b] and computational[10] evidence that π donors provide stabilization for the singlet states of cyclopentane-1,3-diyls which are geminally substituted at C2 with fluoro or alkoxyl substituents.

To investigate the contributions of these different possible effects of the fluorines at C1 and C4 to reducing the barrier to ring inversion in **1d**, we have performed ab initio calculations on bicyclo[2.1.0]pentanes **1a**−**d** and on the singlet and triplet states of cyclopentane-1,3-diyls **2a**−**d**. Our calculations indicate that the four fluorines in **1d** provide synergistic stabilization of the singlet diradical (**2d**) that serves as the transition structure (TS) for ring inversion.

We have also performed calculations on ring inversion in **1e** and **1f**, which have cyano substituents at C1 and C4. Our computational results show that, unlike the π electron-donating fluoro substituents at C1 and C3 in singlet **2d**, the π electron-accepting cyano substituents at these two carbons in singlet **2f** actually compete with the π electron-accepting pair of C−F bonds at C2 in providing stabilization of the TS for ring inversion of **1f**.

Computational Methodology

Geometry optimizations and vibrational analyses were performed, using complete active space self-consistent-field (CASSCF) calculations[11] with the 6-31G* basis set.[12] For **1a**−**d**, the orbitals in the active space consisted of the bonding and antibonding MOs of the C1−C4 σ bond, which correlate with, respectively, the in-phase and out-of-phase combinations of the 2p-π AOs at C1 and C3 in **2a**−**d**. The calculations on these molecules are designated (2/2)-CASSCF. For the calculations on **1e**/**2e** and **1f**/**2f**, a π and π* MO and a pair of π electrons on each cyano group were added to the active space, making the calculations on these molecules (6/6)-CASSCF.

The (2/2)- and (6/6)CASSCF vibrational analyses were used to characterize each stationary point as a minimum, transition structure (TS), or hill top. The unscaled vibrational frequencies were used to obtain the zero-point energies and heat capacities that were necessary to convert both the CASSCF and CASPT2 differences in electronic energies into differences in enthalpies at 298 K.

Single-point CASPT2 calculations[13] were performed at each of the CASSCF stationary points, to provide correlation for the electrons in the strained C−C bonds of **1** and to include the effects of dynamic electron correlation.[14] The single-point CASPT2 calculations were carried out with both the 6-31G*[12] and 6-311G** basis sets.[15] The CASSCF and CASPT2 calculations were performed with, respectively, the Gaussian 03[16] and MOLCAS 6.2[17] suites of electronic structure programs.

Results and Discussion

Table 1 shows the results of our calculations. The first line of the table gives the calculated enthalpies of activation at 298 K for interconversion of **1a** and **1a′** via a TS that corresponds to the singlet state of diradical **2a**. Also provided in the first line of Table 1 are the enthalpy differences computed between **1** and the lowest energy conformation of the triplet state of diradical **2a**.[18]

As shown in the first row of Table 1, the CASPT2 enthalpies of activation for interconversion of **1a** and **1a′** at 298 K are somewhat lower than the experimental value of $\Delta H^{\ddagger} = 36.6$ kcal/mol, which was measured around 480 K.[7] This is the case with both the 6-31G* and 6-311G** basis sets. Recomputing the (2/2)CASSCF thermal corrections for **1a** and for TS **2a** at

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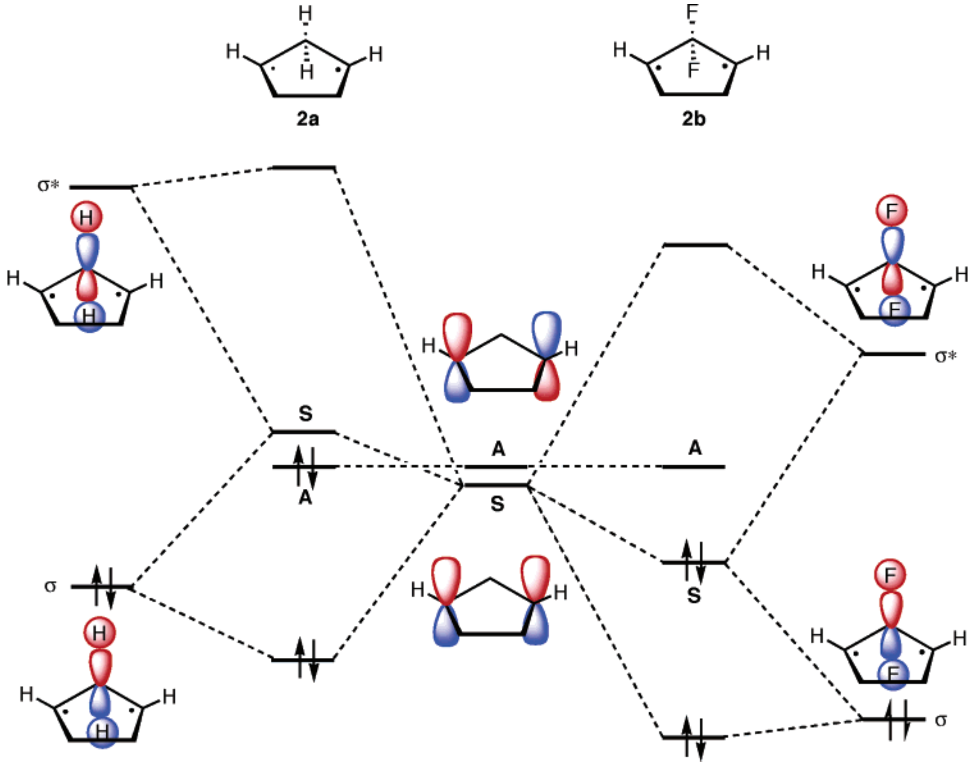

FIGURE 1. Schematic orbital interaction diagrams for cyclopentane-1,3-diyl (**2a**) and 2,2-difluorocyclopentane-1,3-diyl (**2b**).

480 K increases the calculated enthalpies of activation, but only by 0.2 kcal/mol.

The entries for **1b**−**f** in Table 1 are the amounts by which the fluoro and cyano substituents in these compounds reduce the enthalpy differences between **1b**−**f** and singlet and triplet **2b**−**f** from the corresponding enthalpy differences between unsubstituted **1a** and unsubstituted singlet and triplet **2a**. For example, the entries for TS **2d** mean that the four fluoro substituents in **1d** are calculated to lower the CASPT2 enthalpy of activation for ring inversion by $\Delta\Delta H^{\ddagger} = 24.8$ kcal/mol with the 6-31G* basis set and by $\Delta\Delta H^{\ddagger} = 26.2$ kcal/mol with the 6-311G** basis set. Thus, at 298 K, the enthalpy of activation for interconversion of **1d** and **1d′** is computed to be $\Delta H^{\ddagger} = 8.9$ kcal/mol by CASPT2/6-31G* and $\Delta H^{\ddagger} = 5.8$ kcal/mol by CASPT2/6-311G**.

The results of the CASSCF/6-31G* vibrational analyses give $\Delta S^{\ddagger} = 3.0$ cal/mol K, so at 298 K, the CASPT2 free energies of activation are computed to be $\Delta G^{\ddagger} = 8.0$ kcal/mol with the 6-31G* basis set and $\Delta G^{\ddagger} = 4.9$ kcal/mol with 6-311G**. These calculated values bracket the experimental value of $\Delta G^{\ddagger} = 6.8 \pm 0.2$ kcal/mol.[8]

Inspection of Table 1 shows that the CASPT2 substituent effects that are calculated with both basis sets are quite similar. For simplicity, we will only discuss the quantitative results obtained with the 6-311G** basis set, but the qualitative features of the CASPT2 results, obtained with both basis sets, are identical.

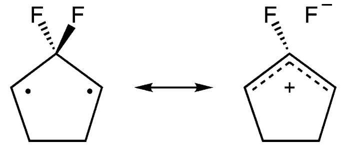

FIGURE 2. Schematic depiction of the stabilization of singlet diradical TS **2b** by hyperconjugation of the geminal C−F bonds at C2 with the 2p-π AOs at C1 and C3.

Effects of the Fluoro Substituents in 1b−d and 2b−d. Ring strain in **1b** presumably accounts for most of the effect of the geminal fluorines on making the enthalpy difference between **1b** and triplet diradical **2b** 5.3 kcal/mol smaller than the enthalpy difference between **1a** and triplet **2a**. However, as discussed previously,[3] the geminal fluorines at C2 stabilize singlet TS **2b** by ca. 11 kcal/mol more than triplet **2b**.

The selective stabilization of the singlet diradical is attributed to the ability of the out-of-phase combination of the C−F σ^* orbitals at C2 to accept electrons from the in-phase (**S**) combination of 2p-π AOs at C1 and C3.[3,6] As shown schematically in the diagram in Figure 1, this is the dominant orbital interaction in **2b**. The effects of this type of orbital interaction can be represented by the hyperconjugated resonance structure in Figure 2.[6]

Table 1 shows that substitution of fluorines at C1 and C4 of **1a** has a much smaller effect on lowering the barrier to ring inversion than substituting a pair of fluorines at C5 of **1a**. In fact, fluorine substitution at C1 and C4 of **1a** is calculated to provide 1.1 kcal/mol more stabilization for triplet **2c** than for singlet TS **2c**.

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(18) (a) The CASSCF geometries of **1a**−**f** and of the singlet and triplet states of **2a**−**f** are available as Supporting Information. Also available are the optimized geometries and energies of the singlet diradical intermediates that were located for **2a**,**c**, and **e**. (b) These intermediates have C_2 symmetry, with radical centers, especially those in **2c**, that are more highly pyramidalized than the radical centers in the diradical TSs for ring inversion. The energies of the singlet diradical intermediate and the TSs differ most for **2c**, for which the CASPT2/6-311G* energy difference is 2.0 kcal/mol. Because of the one fewer real vibrational frequency in the TS than in the intermediate, the CASPT2/6-311G* enthalpies of these two species differ by only 1.3 kcal/mol.

The reason for the very modest stabilization of singlet diradical **2c** by the fluorines at C1 and C3 is that, in contrast to the C−F bonds at C2 in **2b**, the C−H bonds at C2 in **2a** and **2c** act as weak, hyperconjugative, electron donors to the **S** combination of 2p-π AOs at C1 and C3.[6a] As shown schematically in the diagram in Figure 1, this is the dominant orbital interaction in **2a**. The lone pair orbitals on the fluorines that are attached to C1 and C3 in **2c** are also π donors, so that the C−H bonds at C2 and the fluorines at C1 and C3 compete with each other to donate electrons into the **S** combination of 2p-π AOs at C1 and C3 in **2c**.

The π lone pair orbitals on the fluorines in **2c** can donate electrons into not only the **S** but also the **A** nonbonding (NB) MO. However, in the singlet state of **2c**, the **A** NBMO is effectively doubly occupied,[19] so that donation of π electrons into the **A** NBMO provides little net stabilization for singlet **2c**. In contrast, in the triplet state of **2c**, the **A** NBMO is singly occupied, so that donation of π electrons into the **A** NBMO does provide net stabilization of triplet **2c.** It is for this reason that addition of fluorine substituents to C1 and C3 of **2a** provides more stabilization for triplet **2c** than for singlet **2c**.

With electron-accepting C−F bonds at C2, as in **2b**, rather than electron-donating C−H bonds, as in **2a**, one would expect the addition of π-donating, fluoro substituents at C1 and C3 to provide more stabilization for the singlet than for the triplet diradical. Inspection of the results in Table 1 confirms that this is, in fact, the case. Addition of fluorines to C1 and C3 of **2b**, forming **2d**, stabilizes the singlet state by 9.2 kcal/mol but stablizes the triplet state by only 5.9 kcal/mol.

The 11.2 kcal/mol stabilization of triplet **2d**, relative to **1d**, by four fluorines is 0.7 kcal/mol less than the sum of the 5.3 and 6.6 kcal/mol stabilization energies of, respectively, triplets **2b** and **2c**. In contrast, the 26.2 kcal/mol stabilization of singlet TS **2d**, relative to **1d**, by four fluorines is actually 3.7 kcal/mol greater than the sum of the 17.0 and 5.5 kcal/mol stabilization energies of, respectively, singlet TSs **2b** and **2c**.

Clearly, the fluorines at C1 and C3 are acting cooperatively with the geminal fluorines at C2 to stabilize TS **2d**. In terms of the orbitals shown in Figure 1, the presence of the electron-accepting C−F bonds at C2 makes donation of the 2p-π lone pair electrons on the fluorines at C1 and C3 into the **A** NBMO in TS **2d** more favorable than donation into the **S** orbital in TS **2c**. In terms of the resonance structures in Figure 2, the presence of the π electron-donating fluorines at C1 and C3 results in a greater contribution from the ionic resonance structure in TS **2d** than from that in TS **2b**.[20]

This type of cooperativity between the geminal fluorines at C2 and the fluorines at C1 and C3 in TS **2d** should manifest itself in the bond lengths in this singlet diradical. In particular, the C1(C3)−F bond lengths should be shorter in TS **2d** than in TS **2c**. However, this comparison is complicated by the possible inductive effects of the geminal fluorines at C2 on the C1(C3)−F bond lengths in TS **2d**.

In contrast to TS **2d**, the enthalpy of triplet **2d** shows no evidence of a cooperative substituent effect. Indeed, as already noted, the stabilization of triplet **2d**, relative to **1d**, by four fluorines is 0.7 kcal/mol less than the sum of the stabilizations of triplets **2b** and **2c**. Therefore, the C1(C3)−F bond lengths in triplet **2d** can be used as a reference to judge the effect of cooperativity on the C1(C3)−F bond lengths in TS **2d**.

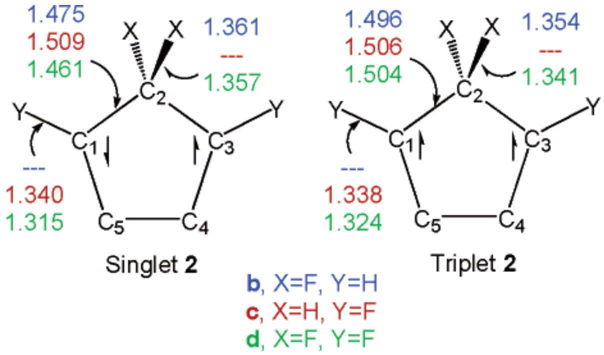

FIGURE 3. Selected C−C and C−F bond lengths (Å) in the (2/2)-CASSCF/6-31G* geometries of singlet and triplet di- and tetrafluorocyclopentane-1,3-diyls (**2b**−**d**).[21]

As shown in Figure 3, the C1(C3)−F bonds in triplet **2d** are 0.014 Å shorter than those in triplet **2c**, suggesting that the geminal C−F bonds at C2 actually do have an inductive effect on the bond lengths in **2d**. However, the C1(C3)−F bonds in singlet **2d** are 0.025 Å shorter than those in singlet **2c** and 0.009 Å shorter than those in triplet **2d**. The shorter C1(C3)−F bond lengths in singlet **2d** are consistent with stabilization of the TS for ring inversion of **1d** by donation of 2p-π lone pair electrons from the fluorines at C1 and C3, in synergy with hyperconjugation by the electron-accepting pair of C−F bonds at C2.

Effects of the Cyano Substituents in 1e,f and 2e,f. Although cyano is a better radical stabilizing substituent than fluorine, unlike fluorine, cyano is a π acceptor rather than a π donor. Therefore, using either Figure 1 or Figure 2, it is easy to predict that the cyano substituents at C1 and C3 in singlet **2f** should compete, rather than cooperate, with the geminal fluorines at C2 in stabilizing the TS for ring inversion of **1f**. Consequently, the net stabilization of TS **2f** by the fluorine and cyano substituents should be less than the sum of the stabilization enthalpies of TSs **2b** and **2e**.

To test this prediction, we carried out (6/6)CASSCF and CASPT2 calculations on **1e** and **2e** and on **1f** and **2f**. The results, which are given in Table 1, support the existence of a competitive substituent effect on the stabilization of TS **2f**.

Because cyano is strongly radical stabilizing, the cyano groups at C1 and C3 in **2e** are computed to make the barrier to ring inversion 14.8 kcal/mol smaller in **1e** than in **1a**. However, this stabilization is not unique to TS **2e**. Table 1 shows that the enthalpy difference between **1e** and triplet **2e** is also computed to be smaller by 15.4 kcal/mol than the enthalpy difference between **1a** and triplet **2a**.

If the lowering of the barriers to ring inversion by the fluorines at C2 in TS **2b** and the cyano groups at C1 and C3 in TS **2e** were additive in TS **2f**, the lowering of the barrier to ring inversion in **1f** would be 17.0 + 14.8 = 31.8 kcal/mol. However, the lowering of the barrier is actually calculated to be only 25.7 kcal/mol, 6.1 kcal/mol less than that predicted by additivity.

On the other hand, if the stabilization enthalpies of triplet **2b** and triplet **2e** are added, the sum is 5.3 + 15.4 = 20.7 kcal/mol. Therefore, the 18.8 kcal/mol, by which the cyano and fluoro substituents actually do make the enthalpy difference between triplet **2f** and **1f** smaller than that between triplet **2a** and **1a**, is just 1.9 kcal/mol less than the reduction expected from additivity.

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(19) The dominant configuration in the CASSCF wave function has the **A** NBMO doubly occupied; however, there is a second configuration, of smaller weight, in which the **S** NBMO is doubly occupied.

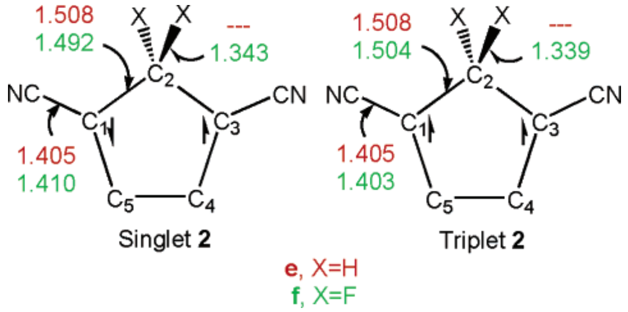

FIGURE 4. Selected C−C and C−F bond lengths (Å) in the (6/6)-CASSCF/6-31G* geometries of singlet and triplet 1,3-dicyanocyclopentane-1,3-diyl (**2e**) and its 2,2-difluoro derivative (**2f**).

The competition between the fluorines at C2 and the cyano groups at C1 and C3 in TS **2f** should manifest itself in the bond lengths in this singlet diradical. In particular, the C−CN bond lengths should be longer in singlet **2f** than in singlet **2e**. Figure 4 shows that this expectation is borne out.

Because the substituent effects on the enthalpy of triplet **2f** are nearly additive, one would not expect the C−CN bond lengths in triplet **2f** to be significantly different from the C−CN bond lengths in triplet **2e**. However, the competition between the geminal C−F bonds at C2 and the cyano groups at C1 and C3 in TS **2f** should result in the C−CN bond lengths in triplet **2f** being shorter than those in this singlet diradical. Figure 3 shows that these expectations regarding the C−CN bond lengths in triplet **2e** and triplet **2f** are also borne out.

Another consequence of the competition between the fluoro and cyano substituents in TS **2f** is that its diradical character should be greater than the diradical character in TS **2b**. If the ratio of the square of the coefficients of the first two configurations in the CASSCF wave function is used as a measure of diradical character (the smaller the ratio, the larger the amount of diradical character),[22] the finding that the ratio is $c_1^2/c_2^2 = 2.21$ in singlet **2f** compared to $c_1^2/c_2^2 = 2.35$ in singlet **2b** confirms the hypothesis that **2f** has more diradical character than **2b**.

On the other hand, the finding that the substituent effects in singlet **2d** are cooperative means that the presence of the π electron-donating fluorines at C1 and C3 should make the diradical character of singlet **2d** smaller than that of singlet **2b**. This conjecture too is confirmed by the ratio of $c_1^2/c_2^2 = 3.60$ in TS **2d**, which is more than 50% larger than the ratio of $c_1^2/c_2^2 = 2.35$ in TS **2b**.

Conclusions

The addition of fluorine substituents to C1 and C4 of **1b** is computed to make the barrier to ring inversion in **1d** lower than that in **1b** by 9.2 kcal/mol. Of this energy lowering, 3.7 kcal/mol is attributable to the cooperative interaction between the π electron-donating fluorines at C1 and C3 and the electron-accepting C−F bonds at C2 in TS **2d**. This cooperative substituent effect contributes to the low barrier to ring inversion in **2d**, measured by Lemal and co-workers.[8]

Our calculations also confirm the conjecture that the interaction between the π electron-accepting cyano groups at C1 and C3 and the electron-accepting C−F bonds at C2 in TS **2f** is competitive. Although the barrier to ring inversion in **1f** is computed to be about the same size as the barrier in **1d**, the lowering of the barrier height in **1f**, relative to **1a**, is 6.1 kcal/mol less than the sum of the lowering of the barrier heights by the geminal fluoro substituents at C2 in **1b** and by the cyano groups at C1 and C4 in **1e**.

We hope that experimental verification of our predictions of the effects of substituents on the barriers to ring inversion in bicyclo[2.1.0]pentanes **1b**, **1c**, **1e**, and **1f** will be forthcoming.

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Supporting Information Available: Geometries and energies of all the minima and TSs on the potential energy surfaces for ring inversion of **1a**−**f**, optimized geometries and energies of triplet diradicals **2a**−**f**, and complete lists of authors for refs 16 and 17 (29 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) There is an obvious analogy between the cooperative stabilization of singlet diradical **2d** and the captodative stabilization of a monoradical by a π donor and a π acceptor attached to the radical center. For a review of the captodative effect, see: Viehe, H. G.; Janousek, Z.; Merenyi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148.

(21) The bond lengths given for singlet **2c** in Figure 2 are actually those in the singlet C_2 diradical intermediate, rather than those in the C_1 TS for ring inversion. TS **2c** connects a C_s intermediate to the C_2 intermediate in the ring inversion of **1c**,[18] and the reaction coordinate in the TS corresponds to inversion of one of the radical centers. Consequently, there is a planar radical center in TS **2c**, and the C−F bond to this nominally sp^2 carbon is anomalously short (1.330 Å), 0.008 Å shorter than the radical center that does not undergo inversion in the TS.

(22) See, for example: Borden, W. T. *Diradicals*; Wiley: New York, 1982; pp 1−61.