the more highly alkyl substituted cation (**6**) to the trihalo cation (**8**) the fluorine substituted cations change from being most stable to least stable by a wide margin. For the ethyl cation (**3**) fluorine and chlorine have identical effects on cation stability.

These results show that it is not possible to make a blanket statement with regard to the relative ability of halogens to stabilize an adjacent cationic center through direct π donation. From the limited examples examined here it appears that electron-releasing substituents favor fluorine and electron-withdrawing substituents favor chlorine. Bromine is found to be uniformly superior to fluorine or chlorine at stabilizing an adjacent carbocation. For bromine, however, the bridged isomer, where possible, is even more stable.

Finally, it is interesting to note that halogens are remarkably good at stabilizing gas-phase carbocations given their high electronegativities. There are many examples of bromine in particular stabilizing cations via bridging, but the calculations reported here argue that cations which place a halogen directly adjacent to the cationic center should also be very favorable, in some cases being competitive with cations of well-known stability such as *tert*-butyl.

Registry No. 1a, 53172-39-7; **1b**, 23134-14-7; **1c**, 20174-90-7; **2a**, 29526-62-3; **2b**, 41797-39-1; **2c**, 20500-81-6; **3a**, 29526-61-2; **3b**, 41797-38-0; **3c**, 83490-90-8; *trans*-**4a**, 78195-76-3; *cis*-**4a**, 78195-75-2; *trans*-**4b**, 78195-74-1; *cis*-**4b**, 78195-73-0; *trans*-**4c**, 52754-93-5; *cis*-**4c**, 52754-94-6; **5a**, 53172-45-5; **5b**, 53172-23-9; **5c**, 143171-84-0; **6a**, 51608-55-0; **6b**, 53176-16-2; **6c**, 143171-85-1; H, 12184-88-2.

Ab Initio Calculations of the Barriers to Rotation in 1,1-Difluoroallyl Radical and an Analysis of the Factors That Govern Rotational Barriers in Fluorinated Allylic Radicals

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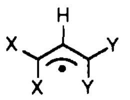
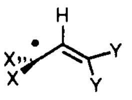
Abstract: The energies required to rotate the CF_2 and the CH_2 group out of conjugation in 1,1-difluoroallyl radical have been calculated at the SD-CI/6-31G*//UHF/6-31G* level of theory. In agreement with experiment, the barrier to CF_2 group rotation in this allylic radical is computed to be much larger than that in 1,1,3,3-tetrafluoroallyl radical. The factors that govern the size of rotational barrieirs in allylic radicals are analyzed, and the origin of the difference in barriers to CF_2 group rotation in these two fluorinated allylic radicals is discussed.

Ab initio calculations[1] have found, in agreement with experiment, that the rotational barrier in 1,1,3,3-tetrafluoroallyl radical (**1**)[2] is considerably lower than that in the parent allyl radical (**2**).[3a,b] The calculations showed that this difference is due to the strong preference of CF_2 radical centers for pyramidal geometries. The pyramidalization energy that is recovered on twisting a CF_2 group out of conjugation in **1** was found to comprise the major part of the difference between the CF_2 rotational barrier in **1** and the CH_2 rotational barrier in **2**.

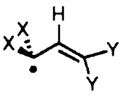
Although, to the best of our knowledge, the CF_2 and CH_2 rotational barriers in 1,1-difluoroallyl radical (**3**) have not been measured precisely, there is experimental evidence[2,3a] that they are both considerably higher than the CF_2 rotational barrier in **1**. This seems rather surprising. One might have expected that in **3**, although the energy required to rotate the CH_2 group out of conjugation would be high and close to that in **2**, the barrier to rotating the CF_2 group would be low and similar to that in **1**.



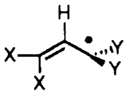
1a, X = Y = F
2a, X = Y = H
3a, X = F, Y = H



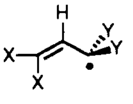
1b, X = Y = F
2b, X = Y = H
3b, X = F, Y = H



1c, X = Y = F
2c, X = Y = H
3c, X = F, Y = H



3d, X = F, Y = H



3e, X = F, Y = H

In this paper we report the results of our calculations on the rotational barriers in **3**. In agreement with experiment, we find that the CF_2 rotational barrier in **3** is substantially higher than that in **1**, whereas the CH_2 rotational barrier in **3** is lower than that in **2**. The results of our calculations permit the factors that govern the rotational barrier heights in **1**–**3** to be analyzed.

Computational Methodology

Reactant and transition state geometries were fully optimized in C_s symmetry at the UHF level,[4] using the 6-31G* basis set.[5] All stationary points were characterized by vibrational analyses. Electron correlation, beyond that in the UHF wave function, was taken into account by performing configuration interaction (CI) calculations at the optimized UHF/6-31G* geometries. All single and double excitations were included (SD-CI). The C and F 1s electrons were frozen in the SD-CI calculations. The calculations were carried out using either the GAUSSIAN 86[6] or GAUSSIAN 90[7] package of ab initio programs.

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Table I. Optimized Bond Lengths (Å) and Bond Angles (deg) and Pyramidalization Angles (deg)[a] for **1**, **2**, and **3** at the UHF/6-31G* Level

	1a	**1b**	**1c**	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**3d**	**3e**
r_1	1.372	1.454	1.473	1.390	1.479	1.479	1.364	1.467	1.480	1.309	1.308
r_2	1.372	1.314	1.309	1.390	1.327	1.327	1.397	1.329	1.316	1.476	1.475
r_3	1.071	1.076	1.072	1.078	1.081	1.082	1.074	1.079	1.079	1.076	1.077
r_4	1.307	1.315	1.319	1.074	1.076	1.076	1.308	1.317	1.322	1.305	1.305
r_5	1.305	1.315	1.319	1.076	1.076	1.076	1.308	1.317	1.322	1.304	1.304
r_6	1.307	1.294	1.296	1.074	1.076	1.075	1.072	1.075	1.075	1.075	1.075
r_7	1.305	1.294	1.296	1.076	1.076	1.076	1.073	1.075	1.075	1.075	1.075
θ_1	117.2	121.1	119.8	117.7	116.7	116.7	115.3	117.7	116.1	116.0	116.0
θ_2	117.2	117.1	118.6	117.7	118.5	118.5	120.5	119.6	121.5	120.1	120.2
θ_3	122.6	123.8	115.1	121.4	121.0	120.5	124.1	123.8	114.9	124.7	124.7
θ_4	112.2	112.5	109.2	117.4	118.0	117.4	111.3	112.4	109.0	109.7	109.7
θ_5	122.6	124.1	124.3	121.4	121.4	121.4	120.4	121.0	121.5	120.9	120.7
θ_6	112.2	110.3	110.2	117.4	116.8	116.8	118.2	117.0	116.9	118.3	118.1
ϕ^a		0.0	43.0		0.0	12.0		0.0	43.6	0.0	7.4

[a] The pyramidalization angle at the rotated terminal group is defined as the angle between the plane of this group and the extension of the C–C bond connected to this group.

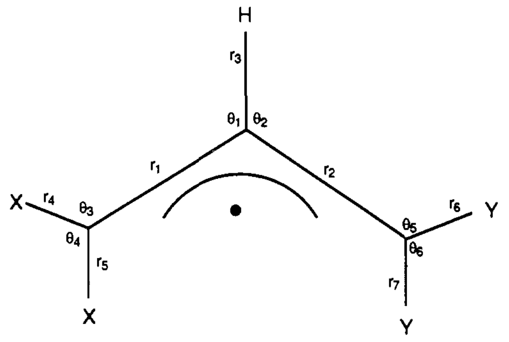

Figure 1. Definition of the bond lengths (r) and the bond angles (θ) in the radicals in Table I, including **b–e**, where one terminal group is orthogonal to the C–C–C plane.

Results and Discussion

The equilibrium geometry of **3** was found to be planar (**3a**). The geometrical parameters of **3a** are defined in Figure 1 and given in Table I. In agreement with the results of a previous INDO study,[8] the bond to the CF_2 group is found to be about 0.03 Å shorter than that to the CH_2 group.

Two transition states were found for the rotation of the CF_2 group. The one of lower energy is **3c**. As shown in Table I, in **3c** the pyramidalization angle, ϕ, at the twisted CF_2 group is 43.6°. The higher energy transition state is similar to **3c**, but the CF_2 group is pyramidalized in the opposite sense. The latter transition state is computed to lie higher in energy than **3c** by 2.5 kcal/mol at the UHF/6-31G* level.

For rotation of the CH_2 group only one transition state (**3e**) was found. As shown in Table I, in **3e** the pyramidalization angle, ϕ, at the twisted CH_2 group is only 7.4°. Unlike the case for the rotated CF_2 group, planarization of the rotated CH_2 group requires so little energy that geometries in which the pyramidalization angle is opposite to that in **3e** can relax to **3e** by passing through a planar geometry, without encountering an energy barrier.

The UHF and SD-CI energies of **3a**, **3c**, and **3d** are given in Table II; and the energies of **3c** and **3e**, relative to **3a**, are given in Table III, including corrections for zero-point energy differences. Table III shows that at the SD-CI level, rotation of the CF_2 group in **3** requires only 2.7 kcal/mol less energy than rotation of the CH_2 group. Including zero-point energies, this difference is reduced to 0.9 kcal/mol.

Table III also gives the rotational barriers calculated for **1** and **2**.[1] Given the greater than 10 kcal/mol difference between the rotational barriers in **1** and **2**, it is surprising that the energy required to form **3c** by rotation of the CF_2 group in **3a**, is calculated to be nearly the same as that required to form **3e** by rotation of the CH_2 group. Table III shows that the reason for this finding is that the energy required for CF_2 group rotation to form **3c** from **3a** is 2.7 times greater than the 4.0 kcal/mol that is necessary to form **1c** from **1a**. This computational result is in agreement with the experimental finding of a substantially larger barrier to CF_2 group rotation in **3** than in **1**.[2,3a]

Table II. UHF/6-31G* and SD-CI/6-31G* Energies (hartrees) at the UHF/6-31G* Optimized Geometries for **1**,[1] **2**,[1] and **3**

	UHF	SD-CI
1a	−511.8620	−512.7436
1b	−511.8375	−512.7235
1c	−511.8545	−512.7392
2a	−116.4681	−116.8142
2b	−116.4383	−116.7896
2c	−116.4385	−116.7898
3a	−314.1695	−314.7832
3b	−314.1306	−314.7476
3c	−314.1496	−314.7679
3d	−314.1453	−314.7635
3e	−314.1454	−314.7636

In order to understand why the energy required for CF_2 group rotation is computed to be considerably larger in **3** than in **1**, the same type of analysis can be applied to the rotational barriers in **3** that was used to understand why the rotational barrier in **1** is much lower than that in **2**.[1] For this analysis the rotation of each CX_2 group (X = F or H) in **3** is divided conceptually into two discrete steps. In the first step the CX_2 group is twisted out of conjugation with the pyramidalization angle at this group fixed at $\phi = 0°$, resulting in formation of **3b** and **3d**. The energies of these two geometries, relative to that of **3a**, are given in Table III. We define these energy changes as the *intrinsic* barriers to rotation in **3**. In the second step the twisted CX_2 group is allowed to relax from a planar to a pyramidalized geometry. The calculated energy lowerings upon pyramidalization are given by the differences in Table III between the energies of **3b** and **3c** and between those of **3d** and **3e**.

As can be seen from the SD-CI energies in Table III, the intrinsic barrier to rotation of a *planar* CX_2 group in **3a** actually requires 10 kcal/mol more energy when X = F (**3a** → **3b**) than when X = H (**3a** → **3d**). Formation of **3c** requires less energy than formation of **3e** only because pyramidalization of the CF_2 group is very exothermic, lowering the energy of **3b** by 12.7 kcal/mol, whereas pyramidalization of the CH_2 group lowers the energy of **3d** by less than 0.1 kcal/mol. Were it not for the much larger pyramidalization energy of CF_2, the barrier to rotating the CF_2 group in **3** would be nearly twice as large as the barrier to rotating the CH_2 group.

In contrast, as shown in Table III, the energy required to rotate a planar CF_2 group in **1a** to form **1b** is actually slightly less than that required to rotate a planar CH_2 group in **2a** to form **2b** and almost the same as that required to rotate a planar CH_2 group in **3a** to form **3d**. The very large (nearly 10 kcal/mol) difference between the energies required for planar CF_2 group rotation in **1a** and **3a** demonstrates that the identity of the rotating CX_2 group

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[8] Kispert, L. D.; Pittman, C. U.; Allison, D. L.; Patterson, T. B., Jr.; Gilbert, C. W., Jr.; Hains, C. F.; Prather, J. *J. Am. Chem. Soc.* **1972**, *94*, 5979.

Table III. Relative Energies (kcal/mol) of Geometries of **1**, **2**, and **3** at UHF/6-31G*, SD-CI/6-31G*, and with Inclusion of Zero-Point Energy (ZPE) Differences between Equilibrium Geometries and Transition States

	1a	1b	1c[a]	2a	2b	2c[a]	3a	3b	3c[a]	3d	3e[a]
UHF	0	15.4	4.7	0	18.7	18.6	0	24.4	12.5	15.2	15.1
SD-CI	0	12.6	2.7	0	15.4	15.3	0	22.3	9.6	12.3	12.3
CI+ZPE	0		4.0	0		14.4	0		10.9		11.8

[a] Transition state for CX_2 rotation.

cannot be the sole factor that determines the intrinsic energies required for CX_2 group rotation in these fluoroallylic radicals.

Clearly, the nature of the other terminal group must play an important role. For example, since **3b** and **3d** are both formed from the same allylic radical (**3a**), the difference in energies required for planar CF_2 and CH_2 group rotation in **3a** could reasonably be attributed to the difference between the energies of the remaining π bonds, $RCH{=}CH_2$ in **3b** and $R'CH{=}CF_2$ in **3d**. However, in order for the difference between the two rotational barriers in **3a** to be attributed primarily to the difference in π bond energies of **3b** and **3d**, it must be shown that there is not a large difference between the interactions of the planar radical centers with the adjacent π bonds in these two twisted geometries. A necessary condition for this to be the case is that the total energy of **3b** and **3d** must not depend on which radical center is attached to which π bond.

Exchanging the nonconjugated CF_2 group in **3b** and the nonconjugated CH_2 group in **3d** gives **1b** plus **2b**. The isodesmic reaction

$$\mathbf{3b} + \mathbf{3d} \rightarrow \mathbf{1b} + \mathbf{2b} \qquad (1)$$

is, in fact, calculated to be almost thermoneutral. The reaction in eq 1 is computed to be endothermic by 0.1 kcal/mol at the UHF level and exothermic by 1.2 kcal/mol at the SD-CI level.

The near thermoneutrality of the isodesmic reaction in eq 1 provides some justification for attributing the difference between the two rotational barriers in **3a** largely to the difference between the π bond energies of the radicals, **3b** and **3d**, that are formed. However, in comparing the intrinsic rotational barriers in different allylic radicals, such as **1**, **2**, or **3**, the energies of the different allylic π systems at the conjugated geometries (**1a**, **2a**, and **3a**) must also be taken into account.

More specifically, as shown schematically in Figure 2 for **3**, the energy that is required to rotate a planar CX_2 group out of conjugation $[\Delta E^{CX_2}(3)]$ is equal to the difference between the π bond energy of the conjugated allylic radical $[E_\pi(\mathbf{3a})]$ and the energy of the π bond that remains in the twisted radical after rotation of the planar CX_2 group $[E_\pi(\mathbf{3b})$ or $E_\pi(\mathbf{3d})]$. Using this relationship between π bond energy differences and the SD-CI barriers to rotation for **1**–**3** in Table III, eqs 2–5 are obtained.

$$E_\pi(\mathbf{3a}) - E_\pi(\mathbf{3b}) = \Delta E^{CF_2}(3) = 22.3 \text{ kcal/mol} \qquad (2)$$

$$E_\pi(\mathbf{3a}) - E_\pi(\mathbf{3d}) = \Delta E^{CH_2}(3) = 12.3 \text{ kcal/mol} \qquad (3)$$

$$E_\pi(\mathbf{1a}) - E_\pi(\mathbf{1b}) = \Delta E^{CF_2}(1) = 12.6 \text{ kcal/mol} \qquad (4)$$

$$E_\pi(\mathbf{2a}) - E_\pi(\mathbf{2b}) = \Delta E^{CH_2}(2) = 15.4 \text{ kcal/mol} \qquad (5)$$

Subtracting eq 3 from eq 2 gives

$$E_\pi(\mathbf{3d}) - E_\pi(\mathbf{3b}) = \Delta E^{CF_2}(3) - \Delta E^{CH_2}(3) = 10.0 \text{ kcal/mol} \qquad (6)$$

Thus, at the SD-CI level the π bond of **3d** is calculated to be 10.0 kcal/mol stronger than that of **3b**.

The π bond in **3d** should be very similar to that of 1,1-difluoroethylene, and the π bond of **3b** should be similar to that in ethylene. Nevertheless, as shown in Table IV, at the GVB-PP(1)/6-31G* level we calculated that the π bond dissociation energy (BDE) of 1,1-difluoroethylene is 63.3 kcal/mol,[9] which is actually 2.3 kcal/mol less than the π BDE that we calculate for ethylene at the same level of theory. Both calculated π BDEs are in excellent agreement with those obtained from experiments.[10,11]

However, in comparing the difference between $E_\pi(\mathbf{3d})$ and $E_\pi(\mathbf{3b})$ with the difference between the π BDEs of 1,1-fluoroethylene and ethylene, it must be noted that $E_\pi(\mathbf{3d})$ in eq 3 is defined with the CF_2 radical center, formed on breaking the π bond in **3d**, constrained to planarity (see Figure 2). In contrast,

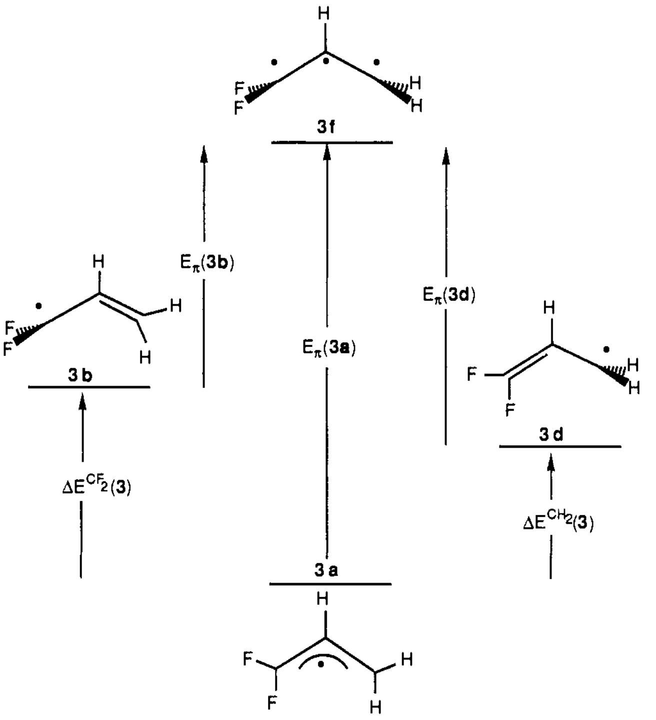

Figure 2. Schematic depiction of the energies of **3a**, **3b**, and **3d**, relative to that of a completely nonconjugated radical with planar terminal groups (**3f**). $\Delta E^{CF_2}(3)$ and $\Delta E^{CH_2}(3)$ are the energies required to rotate, respectively, the planar CF_2 and CH_2 groups out of conjugation in **3a**.

Table IV. GVB-PP(1)/6-31G* Energies (hartrees) for Ethylene, 1,1-Difluoroethylene, and Tetrafluoroethylene and the Energies (kcal/mol) Required To Form Singlet Diradicals by Rotation about the C–C Bond, with the CX_2 and CY_2 Constrained to Planarity and Allowed to Pyramidalize

		equilibrium geometry	rotated geometries		
X	Y	$E(X_2C{=}CY_2)$	CX_2, CY_2 planar	CX_2 planar, CY_2 pyramidalized	CX_2, CY_2 pyramidalized[a]
H	H	−78.0603	65.6	65.6	65.6
H	F	−275.7667	74.8	63.4	63.3
F	F	−473.4444	68.3	60.8	50.3

[a] Transition state for rotation about the C–C bond.

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(9) For previous calculations and discussions, see: (a) Nagase, S.; Morokuma, K. *J. Am. Chem. Soc.* **1978**, *100*, 1661. (b) Epiotis, N. D.; Larson, J. R.; Yates, R. L.; Cherry, W. R.; Shaik, S.; Bernardi, F. *J. Am. Chem. Soc.* **1977**, *99*, 7460. (c) Larson, J. R.; Epiotis, N. D.; Larson, L. R. *Tetrahedron* **1981**, *37*, 1557. (d) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 1585.

(10) (a) Pickard, J. M.; Rodgers, A. S. *J. Am. Chem. Soc.* **1977**, *99*, 695. (b) Pickard, J. M.; Rodgers, A. S. *J. Am. Chem. Soc.* **1976**, *98*, 6115.

(11) (a) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315. (b) Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502. (c) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976; pp 63–65. (d) Using the thermodynamic definition of Benson, the π bond energy of ethylene was initially underestimated, because the calculations employed a heat of formation of the ethyl radical that was too low. Upwardly revised estimates of the heat of formation of the ethyl radical (Parmar, S. S.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 57 and references therein) give a π BDE for ethylene of 64 kcal/mol, which is in excellent agreement with that obtained from kinetics by Rabinovitch and co-workers.

the π BDE of 1,1-difluoroethylene contains a contribution from CF_2 radical pyramidalization. As shown in Table IV, constraining the CF_2 radical center to planarity in the diradical formed by breaking the π bond in 1,1-difluoroethylene raises the π BDE by 11.5 kcal/mol to 74.8 kcal/mol. Thus, the π bond in 1,1-difluoroethylene is intrinsically 9.2 kcal/mol stronger than the π bond of ethylene. The difference of 9.2 kcal/mol between the *intrinsic* π bond strength of 1,1-difluoroethylene and that of ethylene is in good agreement with the difference of 10.0 kcal/mol calculated between E_π(**3b**) and E_π(**3d**).

This agreement provides additional evidence that, when a terminal group is twisted out of conjugation in **3**, the barrier heights are not significantly affected by differences between the interactions of the nonconjugated radical centers with the π bonds that remain. The near-thermoneutrality of eq 1 allows this conclusion to be extended to **1** and **2** as well. Therefore, since **1b** and **3d** each contain a $C{=}CF_2$ π bond and **2b** and **3b** each contain a $C{=}CH_2$ π bond, setting E_π(**1b**) $\approx$ E_π(**3d**) and E_π(**2b**) $\approx$ E_π(**3b**) appear to be reasonable approximations. Using these approximate equalities, eqs 2–5 can be solved for the differences between the intrinsic π bond energies of the conjugated allylic radicals.

For example, substituting E_π(**1b**) $\approx$ E_π(**3d**) in eq 4, and then subtracting eq 3 from eq 4 yields

$$E_\pi(\mathbf{1a}) - E_\pi(\mathbf{3a}) = \Delta E^{CF_2}(1) - \Delta E^{CH_2}(3) = 0.3 \text{ kcal/mol} \quad (7)$$

which indicates that allylic radicals **1a** and **3a** have very similar intrinsic π bond energies. In contrast, the intrinsic π bond energy of **2a** is calculated to be different from and considerably smaller than those of **1a** and **2a**. Substituting E_π(**2b**) $\approx$ E_π(**3b**) in eq 5 and then subtracting eq 5 from eq 2 gives

$$E_\pi(\mathbf{3a}) - E_\pi(\mathbf{2a}) = \Delta E^{CF_2}(3) - \Delta E^{CH_2}(2) = 6.9 \text{ kcal/mol} \quad (8)$$

The π bond energy differences in eqs 7 and 8 imply that, unlike the isodesmic reaction in eq 1 for the nonconjugated radicals, the isodesmic reaction

$$\mathbf{3a} + \mathbf{3a} \rightarrow \mathbf{1a} + \mathbf{2a} \quad (9)$$

for the conjugated allylic radicals should be endothermic by 6.6 kcal/mol, since, although the intrinsic π bond energies of **1a** and **3a** are nearly the same, the partial π bonds in **3a** are intrinsically about 7 kcal/mol stronger than those in **2a**. This reaction is actually computed to be endothermic by 5.4 kcal/mol, using the SD-CI energies in Table II.[12]

The fact that the partial π bonds in allylic radicals **1a** and **3a** are intrinsically stronger than those in **2a** is obviously related to the fact, discussed above in connection with the relative energies of **3b** and **3d**, that the π bond in 1,1-difluoroethylene is intrinsically stronger than that in ethylene. As shown in Table IV, the *intrinsic* π bond strength of 1,1-difluoroethylene (74.8 kcal/mol) is not only greater than that of ethylene (65.6 kcal/mol) but also than that of tetrafluoroethylene (68.3 kcal/mol).[13]

Based on the intrinsic π bond energies for these three alkenes, one would expect the isodesmic reaction, analogous to that in eq 9,

$$H_2C{=}CH_2 + F_2C{=}CF_2 \rightarrow 2H_2C{=}CF_2 \quad (10)$$

to be exothermic by 15.7 kcal/mol. Using the GVB-PP(1)/6-31G* energies for the alkenes in Table IV, the actual exothermicity is calculated to be 18.1 kcal/mol.[15] As with eq 9, the difference of 2.4 kcal/mol between the actual exothermicity and that estimated from intrinsic π bond strengths is due to the fact that the analogous reaction for the twisted alkenes is computed to be exothermic by this amount.

The exothermicity of the reaction in eq 10 can be related to the more general observation, made by Pauling,[17] that the reaction

$$A_2 + B_2 \rightarrow 2AB \quad (11)$$

is almost invariably exothermic. Pauling argued that the exothermicity of the reaction in eq 11 depends on the electronegativity difference between A and B, since the necessarily homopolar bonds in A_2 and B_2 are replaced by a heteropolar bond in AB, thus allowing the more electronegative of the two atoms to acquire the greater electron density. The same type of argument can be made for the reaction in eq 10, which replaces the necessarily homopolar σ and π C–C bonds in ethylene and tetrafluoroethylene with the heteropolar σ and π C–C bonds in 1,1-difluoroethylene.[18]

Our finding that the intrinsic π bond energy of **2a** is smaller than that of both **1a** and **3a** can be similarly understood, since the former allylic radical does not contain CF_2 groups, which polarize the partial π bonds by acting as π electron donors[19] in the latter two allylic radicals. It is of some interest that the single CF_2 group in **3a** is calculated to have a stabilizing effect on the allylic π bond that is only slightly smaller than the pair of CF_2 groups in **1a**. Presumably, this is a consequence of the fact that in **3a**, unlike the case in **1a**, the pair of π-donating fluorines at C_1 do not have to compete with a second pair at C_3.

Conclusions

Although, as shown in Tables III and IV, the precise amount of energy lowering that results from allowing pyramidalization at a nonconjugated CF_2 radical center depends on the type of group to which it is bonded,[21] the stabilization usually amounts to about 10–12 kcal/mol.[14,22] It is CF_2 group pyramidalization that makes the barrier to CF_2 rotation in **1** considerably less than that in **2**[1,23] and the π bond energy of tetrafluoroethylene significantly less than that of ethylene.[14] However, when CF_2 group planarity is enforced, the intrinsic barrier to rotation in **1** [$\Delta E^{CF_2}(1)$

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(12) The value of 6.6 kcal/mol, predicted from eqs 7 and 8, for the endothermicity of the reaction in eq 9 is 1.2 kcal/mol greater than that actually computed at the SD-CI level, because eqs 7 and 8 are derived with the tacit assumption that the change in energy for the isodesmic reaction in eq 1 is exactly zero. As discussed in the text, using the SD-CI energies, the reaction in eq 1 is actually exothermic by 1.2 kcal/mol. The calculated exothermicity probably arises from a synergistic interaction between the CF_2 groups in **1b**, since the pair of fluorines attached to the conjugated carbon can act as π donors, while the appropriate combination of the C–F antibonding σ orbitals at the nonconjugated carbon can act as a good π acceptor.

(13) At MP2/6-31G*, with triplet UMP2 for the diradical formed by breaking the π bond in tetrafluoroethylene, the intrinsic π bond energy is computed to be 62.6 kcal/mol.[14] Because of the use of the triplet diradical as reference, this value for the intrinsic π bond energy of tetrafluoroethylene is almost certainly too low. An alternative definition of intrinsic π bond strength, which is based on monoradicals as the reference, yields 69.6 kcal/mol.[14]

(14) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282.

(15) This GVB-PP(1)/6-31G* value is in reasonably good agreement with the experimental value, based on heats of formation, of −14.6 ± 1.5 kcal/mol[16] and in slightly better agreement with the experimental value than when SCF energies are used.[9d]

(16) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; Vol 3, 1986; VCH Publishers: Deerfield Beach, FL, Chapter 4.

(17) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 3.

(18) This argument has previously been used to rationalize the greater thermodynamic stability of 1,1- relative to 1,2-disubstituted ethylenes.[9b,19] However, this argument has been criticized when applied to 1,1- and 1,2-difluoroethylenes,[20] since attachment to two fluorines to the same saturated carbon center is known to be stabilizing.[16]

(19) Bock, C. W.; George, P.; Mains, G. J.; Trachtman, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 8.

(20) (a) Kollman, P. *J. Am. Chem. Soc.* **1974**, *96*, 4363. (b) Cremer, D. *J. Am. Chem. Soc.* **1981**, *103*, 3633.

(21) Comparison of the planarization energies of the nonconjugated CF_2 groups in **1** and **3** indicates it is slightly easier to planarize a nonconjugated CF_2 group that is adjacent to a double bond which is substituted at the other end with π electron donating fluorines. Consistent with the premise that an electron-rich π orbital lowers the energetic cost of planarizing an adjacent, nonconjugated CF_2 group is the comparison in Table IV between the energy required for CF_2 planarization in twisted 1,1-difluoroethylene and tetrafluoroethylene. The energetic cost of 11.4 kcal/mol in the former molecule is reduced to 7.5 kcal/mol in the latter upon replacement of the planar CH_2 group by a planar CF_2 group. Also as shown in Table IV, with one CF_2 group in twisted tetrafluoroethylene allowed to remain pyramidal, the energetic cost of planarizing the second CF_2 group increases to 10.5 kcal/mol. This effect has been noted previously.[14]

(22) (a) Paddon-Row, M. N.; Thompson, C.; Ball, J. R. *J. Mol. Struct.* **1987**, *150*, 93. (b) Chen, Y.; Rauk, A.; Tschuikow-Roux, E. *J. Chem. Phys.* **1990**, *93*, 1187.

(23) CF_2 pyramidalization has even a larger effect on reducing the barriers to rotation in fluorinated allylic anions: Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Phys. Org. Chem.* **1988**, *1*, 153. Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Phys. Org. Chem.* **1990**, *3*, 635.

= 12.6 kcal/mol] is nearly the same as the barrier to CH_2 rotation in **2** [$\Delta E^{CH_2}(\mathbf{2})$ = 15.4 kcal/mol], and the intrinsic π bond strength of tetrafluoroethylene (68.3 kcal/mol) is comparable to that in ethylene (65.6 kcal/mol).

Our calculations indicate that the intrinsic strength of the π bond in 1,1-difluoroethylene is greater by 9–10 kcal/mol than the strength of the π bond in ethylene. This difference in intrinsic π bond strengths is about the same size as the energy lowering on CF_2 group pyramidalization. The similarity of these two different types of energies accounts for the fact that in **3** rotation of the CH_2 and CF_2 groups are predicted to require comparable energies. Rotation of the CH_2 group in **3** leaves behind a stronger π bond, but this energetic advantage is overcome by the slightly larger energy lowering on CF_2 pyramidalization.[24]

The same type of near cancellation accounts for the fact that, in excellent agreement with experiment,[10,11] our computed value for the π bond dissociation energy in 1,1-difluoroethylene is nearly the same as that in ethylene. The intrinsically greater strength of the π bond in 1,1-difluoroethylene is again slightly more than cancelled by the energy lowering upon CF_2 pyramidalization.

When the intrinsic barriers to CX_2 group rotation in different allylic radicals are compared, $\Delta E^{CX_2}(\mathbf{n})$ depends, of course, on not just the intrinsic energy of the π bond that remains in the twisted radical but also on the intrinsic energy of the π system in the planar allylic radical. For example, although rotating a CH_2 group in **2** and the CF_2 group in **3** leaves behind the same type of π bond, the intrinsic barrier to planar CF_2 group rotation in **3**, $\Delta E^{CF_2}(\mathbf{3})$, is calculated to be about 7 kcal/mol larger than the barrier to CH_2 group rotation in **2**, $\Delta E^{CH_2}(\mathbf{2})$. We attribute this finding to π bonding in **3a** that is intrinsically 7 kcal/mol stronger than that in **2a**. However, since the difference between the intrinsic energies required for CH_2 group rotation in **2** and CF_2 group rotation in **3** is more than offset by the energy lowering upon CF_2 pyramidalization in **3**, the actual barrier to CH_2 rotation in **2** is computed to be slightly larger than the barrier to CF_2 rotation in **3**.

The computational finding, that formation of the same type of double bond by planar CF_2 group rotation in **1** or by CH_2 group rotation in **3** requires comparable energies, is indicative of very similar intrinsic energies for the conjugated π systems of these two allylic radicals, **1a** and **3a**. This is why the difference between the calculated barrier heights for CF_2 rotation in **1** and CH_2 rotation in **3** is due almost solely to the pyramidalization energy of the CF_2 group.[1]

In summary, our computational study predicts that rotation of either terminal group in **3** will require nearly the same energy. This energy is calculated, in agreement with experiment,[3a] to be substantially higher than that required for CF_2 rotation in **1**. Our calculations further predict that careful measurement of the rotational barriers in **3** should find them to be slightly lower than that for CH_2 rotation in **2**.[1,3b] The predicted barrier heights to terminal group rotation in **1**–**3** can be understood on the basis of (1) the preference of CF_2 radical centers for pyramidal geometries, (2) the greater intrinsic strength of the π bond in $RCH{=}CF_2$, compared to that in $R'CH{=}CH_2$, and (3) intrinsic π bond strengths in fluorinated allylic radicals **1** and **3** that are comparable and both larger than that in the parent allyl radical (**2**).

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[24] CH_2 rotation lowers the zero-point energy because of the decrease in the force constant for pyramidalization at the rotated CH_2 group. In contrast, CF_2 rotation has just the opposite effect, since the latter group has a strong preference for a pyramidal geometry.[1] These changes in zero-point energies tend to decrease by about 2 kcal/mol the preference for CF_2 over CH_2 rotation. Moreover, upon CF_2 group rotation, the increase in the frequencies of vibrations that have low frequencies at the fully conjugated geometry results in a decrease in entropy. The entropy of activation for CF_2 group rotation is computed to be −6.9 cal/mol·K in **1** (UHF/3-21G)[1] and −3.2 cal/mol·K in **3** (UHF/6-31G*). Unlike the case in **2**,[1] in which the calculated (UHF/3-21G) entropy of activation for CH_2 group rotation is essentially zero,[1] in **3** the entropy of activation for CH_2 group rotation is computed (UHF/6-31G*) to be −1.5 cal/mol·K. The small but negative change in entropy on going from **3a** to **3e** is a consequence of the fact that formation of a full double bond to the CF_2 group increases the frequencies of vibrational modes that involve CF_2 pyramidalization. The same effect also contributes to the much more negative entropy of activation that is computed for CF_2 group rotation in **1**.