Structures and Stabilities of Fluorinated Carbanions: Evidence for Anionic Hyperconjugation

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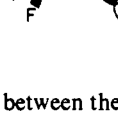
Abstract: Ab initio molecular orbital calculations have been performed on CF_3^-, $CF_3CH_2^-$, $CF_3CF_2^-$, $(CF_3)_2CF^-$, and $(CF_3)_3C^-$. The geometries were gradient optimized with a double-ζ basis set augmented by a set of polarization functions on carbon. The fluorines on C_β anti to the lone pair on C_α^- are shown to have long bond lengths. The C_α^-–C_β bond lengths decrease with increasing CF_3 substitution on C_α^-. These geometric results are interpreted as providing evidence for the presence of negative anionic hyperconjugation in fluorocarbanions. Analysis of relative energetics, HOMO eigenvalues, and Mulliken charges substantiates the hyperconjugation arguments. The fluoride affinities of $CF_2{=}CF_2$, $CF_2{=}CH_2$, $CF_3CF{=}CF_2$, and $(CF_3)_2C{=}CF_2$ were calculated to derive the approximate heats of formation (kcal/mol): −256.3 ($CF_3CF_2^-$), −144.1 ($CF_3CH_2^-$), −374.3 ($(CF_3)_2CF^-$), −504.3 ($(CF_3)_3C^-$). From isodesmic reaction energies, the order of carbanion stabilities is $(CF_3)_3C^- > (CF_3)_2CF^- > CF_3CF_2^- \simeq CF_3^- > CF_3CH_2^-$. The $(CF_3)_3C^-$ anion was found to be 40.8 kcal/mol more stable than CF_3^-.

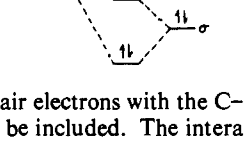
The concept of negative anionic hyperconjugation (HCJ) was introduced in 1950,[1] fell into disrepute around 1970,[2-4] and is in vogue again[5-9] in the 80's. In terms of resonance theory, negative anionic HCJ is represented by a no-bond resonance structure, e.g., A ↔ B. In terms of molecular orbital theory, the description

$$CF_3-\bar{C}F_2 \longleftrightarrow F^-\ CF_2{=}CF_2$$

A B

of the effect is based on stabilization of the lone pair (n) electrons on C^- by the C–F σ^* orbital on the β carbon. The effect of





interaction between the lone pair electrons with the C–F bonding σ orbital, of course, also must be included. The interaction with σ^* is stabilizing, whereas that with σ is destabilizing. The energetic balance of the two effects determines the overall stabilization or destabilization due to HCJ. For β-fluorocarbanions, the orbital energies are such that interaction with σ^* is larger than that with σ, simply because of the low-lying σ^* orbital of the C–F bond. Thus, anionic HCJ of the C–F bond is overall stabilizing.

There have been several theoretical studies of anionic fluorine HCJ,[6,8,9-14] but none to date has examined perfluorinated systems.

Table I. Calculated Geometries for the β,β,β-Trifluoroethyl Anion

parameter	DZ + D_C[a]	3-21+G[b]
$r(C_\beta-F_{anti})$[c]	1.409	1.499
$r(C_\beta-F_\beta)$	1.361	1.407
$r(C_\alpha-C_\beta)$	1.446	1.389
$r(C_\alpha-H)$	1.090	1.072
$\theta(C_\alpha C_\beta F_{anti})$[d]	119.4	120.6
$\theta(F_\beta C_\beta F_\beta)$	105.1	105.6
$\theta(HC_\alpha H)$	110.0	119.7

[a] This work. Total energy = −375.242 586 au for C_s structure shown in text. [b] Reference 9. [c] Bond lengths in Å. [d] Bond angles in deg.

Initial theoretical work focused on the β-fluoroethyl anion, $FCH_2CH_2^-$, but it recently has been shown that this anion is not a minimum on the potential energy surface and it undergoes complete F^- dissociation upon geometry optimization.[9,13,15] The stable structure is actually one involving a strong hydrogen bond between CH_2CH_2 and fluoride ion.[9] This is consistent with the experimental results for the fluoride affinity of CH_2CH_2.[16] Apielog[6a] partially optimized the geometry of $CF_3CH_2^-$ and found a lengthening of the C–F bond anti to the lone pair and a shortened C–C bond. Schleyer and co-workers[9] fully optimized the structures of $CF_3CH_2^-$ with a 3-21G basis set augmented by diffuse functions on the heavy atoms. Their results confirmed Apielog's findings and indicated that anionic HCJ accounted for the structural differences. Using Schleyer's geometry, Allen and co-workers[11] examined electron density plots for the HOMO of $CF_3CH_2^-$ and adduced evidence for delocalization from the lone pair into the region of the C–F bond.

It is well established that calculations with small double-ζ basis sets give overcontracted C=C bonds and overelongated C–F bonds,[17] and thus the reported geometry parameters for $CF_3CH_2^-$ might be questionable. Furthermore, the fluoride affinity of CF_2CH_2 at the CF_2 carbon is calculated to be very small (ca. 4 kcal/mol, see below), and experiment suggests that the lowest point on the potential surface is not $CF_3CH_2^-$ but is a $CF_2CH_2{\cdots}F^-$ hydrogen bonded structure.[16b] Thus, to date there have been no

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(1) Roberts, J. D.; Webb, R. L.; McElhill, E. A. *J. Am. Chem Soc.* **1950**, *72*, 408.

(2) (a) Holtz, D. *Prog. Phys. Org. Chem.* **1971**, *8*, 1. (b) Holtz, D. *Chem. Rev.* **1971**, *71*, 1.

(3) Klabunde, K. J.; Burton, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 820, 5985.

(4) Streitweiser, A.; Holtz, D.; Ziegler, G. R.; Stoffer, J. O.; Brokaw, M. L.; Guibe, F. *J. Am. Chem. Soc.* **1976**, *98*, 5229.

(5) Sleigh, J. H.; Stephens, R.; Tatlow, R. C. *J. Fluorine Chem.* **1980**, *15*, 411.

(6) (a) Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 396. (b) Apeloig, Y.; Rappaport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095.

(7) Stock, L. M.; Wasielewski, M. R. *Prog. Phys. Org. Chem.* **1981**, *13*, 253.

(8) See Streitweiser et al. (Streitweiser, A., Jr.; Berke, C. M.; Schriver, G. W.; Grier, D.; Collins, J. B. *Tetrahedron, Suppl. 1* **1981**, *37*, 345) for opposite conclusions.

(9) Schleyer, P. von R.; Kos, A. J. *Tetrahedron* **1983**, *39*, 1141.

(10) Farnham, W. B.; Smart, B. E.; Middleton, W. J.; Calabrese, J. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 4565.

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(12) Pross, A.; Radom, L. *Aust. J. Chem.* **1980**, *33*, 241.

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(14) Hoffman, R.; Radom, L.; Pople, J. A.; Schleyer, P. von R.; Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 6221.

(15) We have reconfirmed this result. For $FCH_2CH_2^-$ in C_s symmetry, the C–C bond length is 1.331 Å and the C–F bond length is 2.83 Å, using the DZ+D_C basis set that is described in the text.

(16) (a) Roy, M.; McMahon, T. B. *Can. J. Chem.* **1985**, *63*, 708. (b) McMahon, T. B., unpublished results.

(17) (a) Gandhi, S. R.; Benzel, M. A.; Dykstra, C. E.; Fukunaga, T. *J. Phys. Chem.* **1982**, *86*, 3121. (b) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 1585.

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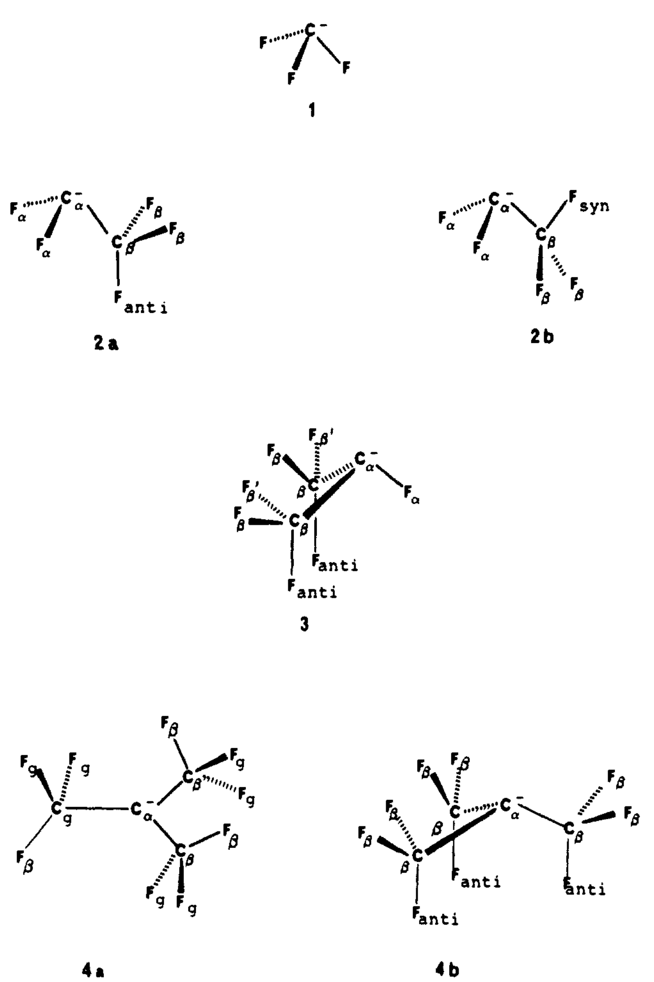


Figure 1. Perfluorocarbanion geometries (see Table II for parameters).

calculations on fluorinated carbanions for which the *lowest energy* structure shows the effects of anionic HCJ.

We have demonstrated recently that calculations using a (9,5)/[3,2] double-ζ basis set augmented by polarization functions on carbon and oxygen accurately reproduce the structure of the CF_3O^- anion and that anionic HCJ adequately explains the unusual structure of this and related perfluorinated alkoxide anions.[10] We have used this basis set to reoptimize the geometry of the $CF_3CH_2^-$ anion and to systematically study the series of $^-CR_1R_2R_3$ anions where R_i = F or CF_3. Our results provide cogent structural and electronic evidence for the importance of negative anionic HCJ.

We also report calculated fluoride affinities for $CF_2{=}CH_2$, $CF_2{=}CF_2$, $CF_3CF{=}CF_2$, and $(CF_3)_2C{=}CF_2$, from which approximate heats of formation of $CF_3CH_2^-$, $CF_3CF_2^-$, $(CF_3)_2CF^-$, and $(CF_3)_3C^-$ are derived. Isodesmic reaction energies that relate the overall stabilities of the carbanions to CF_3^- are discussed.

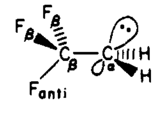
Calculations. The calculations were done with the HONDO program[18] package on an IBM 3083 computer. The geometries were gradient[19] optimized in the following symmetry point groups: CF_3^- (C_{3v}), $CF_3CF_2^-$ (C_s), $(CF_3)_2CF^-$ (C_s), and $C(CF_3)_3^-$ (C_{3v} or C_{3h}) as shown in Figure 1. The basis set for the calculations is of double-ζ quality in the valence space with exponents and coefficients from Dunning and Hay.[20] The basis set is augmented by a set of d polarization functions on each carbon[20] and has the form (9,5,1/9,5/4)/[3,2,1/3,2/2] in the order C, F, H. Since a six-component d function is used, a "diffuse" type s orbital on each carbon is provided. This DZ+D_C basis gives good structures for fluorocarbons at the SCF level and previous work has shown that d orbitals on C are significantly more important than d orbitals on F at the SCF level.[10,17b] The largest calculations for this series of perfluorocarbanions involved 141 basis functions.

Table II. Geometry Parameters for Perfluoroalkyl Anions

bond parameter	calcd (Å)	angle parameter	calcd (deg)
		1	
C–F	1.417	FCF	99.5
		2a	
C_α–C_β	1.523	$F_\alpha C_\alpha C_\beta$	101.4
C_α–F_α	1.423	$F_\alpha C_\alpha F_\alpha$	101.4
C_β–F_{anti}	1.350	$F_{anti}C_\beta C_\alpha$	118.0
C_β–F_β	1.342	$F_{anti}C_\beta F_\beta$	104.9
		$F_\beta C_\beta C_\alpha$	111.1
		$F_\beta C_\beta F_\beta$	105.9
		2b	
C_α–C_β	1.558	$F_\alpha C_\alpha C_\beta$	102.9
C_α–F_α	1.418	$F_\alpha C_\alpha F_\alpha$	100.6
C_β–F_{syn}	1.350	$F_{syn}C_\beta C_\alpha$	110.3
C_β–F_β	1.343	$F_{syn}C_\beta F_\beta$	104.2
		$F_\beta C_\beta C_\alpha$	115.8
		$F_\beta C_\beta F_\beta$	105.4
		3	
C_α–C_β	1.483	$F_\alpha C_\alpha C_\beta$	104.7
C_α–F_α	1.427	$C_\beta C_\alpha C_\beta$	112.1
C_β–F_{anti}	1.359	$F_{anti}C_\beta C_\alpha$	117.5
C_β–F_β	1.343	$F_{anti}C_\beta F_\beta$	104.8
C_β–$F_{\beta'}$	1.340	$F_{anti}C_\beta F_{\beta'}$	103.8
		$F_\beta C_\beta C_\alpha$	111.8
		$F_\beta C_\beta F_{\beta'}$	106.1
		$F_{\beta'}C_\beta C_\alpha$	111.9
		4a	
C_α–C_β	1.458	$C_\beta C_\alpha C_\beta$	120.0
C_β–F_{gauche}	1.354	$F_{gauche}C_\beta C_\alpha$	115.9
C_β–F_β	1.344	$F_{gauche}C_\beta F_{gauche}$	102.6
		$F_{gauche}C_\beta F_\beta$	104.9
		$F_\beta C_\beta C_\alpha$	111.5
		4b	
C_α–C_β	1.475	$C_\beta C_\alpha C_\beta$	114.6
C_β–F_{anti}	1.366	$F_{anti}C_\beta C_\alpha$	116.1
C_β–F_β	1.339	$F_{anti}C_\beta F_\beta$	103.8
		$F_\beta C_\beta C_\alpha$	113.2
		$F_\beta C_\beta F_\beta$	105.5

Results and Discussion

Geometries. β,β,β-Trifluoroethyl Anion. The geometry for $CF_3CH_2^-$ in the minimum-energy C_s conformation shown below was optimized with the DZ+D_C basis set, and in Table I the structural parameters are compared to those previously obtained with a 3-21+G basis set.



As expected, the larger DZ+D_C basis set gives appreciably longer C–C and shorter C–F bonds. The C–F_{anti} bond in $CF_3CH_2^-$ that is most favorably disposed for HCJ (lone pair C_α–C_β–F_{anti} dihedral angle = 180°) is 0.048 Å longer than the C–F_β bonds, which are gauche to the lone pair. The difference between these C–F bond lengths is nearly twice as large with the 3-21+G basis set. The DZ+D_C values show that the C–F_{anti} bond is elongated by 0.078 Å relative to the C–F bonds in CF_3CH_3, and the C–C bond is shortened by 0.058 Å.[21] The 3-21+G results show

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[18] (a) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111. (b) King, H. F.; Dupuis, M.; Rys, J. *National Resource for Computer Chemistry Software Catalog*; Vol. 1, Program QH02 (HONDO), 1980.

[19] Pulay, P. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 153.

[20] Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; p 1.

[21] For CF_3CH_3, r(C–F) = 1.331 Å (DZ+D_C), 1.370 Å (3-21G),[9] 1.340 (2) Å (experimental);[22] r(C–C) = 1.504 Å (DZ+D_C), 1.491 Å (3-21G),[9] 1.494 (3) Å (experimental).[22]

[22] Beagley, B.; Jones, M. O.; Zanjanchi, M. A., Jr. *J. Mol. Struct.* **1979**, *56*, 215.

substantially larger differences of 0.129 Å and 0.102 Å for the C–F and C–C bonds, respectively, in $CF_3CH_2^-$ vs. CF_3CH_3.[21]

Although our DZ+D_C and the 3-21+G results, as well as the earlier 4-31G calculations,[12] show the same trends for changes in geometry that substantiate the importance of anionic HCJ, the predicted effects differ quantitatively. Considering the demonstrated accuracy of the polarized DZ basis set optimized geometries for the related CF_3O^- anion[10] and fluoroolefins,[17b] we believe our results for the $CF_3CH_2^-$ anion are more reliable.

Perfluorocarbanions. The optimized geometry parameters for the CF_3^-, $CF_3CF_2^-$, $(CF_3)_2CF^-$, and $(CF_3)_3C^-$ anions (Figure 1) are listed in Table II. Several notable trends are evident. For CF_3^- (**1**) and $CF_3CF_2^-$ (**2a** and **2b**), the bond angles at C_α^- are much less than tetrahedral, and our calculated FCF bond angle of 99.5° for CF_3^- agrees well with that of 99.6° determined with a large Slater basis set.[23] As more CF_3 groups are added, the sum of the angles at C_α^- increases. The value for $r(C_\alpha^- – F_\alpha)$ also increases with increasing CF_3 substitution. The bond distances for the $C_\alpha^-–F_\alpha$ bond are significantly longer than those in comparable neutral compounds (the C–F bonds range from 1.306 Å in CF_4 to 1.377 Å in CH_3F with this basis set).[24] The $C_\alpha^-–C_\beta$ bond length decreases from 1.523 to 1.458 Å as the number of CF_3 groups is increased. The length of the C_β–F bond nominally anti to the lone pair on C_α^- increases with increasing CF_3 substitution. This bond is always longer than the other C–F bonds on the same group, and the $C_\alpha^-–C_\beta–F_{anti}$ bond angle is always larger than the remaining $C_\alpha^-–C_\beta–F_\beta$ bond angles.

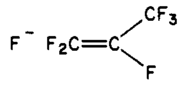
The $C_\beta–F_{anti}$ bond in $CF_3CF_2^-$ (**2a**) is 0.036 Å longer than that in CF_3CF_2H, and the $C_\alpha^-–C_\beta$ bond is 0.009 Å shorter.[25] These differences are significantly smaller than those found for $CF_3CH_2^-$ and CF_3CH_3 (see above). This can be explained in part by comparing the relative importance of anionic HCJ in $CF_3CH_2^-$ vs. $CF_3CF_2^-$. Substitution of two fluorine atoms for hydrogens on C_α^- lowers the energy of the lone pair orbital (n), which increases the energy difference between $\sigma^*(C–F_\beta)$ and the lone pair electrons. (The electronegativity perturbation by F also lowers somewhat the energy of $\sigma^*(C–F_\beta)$, but its effect is greater on C_α^-.) The stabilizing interaction between $\sigma^*(C–F_\beta)$ and the lone pair electrons on C_α^- thus is smaller in $CF_3CF_2^-$ than in $CF_3CH_2^-$; also, the stabilization of the energy of the lone pair for **2a** leads to an increased repulsive interaction with $\sigma(C–F_\beta)$. Consequently, the geometric influence of HCJ is greater in $CF_3CH_2^-$.

For $CF_3CF_2^-$ and $(CF_3)_3C^-$, other conformations were investigated. The conformation for $CF_3CF_2^-$ with the unique F syn (eclipsing) to the lone pair (**2b**) was optimized and was found to be 6.3 kcal/mol *less stable* than the anti structure, **2a**. Although the structure of the CF_3 group changes only slightly, the $C_\alpha^-–C_\beta$ bond length increases significantly, whereas $r(C_\alpha^-–F_\alpha)$ decreases slightly. For the $(CF_3)_3C^-$ ion, the C_{3v} structure wherein one C–F on each CF_3 group was oriented anti to the lone pair (**4b**) was optimized first. (The C_{3v} structure with $\angle C_\beta C_\alpha C_\beta = 120°$ was found to be ca. 6 kcal/mol above **4b**, and it converged to **4b**.) A C_{3h} structure with three fluorines in the plane of the four carbons (**4a**), however, was lower in energy than **4b** by 2.5 kcal/mol. The $C_\beta–F_\beta$ bond in **4a** is shorter than the two C–F bonds which are gauche to the one pair. The $C_\alpha^-–C_\beta$ bond in **4a** is shorter than the $C_\alpha^-–C_\beta$ bond in **4b**. The $C_\beta^-–F_{anti}$ bond in **4b** is the longest such bond (1.366 Å), found in our study.

Table III. Total Energies, HOMO Eigenvalues, and Mulliken Populations for **1–4**

ion	atom	charge (e)	HOMO energy (au)	total energy (au)
CF_3^- (**1**)	C	+0.188	–0.1367	–336.205 80
	F	–0.396		
$CF_3CF_2^-$ (**2a**)	C_α	0.000	–0.1463	–573.004 71
anti	F_α	–0.398		
	C_β	+0.580		
	F_{anti}	–0.267		
	F_β	–0.259		
$CF_3CF_2^-$ (**2b**)	C_α	0.000	–0.1399	–572.994 61
syn	F_α	–0.390		
	C_β	+0.564		
	F_{syn}	–0.264		
	F_β	–0.252		
$(CF_3)_2CF^-$ (**3a**)	C_α	–0.245	–0.1675	–809.822 07
	F_α	–0.393		
	C_β	+0.583		
	F_{anti}	–0.268		
	F_β	–0.247		
	$F_{\beta'}$	–0.249		
$(CF_3)_3C^-$ (**4a**)	C_α	–0.570	–0.1925	–1046.658 33
	C_β	+0.622		
	F_β	–0.246		
	F_g	–0.260		
$(CF_3)_3C^-$ (**4b**)	C_α	–0.540	–0.1983	–1046.654 29
	C_β	+0.590		
	F_{anti}	–0.267		
	F_β	–0.238		

As shown by the above MO diagram, the conformation with F anti to the lone pair on C_α^- should have the maximum energetic effect since the overlap is largest here. (If the F is gauche, less overlap occurs and the energetic consequences of hyperconjugation are diminished.) The results for $CF_3CF_2^-$ are consistent with this simple model since the anti form **2a** is more stable than the syn form **2b**. In **2b** there is significant electronic repulsion between the various electron pairs; consequently, the $C_\alpha^-–C_\beta$ bond lengthens. A similar result is found for C_2F_6 where the D_{3d} form has a C–C bond length of 1.534 Å and the eclipsed D_{3h} form has a C–C bond length of 1.562 Å.[27] We note that the C–C bond length in the anti form of $CF_3CF_2^-$ is shorter than the bond in C_2F_6 (D_{3d}), which reflects the importance of resonance structure B. For $(CF_3)_2CF^-$ (3), the $C_\beta–F_{anti}$ bonds are even longer and the $C_\alpha^-–C_\beta$ bonds are shorter. Because the C–C bond in $CF_3C-F_2CF_3$ is actually longer than that in C_2F_6,[27] resonance structures of the form C play an even larger role in **3**. Two effects are competing in $(CF_3)_3C^-$: hyperconjugation and steric repulsions between the fluorines. The lowest energy C_{3h} structure **4a** has minimal steric effects, whereas the C_{3v} structure **4b** has the best orientation of the CF_3 groups to maximize HCJ. Structure **4a** does have weaker hyperconjugative gauche interactions, but there is still sufficient interaction to increase the $C_\beta–F_{gauche}$ bond lengths, although the effect is smaller than that found for the C_{3v} structure.



C

Electronic Properties. The eigenvalues of the HOMO are consistent with the geometric description given above for $CF_3CF_2^-$ and $(CF_3)_3C^-$ (see Table III). Notably, all of the HOMO's are significantly bound for these anions. The HOMO of **2a** is lower in energy than that of the **2b** by 4.0 kcal/mol. A lower energy HOMO would be indicative of additional HCJ. The rotation barrier in C_2F_6 is 3.9 kcal/mol,[28] and this should be a reasonable estimate for the steric repulsions in **2b**. The remainder of the 6.3 kcal/mol energy difference between **2b** and **2a**, 2.4 kcal/mol, can

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(23) Marynick, D. S. *J. Mol. Struct* (*THEOCHEM*) **1982**, *87*, 161. The value for r(C–F) is 1.434 Å with the STO basis set.

(24) Dixon, D. A., unpublished results.

(25) For CF_3CF_2H, DZ+D_C values: $r(C–F_\beta)_{anti}$ = 1.314 Å, $r(C–F_\beta)$ gauche = 1.321 Å, $r(C–F_\alpha)$ = 1.334 Å, r(C–C) = 1.532 Å, r(C–H) = 1.078 Å. Experimental:[26] $r(C–F_\beta)$ = 1.327 Å (average), $r(C–F_\alpha)$ = 1.347 Å (estimated), r(C–C) = 1.525 (4) Å, r(C–H) = 1.097 (2) Å.

(26) Beagley, B.; Jones, M. O.; Yavari, P. *J. Mol. Struct.* **1981**, *71*, 203.

(27) 6-31G*(C), values: Dixon, D. A.; Van Catledge, F. A., unpublished results.

(28) 6-31G*(C) value: 3.80 kcal/mol.[27] Experimental Values: 3.7–4.3 kcal/mol.[29]

(29) Gallaher, K. L.; Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1974**, *78*, 2389 and references cited therein.

Table IV. Total Energies and Fluoride Affinities of Carbonyl Fluoride and Fluoroolefins

molecule A	E(A)[a]	AF$^-$ [b]	ΔFA[c]	abs FA[c]
$CF_2{=}O$	−311.670 165	CF_3O^-	0.0	42.6[d]
$CF_2{=}CH_2$	−275.785 037	$CF_3CH_2^-$	−38.4	4.2
$CF_2{=}CF_2$	−473.492 467	**2a**	−4.1	38.5
$CF_3CF{=}CF_2$	−710.294 354	**3**	+5.6	48.2
$(CF_3)_2C{=}CF_2$	−947.106 080	**4a**	+21.1	63.7

[a] Total energies in au. [b] See Table I, footnote *a*, and Table III for total energies. For CF_3O^-, total energy = −411.188 911 au (Ref 10). [c] Relative and absolute fluoride affinities in kcal/mol. [d] Reference 30a.

be attributed to the effects of HCJ in **2a** and is consistent with the 4-kcal/mol difference in HOMO eigenvalues. For $(CF_3)_3C^-$, the HOMO of the C_{3v} structure **4b** is 3.6 kcal/mol lower in energy than that of the more stable D_{3h} form, **4a**. This agrees with our previous conclusion that there is more HCJ in **4b** than in **4a** but that the former is destabilized by steric effects.

The Mulliken populations are also given in Table III and are useful for examining trends in the anions. For comparison, the Mulliken populations are $q_C = +0.617e$ and $q_F = -0.154e$ in CF_4 and $q_C = +0.512e$ and $q_F = -0.171$ e in C_2F_6. In CF_3^-, the fluorines carry a large amount of the negative charge. Even with increasing CF_3 substitution, the values for q_F when F is bonded to C_α^- do not show a large variation. The negative charges for all of the fluorines bonded to C_α^- are always greater than those in C_2F_6. The largest negative charge on a fluorine bonded to C_β is always found for the fluorine with the best geometric arrangement for hyperconjugation, i.e., the F in the anti position. The anti F in the C_{3v} structure of $(CF_3)_3C^-$ has more negative charge than do the two gauche F's in the C_{3h} structure. This further supports our conclusion that the C_{3v} structure has more hyperconjugation.

Fluoride Affinities. The fluoride afflnity (FA) of molecule A is defined as $-\Delta H°$ for reaction 1.[30] Rather than calculate

$$A + F^- \rightarrow AF^- \qquad (1)$$

absolute fluoride affinities directly, which would necessitate very accurate calculations on F^-, we computed relative fluoride affinities. We chose as a standard carbonyl fluoride, CF_2O, whose fluoride affinity is known reasonably accurately from experiment (42.6 ± 2 kcal/mol)[30a] and whose fluoride adduct has a well-established structure with F^- directly bonded to carbon. The $\Delta H°$ for reaction 2 gives FA(A) relative to that for CF_2O.[31]

$$CF_3O^- + A \rightarrow CF_2O + AF^- \qquad (2)$$

The required total energies for CF_2O and CF_3O^- with the DZ+D$_C$ basis set are available from our previous work,[10] and the fluorinated carbanion energies are listed in Table III. For the neutral compounds A (fluoroolefins), the structures were geometry optimized with the DZ+D$_C$ basis set.[17b] Their DZ+D$_C$ total energies, calculated relative fluoride affinities, and absolute fluoride affinities are given in Table IV.

Experimental fluoride affinities for these olefins have not yet been determined from equilibrium measurements owing to high kinetic barriers for fluoride transfer from polyfluorinated carbanions.[16b] Only the fluoride affinity of C_2F_4 can be determined from available thermochemical data. From the experimental gas-phase proton affinity of $CF_3CF_2^-$ (372.6 ± 3.9 kcal/mol)[30b,32] and the heats of formation of H^+ (365.7 kcal/mol)[33] and CF_3CF_2H (−264.0 ± 1.5 kcal/mol),[34] $\Delta H_f°(CF_3CF_2^-) = -257.1 \pm 5.4$ kcal/mol. Thus, by using $\Delta H_f°(F^-) = -59.9$ kcal/mol[36] and $\Delta H_f°(C_2F_4)$[37] = −157.9 ± 0.4 kcal/mol, FA(C_2F_4) = 39.3 ± 5.8 kcal/mol. Within experimental uncertainty, our calculated value of 38.5 kcal/mol (Table IV) is identical with the experimental value.

Table V. Heats of Formation of Fluorinated Carbanions

carbanion	calcd (kcal/mol)	exptl (kcal/mol)
CF_3^-		−157.1 ± 2.4[a]
$CF_3CF_2^-$ (**2a**)	−256.3	−257.1 ± 5.4[b]
$CF_3CH_2^-$	−144.1	(−169.7)[c]
$(CF_3)_2CF^-$ (**3**)	−374.3	−380.9 ± 4.6[d]
$(CF_3)_3C^-$ (**4a**)	−504.3	−513.9 ± 4.6[d]

[a] Bartmess, J. E. *J. Phys. Chem. Ref. Data*, to be submitted. See also: Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11. [b] From proton affinity data (ref 30b, 32); see text. [c] On the basis of reported proton affinity of $CF_3CH_2^-$ (374 kcal/mol), ref 32. See text. [d] Estimated from dissociative electron attachment data: (a) Spyrou, S. M.; Sauers, I.; Christophorou; L. G. *J. Phys. Chem.* **1983**, *78*, 7200. (b) Spyrou, S. M.; Hunter, S. R.; Christophorou, L. G. *J. Chem. Phys.* **1985**, *83*, 641.

Substitution of one F by CF_3 in C_2F_4 increases the fluoride affinity by 9.7 kcal/mol, whereas it increases by 25.2 kcal/mol upon substitution by two (geminal) CF_3 groups (see Table IV). The effect of CF_3 substitution is clearly nonadditive, and the relationship of relative fluoride affinities to the relative stabilities of the $CF_3CF_2^-$, $(CF_3)_2CF^-$, and $(CF_3)_3C^-$ anions is discussed below.

Thermochemistry and Relative Fluorocarbanion Stabilities. Approximate heats of formation[31] of the fluorinated carbanions can be immediately derived from the calculated absolute fluoride affinities by using eq 3, if the heats of formation of the corresponding fluoroolefins (A) are known. The experimental heats of formation of $CF_2{=}CF_2$ and $CF_2{=}CH_2$[37] were used to obtain the values for $CF_3CF_2^-$ (**2a**) and $CF_3CH_2^-$ in Table V. For

$$\Delta H_f°(AF^-) = \Delta H_f°(A) - \Delta H_f°(F^-) - FA(A) \qquad (3)$$

$\Delta H_f°(CF_3CF{=}CF_2)$, an estimated value of −266.4 kcal/mol[39] and a value of −267.8 kcal/mol based on early experimental data[42] are available. From the computed ΔE of −5.3 kcal/mol for isodesmic reaction 4[44] and the experimental $\Delta H_f°$'s of C_2H_3F, $C_3H_3F_3$, and C_2F_4,[37] we estimate $\Delta H_f°(CF_3CF{=}CF_2)$ to be −266.2 kcal/mol. This value was used in eq (3) to derive $\Delta H_f°$(**3**).

$$CH_2{=}CHF + CF_3CF{=}CF_2 \rightarrow CH_2{=}CHCF_3 + CF_2{=}CF_2 \qquad (4)$$

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(30) (a) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766. (b) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944.

(31) We are making the approximation that $\Delta E \simeq \Delta H°$, which ignores corrections for differences in zero-point energies. This should be a reasonable approximation for these systems. Any errors introduced should be smaller than uncertainties in the experimental heats of formation and the COF_2 fluoride affinity. See ref 17b.

(32) (a) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160; (b) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5017.

(33) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(34) From $\Delta H_f°(C_2F_5^{\bullet}) = -213.4 \pm 1$ kcal/mol,[35] $\Delta H_f°(H^{\bullet}) = 52.1$ kcal/mol,[35] and $D°(CF_3CF_2{-}H) = 102.7 \pm 0.5$ kcal/mol,[35] $\Delta H_f°(CF_3CF_2H) = -264.0 \pm 1.5$ kcal/mol.

(35) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(36) Woof, A. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 1.

(37) The following thermochemical values used in this work are from Pedley and Rylance's compilation of internally consistent, computer analyzed thermochemical data:[38] $\Delta H_f°(CF_2CF_2) = -157.9 \pm 0.4$ kcal/mol, $\Delta H_f°(CF_2{=}CH_2) = -80.0 \pm 0.8$ kcal/mol, $\Delta H_f°(CH_2{=}CHF) = -33.2 \pm 0.4$ kcal/mol, $\Delta H_f°(CH_2{=}CHCF_3) = -146.8 \pm 1.6$ kcal/mol, $\Delta H_f°(CF_3CF_3) = -322.7 \pm 0.5$ kcal/mol, $\Delta H_f°(CF_3CH_3) = -178.0 \pm 0.4$ kcal/mol, $\Delta H_f°(CF_3CF_2CF_3) = -426.2 \pm 1.7$ kcal/mol.

(38) Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*; University of Sussex: Sussex, Brighton, 1977.

(39) From the experimental heat of chlorination of $CF_3CF{=}CF_2$ (47.1 kcal/mol)[40] and $\Delta H_f°(CF_3CFClCF_2Cl) \simeq -315.5$ kcal/mol estimated from group increments,[41] $\Delta H_f°(CF_3CF{=}CF_2) \simeq -266.4$ kcal/mol.

(40) Lacher, J. R.; Kianpour, A.; Park, J. D. *J. Am. Chem. Soc.* **1957**, *61*, 584.

(41) (a) Bryant, W. M. D. *J. Polym. Sci.* **1962**, *56*, 277. (b) Kauschka, V. G.; Kolditz, L. *Z. Chem.* **1976**, *16*, 3772.

(42) From experimental heats of combustion,[43] $3C_2F_4 \rightarrow 2CF_3CF{=}CF_2 + 20.6$ kcal. Using $\Delta H_f°(C_2F_4) = -157.9$ kcal/mol,[37] $\Delta H_f°(CF_3CF{=}CF_2) = -267.8$ kcal/mol.

(43) Duus, H. C. *Ind. Eng. Chem.* **1955**, *47*, 1445.

(44) Total energies (DZ+D$_C$): −176.912 823 au ($CH_2{=}CHF$), −413.723 148 au ($CF_3CH{=}CH_2$).

Since there are no experimental thermochemical data on $(CF_3)_2C{=}CF_2$, we used the calculated ΔE of -6.2 kcal/mol for eq 5 and our approximate $\Delta H_f°(CF_3CF{=}CF_2)$ to derive $\Delta H_f°((CF_3)_2C{=}CF_2) \simeq -380.7$ kcal/mol. This value was used to obtain $\Delta H_f°$(**4a**) in Table V. There is excellent agreement between the calculated and experimental heats of formation of $CF_3CF_2^-$, $(CF_3)_2CF^-$, and $(CF_3)_3C^-$, especially considering the approximations in both the experimental and theoretical values for the last two anions. (The "experimental" values for $(CF_3)_2CF^-$ and $(CF_3)_3C^-$ are based on heats of formations of perfluoroalkanes and radicals that were *estimated* from group additivity schemes; see Table V, footnote *d* and ref 41.) By contrast, the theoretical $\Delta H_f°(CF_3CH_2^-)$ differs by about 26 kcal/mol from the value that is derived from proton affinity data. This discrepancy is well outside any reasonable experimental or theoretical error limits. We believe this indicates that the most stable species produced in the gas-phase deprotonation of CF_3CH_3 is not $CF_3CH_2^-$ but is instead a hydrogen-bonded species $CF_2{=}CH_2{\cdots}F^-$ which lies about 26 kcal/mol lower in energy. A similar conclusion has been reached concerning the anomalous gas-phase acidity of FCH_2CH_3.[16a] Notably, the estimated differences in energy between $FCH_2CH_2^-$ and $CH_2{=}CH_2{\cdots}F^-$, 28–31 kcal/mol,[9,16a] are very close to the difference that we deduce for $CF_3CH_2^-$ vs. $CF_2{=}CH_2{\cdots}F^-$.

$$2CF_3CF{=}CF_2 \rightarrow (CF_3)_2C{=}CF_2 + CF_2{=}CF_2 \qquad (5)$$

To assess the relative effects of α- vs. β-fluorination on carbanion stability, the energies of isodesmic reactions 6 and 7 were calculated.[45] (The enthalpies of (6) and (7) are equivalent to relative proton affinities of the anions.) The exothermicities indicate that $CF_3CF_2^-$ is about 22 kcal/mol more stable than $CF_3CH_2^-$,[46] whereas $CF_3CF_2^-$ is about 35 kcal/mol more stable than $CH_3CF_2^-$. Thus, three β-fluorines appear to stabilize the ethyl carbanion roughly 13 kcal/mol more than two α-fluorines. (Isodesmic reactions that more properly relate the fluorinated carbanions to $CH_3CH_2^-$ or CH_3^- were not considered because the hydrocarbon anions may not be bound species.[49,50]) The much greater stability of $CF_3CF_2^-$ relative to $CF_3CH_2^-$, due to the α-fluorines, supports the qualitative PMO argument for greater anionic HCJ in the latter (see Geometries Section).

$$CF_3CH_2^- + CF_3CF_2H \rightarrow CF_3CH_3 + CF_3CF_2^- \qquad (6)$$

$$\Delta E = -21.9 \text{ kcal/mol}$$

$$CH_3CF_2^- + CF_3CF_2H \rightarrow CH_3CF_2H + CF_3CF_2^- \qquad (7)$$

$$\Delta E = -35.3 \text{ kcal/mol}$$

Isodesmic reactions 8–10 were used to relate the stabilities of perfluorinated carbanions. (The enthalpies of (8) and (9) are equivalent to relative F^+ affinities of the carbanions.) Experimental heats of formation were used for the neutrals[37] and CF_3^- and calculated values (Table V) for the other carbanions.

$$CF_3^- + CF_3CF_3 \rightarrow CF_4 + CF_3CF_2^- \qquad (8)$$

$$\Delta H = 0.1 \text{ kcal/mol}$$

$$CF_3^- + CF_3CF_2CF_3 \rightarrow CF_4 + (CF_3)_2CF^-$$

$$\Delta H = -14.4 \text{ kcal/mol} \qquad (9)$$

$$2(CF_3)_2CF^- \rightarrow (CF_3)_3C^- + CF_3CF_2^-$$

$$\Delta H = -11.9 \text{ kcal/mol} \qquad (10)$$

The essentially thermoneutral reaction 8 indicates that CF_3^- and $CF_3CF_2^-$ have the same stability, whereas from reaction 9, $(CF_3)_2CF^-$ is 14.4 kcal/mol more stable than CF_3^-. Since $(CF_3)_2CF^-$ is 14.5 kcal/mol more stable than $CF_3CF_2^-$, the approximate enthalpy of reaction 10 implies that $(CF_3)_3C^-$ is 26.4 kcal/mol lower in energy than $(CF_3)_2CF^-$, or 40.9 kcal/mol lower than $CF_3CF_2^-$.

The differences in fluoride affinities of $CF_2{=}CF_2$, $CF_3CF{=}CF_2$, and $(CF_3)_2C{=}CF_2$ (Table IV) clearly do not fully reflect the relative stabilities of the corresponding fluoride adducts. For instance, the isodesmic stabilities of $(CF_3)_3C^-$ and $CF_3CF_2^-$ differ by 40.9 kcal/mol, but the fluoride affinities of $(CF_3)_2C{=}CF_2$ and $CF_2{=}CF_2$ differ by only 25.2 kcal/mol. Since the difference between the stabilities of the product perfluorocarbanions is not equal to the difference between the reaction enthalpies (fluoride affinities), obviously the reactant perfluoroolefins must have different thermodynamic stabilities. Since $FA(CF_3CF{=}CF_2) - FA(CF_2{=}CF_2) = 9.7$ kcal/mol, but $(CF_3)_2CF^-$ is 14.5 kcal/mol lower in energy than $CF_3CF_2^-$, it follows that $CF_2{=}CF_2$ is 4.8 kcal/mol thermodynamically *less* stable than $CF_3CF{=}CF_2$.[51] Similarly, with $FA((CF_3)_2C{=}CF_2) - FA(CF_3CF{=}CF_2) = 15.5$ kcal/mol and $(CF_3)_3C^-$ 26.4 kcal/mol in energy below $(CF_3)_2CF^-$, $(CF_3)_2C{=}CF_2$ is 10.9 kcal/mol *more* stable than $CF_3CF{=}CF_2$. (From these deduced relative stabilities reaction 5 is predicted to be exothermic by 6.1 kcal/mol, which compares to the calculated enthalpy of -6.2 kcal/mol!)

The isodesmic reaction energies provide a quantitative ordering of the overall stabilities of fluorinated carbanions, $(CF_3)_3C^- > (CF_3)_2CF^- > CF_3CF_2^- \simeq CF_3^- > CF_3CH_2^- > CH_3CF_2^-$, but there does not appear to be any way to unambiguously differentiate between the inductive and hyperconjugative contributions to their stabilities.[52] Nonetheless, the importance of fluorine negative HCJ is indisputable. The abnormal structures of β-fluorocarbanions and their charge distributions are compelling evidence for the phenomenon.

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[45] Total energies (DZ+D$_C$): −573.610773 au (CF_3CF_2H), −375.883519 au (CF_3CH_3), −276.333381 au ($CH_3CF_2^-$), −276.995760 au (CH_3CF_2H).

[46] A similar result is obtained from the isodesmic reaction $CF_3CH_2^- + CF_2{=}CF_2 \rightarrow CF_3CF_2^- + CF_2{=}CH_2$, for which $\Delta E = -34.3$ kcal/mol. After correcting for the relative stabilities of $CF_2{=}CF_2$ and $CF_2{=}CH_2$, which can be equated to the difference of their π-bond strengths[17b,47] (ca. 10.5 kcal/mol),[48] $CF_3CF_2^-$ is deduced to be 23.8 kcal/mol more stable than $CF_3CH_2^-$.

[47] Smart, B. E. In *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; Verlag Chemie: Deerfield, FL, 1986; Vol. 3, Chapter 4.

[48] (a) Wu, E.-C.; Rodgers, A. S. *J. Am. Chem. Soc.* **1976**, *98*, 6112. (b) Pickard, J. M.; Rodgers, A. S. *J. Am. Chem. Soc.* **1977**, *99*, 695.

[49] (a) Christodoulides, A. A.; McCorkle, D. L.; Christophorou, L. G. In *Electron-Molecule Interactions and Their Applications*; Christophorou, L. G., Ed.; Academic Press: Orlando, FL, 1984; Vol. 2, Chapter 6. (b) Janousek, B. K.; Brauman, J. I. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol 2, Chapter 10.

[50] The electron affinity of CH_3 has been reported to be 1.8 ± 0.7 kcal/mol: Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556. It has been suggested, however, that CH_3 cannot bind an additional electron; see: Marynick, D. S.; Dixon, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 410.

[51] From the underlying isodesmic relationships that we are using, this more precisely means that $CF_2{=}CF_2$ is thermodynamically less stable than $CF_3CF{=}CF_2$ with regard to F_2 addition. This is equivalent to using the isodesmic equation $CF_3CF{=}CF_2 + CF_3CF_3 \rightarrow CF_2{=}CF_2 + CF_3CF_2CF_3$ ($\Delta H° = 4.8$ kcal/mol) to relate the stabilities of the olefins.

[52] Neither the relative inductive (i.e., field component) or hyperconjugative contributions of anti, syn, and gauch β-fluorines nor the effect of α-fluorination on β-fluorine hyperconjugation can be quantified energetically. In fact, from the available data it is difficult to see how to reliably assess even the gross effects of α- vs. β-fluorination. To illustrate the complications, we note that the effect of substituting CF_3 by F on the isodesmic stabilities of the perfluorocarbanions not only is nonadditive but also exhibits "saturation" (i.e., the difference in the stabilities of $(CF_3)_3C^-$ and $(CF_3)_2CF^-$ is nearly twice that of $(CF_3)_2CF^-$ and $CF_3CF_2^-$, but $CF_3CF_2^-$ and CF_3^- have the same stability). We thank a referee for drawing our attention to this curious saturation effect.