

Effect of Fluorine Substitution on the Carbon Acidity of Methane, Methyl Isocyanide, Acetonitrile, Acetaldehyde, and Nitromethane

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The effect of fluorine substitution on the acidity of the title compounds has been examined via ab initio molecular orbital theory. Multiple fluorine substitution has a synergetic effect on the acidity of methane. In the case of substituted methanes, the acidity of methyl isocyanide increases linearly with the fluorine substitution while a smaller effect is observed with acetonitrile, and little effect is found with acetaldehyde and nitromethane. The acetaldehydes are unique in that the anion of difluoroacetaldehyde remains planar, whereas all of the other difluoroanions become markedly pyramidal with large inversion barriers. The ionization process was examined in terms of the changes in atomic charges and bond orders. Fluorine has a larger effect on the acidity of compounds with pyramidal anions than those with planar ones. The stabilization appears to be a consequence of the competition for p character by the fluorine atoms which tends to place the anionic charge into an orbital with high s character.

1. Introduction

Nitromethane and acetaldehyde are two of the more acidic monosubstituted methane derivatives. On ionization, the anions are stabilized through the formation of a π system with substituents that allow delocalization of the charge at the anionic carbon. This increases the acidity of methane by about 51 and 61 kcal/mol on going to acetaldehyde and nitromethane, respectively. It has been shown that the π system contributes to this stabilization by 34 kcal/mol in the case of acetaldehyde and 28 kcal/mol with nitromethane,¹ and the remaining stabilization is due to the inductive effect of the substituent. Acetonitrile also has increased acidity (44 kcal/mol with respect to methane), but here σ - π partitioning of the stabilization cannot be done due to the rotational degeneracy of the π system in the cyano group.

We have examined the changes in electron density that occur when these weak organic acids are converted to their anions. The charge transfer from the anionic center to the substituent was studied, and both σ and π components were found (Table 1). Acetaldehyde and nitromethane were found to have the largest π transfers. They also had the highest acidities. A cyano group gave significantly less charge transfer. The common feature with all these groups is that they stabilize the anionic charge to a major extent via a π interaction with the anionic center.

Fluorine is an example of a substituent that should stabilize anions largely via σ charge transfer due to its high electronegativity and the relatively high σ^* energy. Thus, we became interested in the relative effects of fluorine and the other substituents in Table 1 on the acidity of the C–H bonds. Here, it should be noted that a recent study reported the effect of fluorine substitution on the acidity of sulfones,^{2,3} and the present investigation provides complementary information.

(1) Wiberg, K. B.; Castejon, H. J. *J. Org. Chem.* **1995**, *60*, 6327.

(2) Raabe, G.; Gais, H.-J.; Fleischauer, J. *J. Am. Chem. Soc.* **1996**, *118*, 4622. They examined the effect of fluorine substitution remote from the anionic center.

(3) For a comparison with the other weak acids, dimethyl sulfone is more acidic than methane by 41 kcal/mol, and the rotational barrier is 9 kcal/mol (Wiberg, K. B.; Castejon, H. *J. Am. Chem. Soc.* **1994**, *116*, 10489).

Table 1. σ and π Electron Shifts to Substituents on Ionization^a

compd	σ	π
methyl isocyanide	0.000	0.337
acetonitrile	0.003	0.385
nitromethane	0.016	0.593
acetaldehyde	0.010	0.555

^a The charge shifts were obtained by integrating the electron density for the σ and π electrons separately in obtaining the Hirshfeld electron populations (ref 1).

Table 2. Calculated Energies at MP2/6-31+G*

compd	precursor		anion	
	zpve ^a	energy	zpve	energy
methane	26.7	-40.334 08	17.0	-39.654 43
fluoromethane	23.7	-139.353 50	13.8	-138.688 32
difluoromethane	20.1	-238.390 86	10.3	-237.749 87
trifluoromethane	15.6	-337.437 36	5.8	-336.831 98
methyl isocyanide	27.3	-132.303 49	18.2	-131.683 27
fluoromethyl isocyanide	23.4	-231.324 38	14.2	-230.718 84
difluoromethyl isocyanide	18.9	-330.359 23	9.5	-329.775 28
acetonitrile	27.4	-132.345 36	18.1	-131.736 74
fluoroacetonitrile	23.6	-231.357 59	14.4	-230.758 52
difluoroacetonitrile	19.2	-330.387 69	9.9	-329.801 26
nitromethane	30.6	-244.351 76	22.1	-243.772 68
fluoronitromethane	26.6	-343.370 79	17.6	-342.795 98
difluoronitromethane	20.1	-442.402 87	12.6	-441.831 16
acetaldehyde	33.6	-153.358 01	25.4	-152.764 74
fluoroacetaldehyde	29.8	-252.374 73	21.1	-251.791 81 ^b
difluoroacetaldehyde	25.5	-351.411 81	16.8	-350.821 38

^a The zero-point energies were calculated at the HF/6-31G* level and were scaled by 0.893. The total energies are given in Hartrees, and the zero-point energies are given in kcal/mol. ^b The *Z* isomer.

2. Calculations

The energies and structures of the compounds in this study were obtained at the MP2/6-31+G* level of theory, and the zero-point energies were calculated at the HF/6-31G* level. The energies are summarized in Table 2. The enthalpies of ionization derived from these energies are given in Table 3 and are compared with the available experimental data.⁴ In most cases, there is good agree-

(4) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *117*, Suppl. 1.

Table 3. Calculated and Experimental Acidities^a

compd	ΔH_{calcd}	ΔH_{obsd}	$\Delta\Delta H$	$\Delta\Delta H$
methane	416.8	416.8 ± 2	0.0	
fluoromethane	406.3		-10.5	0.0
difluoromethane	391.3	386.7 ± 7	-25.5	-15.0
trifluoromethane	368.9	376.9 ± 2	-47.9	-37.4
methyl isocyanide	380.1		-36.7	0.0
fluoromethyl isocyanide	370.8		-46.0	-9.3
difluoromethyl isocyanide	357.1		-59.7	-23.0
acetonitrile	373.5	373 ± 3	-43.3	0.0
fluoroacetonitrile	366.8		-50.0	-6.7
difluoroacetonitrile	358.7		-58.1	-14.8
nitromethane	354.9	356.4 ± 3	-61.9	0.0
fluoronitromethane	350.4		-66.4	-4.5
difluoronitromethane	348.2		-68.6	-6.7
acetaldehyde	364.1	365.9 ± 3	-52.7	0.0
fluoroacetaldehyde	357.1		-59.7	-7.0
difluoroacetaldehyde	360.8		-56.0	-3.3

^a kcal/mol.**Table 4. Geometry and Bond Orders in Fluoromethanes**

	bond	neutral	anion	diff
(a) Geometry Changes				
CH ₄	C-H	1.091	1.102	+0.011
CH ₃ F	C-H	1.091	1.111	+0.020
	C-F	1.407	1.521	+0.114
CH ₂ F ₂	C-H	1.089	1.113	+0.024
	C-F	1.376	1.488	+0.112
CHF ₃	C-H	1.088		
	C-F	1.351	1.448	+0.097
(b) Bond Orders				
CH ₄	C-H	0.976	1.088	
CH ₃ F	C-H	0.938	1.014	
	C-F	0.778	0.789	
CH ₂ F ₂	C-H	0.895	0.940	
	C-F	0.724	0.758	
CHF ₃	C-H	0.850		
	C-F	0.658	0.712	

Table 5. Pyramidalization (θ) and Internal Angles in Fluoromethanes

anion	angle (deg)			θ
	H-C-H	H-C-F	F-C-F	
CH ₃ ⁻	110.74			46.8
CH ₂ F ⁻	105.59	101.00		71.6
CHF ₂ ⁻		98.43	100.44	74.5
CF ₃ ⁻			99.55	75.1

Table 6. Charges in Fluoromethanes

	atom	neutral	anion	diff
CH ₄	C	-0.137	-0.747	-0.610
	H	0.034	-0.083	-0.117
CH ₃ F	C	0.475	-0.130	-0.605
	H	0.061	-0.081	-0.142
	F	-0.659	-0.708	-0.049
CH ₂ F ₂	C	1.123	0.452	-0.671
	H	0.097	-0.052	-0.149
	F	-0.658	-0.700	-0.042
CHF ₃	C	1.819	1.104	-0.715
	H	0.146		
	F	-0.655	-0.701	-0.046

ment, but with trifluoromethane the calculated ΔH was significantly less endothermic than the experimental value.

Except for the fluoromethanes, there are no data for the ionization of the fluorinated derivatives of the weak acids. One might reasonably expect that any errors in the calculations will cancel between the different compounds and that useful comparisons could be made using the calculated energies.

The net effect of the substituents (F, NO₂, CHO, etc.) is given in the column marked $\Delta\Delta H$. The effect of fluorine substitution alone is shown in the column $\Delta\Delta H$. The latter quantity is largest with substitution on fluo-

romethane and decreases as the initial substituent goes through the series isocyno, cyano, nitro, and aldehyde.

3. Fluoromethanes

A large increase in acidity is found on progressive fluorine substitution on methane. The structural changes that accompany deprotonation are summarized in Table 4. The C-H bonds uniformly increase in length by about 0.02 Å. A much larger effect is found in the C-F bonds (0.11 Å), and it is almost independent of the degree of fluorine substitution. The C-F covalent bond orders⁵ decrease with increasing fluorine substitution, reflecting the increasing ionic character of these bonds.

The degree of pyramidalization (planar = 0°) and the bond angles in the anions are given in Table 5. Finally, the changes in electron population derived from deprotonation are summarized in Table 6. Here, there is a small increase in the negative charge at fluorine on going to the anions, but a larger change is found at the hydrogens. In carbanions, it is usually found that much of the negative charge is transferred to the hydrogens.⁶

Methide ion is pyramidal⁷ with a 110.7° H-C-H bond angle and a 47° pyramidalization angle. The corresponding angles for a CH₃ fragment of methane are 109.47° and 60°. Thus, the anion is partway toward becoming planar, but the change from methane is not large. The introduction of one fluorine reduces the H-C-H angle in the anion to 105.6° and increases the pyramidalization to 71.6°. Further fluorine substitution continues to decrease the bond angles, and increases the pyramidalization angle to 75°.

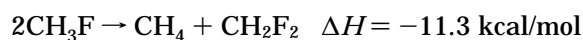
Fluorine is known to prefer to be bonded to a carbon orbital with high *p* character, and lone pairs would be expected to prefer an orbital with high *s* character.⁸ These two effects are synergetic, giving for CF₃⁻ a bond angle (α) of 99.6° and a pyramidalization angle (θ) of 75° (Figure 1). The angle, θ , is defined as follows:



The two effects combine to lead to large increases in acidity on successive fluorine substitution.

4. Incremental Geminal Stabilization Effect

Fluorine is known to exert what is called the incremental geminal stabilization effect, which is defined as the increase in the stabilization of a geminally substituted compound relative to the corresponding monosubstituted compounds.⁹ The amount of stabilization can be derived from the following isodesmic reactions for the effect on methane:



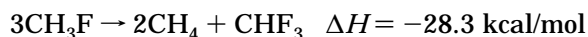
(5) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142. Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644.

(6) Wiberg, K. B.; Schleyer, P. v. R.; Streitwieser, A. *Can. J. Chem.* **1996**, *74*, 892.

(7) Ellison, G. B.; Engleking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556.

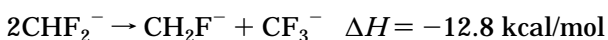
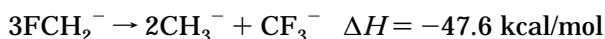
(8) Bent, H. *Chem. Rev.* **1961**, *61*, 275.

(9) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 1663.



We have examined the origin of the stabilization derived from multiple fluorine substitution.¹⁰ Each additional fluorine accepts the same electron population from the carbon. The increase in positive charge of the carbon with increasing F substitution leads to increased Coulombic attraction between carbon and fluorine and to stronger and shorter C–F bonds. Although one might have expected the electron transfer to fluorine to diminish with increasing fluorine substitution, the constant electron transfer has been confirmed by other studies.¹¹

The corresponding reactions for the anions are as follows:



These reactions show that the fluorine exerts a stronger stabilization effect on the anions than on the neutral molecules, which accounts for the increase in acidity of fluoromethane with increasing fluorine substitution.

The fluoromethyl anions also show a decrease in the C–F bond length with increasing fluorine substitution. This could be due to the same Coulombic factors as proposed for the fluoromethanes. The change in C–F bond length on ionization is essentially constant at 0.11 Å (Table 4), and there is only a small and constant increase in the charge at the fluorines on ionization (Table 6). The charge at the carbon of the fluoromethyl anion is small and negative, and it becomes progressively more positive as the number of fluorines increases leading to an increase in the Coulombic attraction between carbon and fluorine. The essentially constant changes in charge and geometry in comparing the fluoromethanes and their anions does suggest that the same Coulombic effects are operative in the two series.

What is the origin of the increased acidity of the fluoromethanes? As noted above, the fluoromethyl anions are strongly pyramidalized (Table 6). This corresponds to the operation of Bent's rule,⁸ which states that electronegative atoms prefer to be bonded to orbitals having high *p*-character. The increasing *p*-character with fluorine substitution will lead to a decrease in the H–C–F and F–C–F angles, which leads to increased pyramidalization. The lone pair then occupies an orbital with high *s* character, which will lead to stabilization. In addition, the fluorine does transfer charge from the anionic carbon via the σ system as can be seen from the charges in Table 6. This leads the overall negative charge to be placed on atoms with high electronegativity, again leading to stabilization.

5. Effect of Fluorine on Acetonitrile and Methyl Isocyanide

With the substituted methanes, both mono- and di-substitution can be examined. The geometries, bond

Table 7. Geometry and Bond Orders in Fluoroacetonitriles

	bond	neutral	anion	diff
(a) Geometry Changes				
CH ₃ CN	C–N	1.181	1.203	+0.022
	C–C	1.464	1.401	–0.063
CH ₂ FCN	C–N	1.181	1.199	+0.018
	C–C	1.470	1.420	–0.050
CHF ₂ CN	C–F	1.399	1.474	+0.075
	C–N	1.181	1.190	+0.009
	C–C	1.477	1.476	–0.001
	C–F	1.369	1.453	+0.084
(b) Bond Orders				
CH ₃ CN	C–N	2.260	2.124	
	C–C	1.034	1.433	
CH ₂ FCN	C–N	2.277	2.151	
	C–C	0.975	1.274	
CHF ₂ CN	C–F	0.773	0.767	
	C–N	2.291	2.167	
	C–C	0.921	1.014	
	C–F	0.715	0.730	

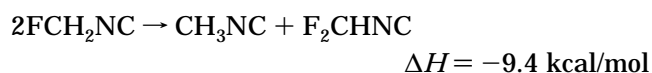
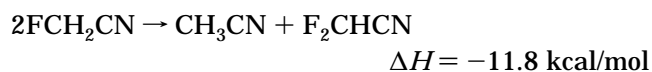
Table 8. Charges in Fluoroacetonitriles

	atom	neutral	anion	diff
CH ₃ CN	N	–1.175	–1.417	–0.242
	C	0.884	0.762	–0.122
	C	0.011	–0.346	–0.358
	H	0.093	0.001	–0.093
	H	0.093	0.001	–0.093
CH ₂ FCN	H	0.093	0.001	–0.093
	N	–1.108	–1.350	–0.242
	C	0.891	0.795	–0.096
	C	0.621	0.214	–0.407
	F	–0.632	–0.677	0.045
CHF ₂ CN	H	0.115	0.014	0.100
	H	0.115	0.014	0.115
	N	–1.055	–1.296	–0.241
	C	0.910	0.871	–0.039
	C	1.276	0.775	–0.501
	F	–0.635	0.674	–0.039
	F	–0.635	0.674	–0.039
	H	0.155		–0.155

Table 9. Geometry and Bond Orders in Fluoroisocyanides

	bond	neutral	anion	diff
(a) Geometry Changes				
CH ₃ NC	N–C	1.188	1.200	0.012
	C–N	1.428	1.404	–0.024
CH ₂ FNC	N–C	1.190	1.197	+0.007
	C–N	1.418	1.420	+0.002
CHF ₂ NC	C–F	1.388	1.480	+0.092
	N–C	1.191	1.193	+0.002
	C–N	1.411	1.464	+0.053
	C–F	1.361	1.444	+0.083
(b) Bond Orders				
CH ₃ NC	N–C	1.838	2.006	
	C–N	0.854	1.013	
CH ₂ FNC	N–C	1.789	1.955	
	C–N	0.789	0.901	
CHF ₂ NC	C–F	0.734	0.736	
	N–C	1.751	1.926	
	C–N	0.723	0.751	
	C–F	0.672	0.697	

orders, and atomic charges for acetonitriles and methyl isocyanides are given in Tables 7–10. Theisodesmic reactions for the effect of fluorine substitution on acetonitrile and methyl isocyanide are as follows:



The stabilization by multiple fluorine substitution in acetonitrile is similar to that in fluoromethanes, whereas methyl isocyanide is somewhat less stabilized. The

(10) Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

(11) Cioslowski, J.; Nanayakkara, A. *J. Am. Chem. Soc.* **1993**, *115*, 11213. Guadagnini, P. H.; Bruns, R. E. *J. Am. Chem. Soc.* **1995**, *117*, 4144.

Table 10. Charges in Fluoroisocyanides

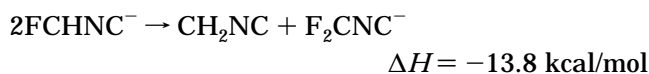
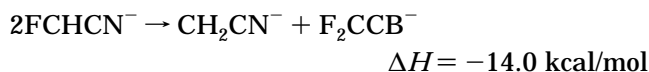
	atom	neutral	anion	diff
CH ₃ NC	C	0.907	0.579	-0.328
	N	-1.543	-1.510	+0.033
	C	0.362	-0.032	-0.395
	H	0.092	-0.018	-0.110
	H	0.092	-0.018	-0.110
CH ₂ FNC	H	0.092	-0.092	-0.092
	C	0.952	0.666	-0.285
	N	-1.551	-1.505	+0.045
	C	0.996	0.524	-0.472
	F	-0.641	-0.683	-0.042
CHF ₂ NC	H	0.118	-0.001	-0.119
	H	0.118	-0.001	-0.118
	C	0.986	0.756	-0.230
	N	-1.542	-1.474	+0.067
	C	1.688	1.089	-0.598
	F	-0.641	-0.685	-0.044
	F	-0.641	-0.685	-0.044
	H	0.155		-0.155

Table 11. Pyramidalization Angles and Inversion and Rotation Barriers for Anions^a

anion	θ	inversion	rotation
CH ₂ CHO ⁻	0.0		36.1
CHFCHO ⁻	2.6		29.9
CF ₂ CHO ⁻	2.0		13.4
CH ₂ NO ₂ ⁻	0.0		32.6
CHFNO ₂ ⁻	38.1	0.93	23.0
CF ₂ NO ₂ ⁻	65.2	10.7	5.6
CH ₂ CN ⁻	33.6	0.15	
CHFCN ⁻	56.0	4.6	
CF ₂ CN ⁻	67.7	59.7	
CH ₂ NC ⁻	52.7	2.5	
CHFNC ⁻	66.9	14.4	
CF ₂ NC ⁻	72.4	43.9	

^a kcal/mol.

corresponding reactions for the anions are as follows:



Although there is a difference in magnitude, here the stabilization effect follows the same trend as with the fluoromethanes; namely, the anions are stabilized more than the parent compounds. Consequently, the acidity of the fluorinated compounds is larger. The anions in these cases exhibit a strong pyramidalization and a large inversion barrier, which increases with increasing fluorine substitution (Table 11). Also, in both cases the charge transfer to the cyano and isocyano groups decreases upon fluorination, and as in the case of fluoromethanes the anionic carbon becomes more positive (Tables 7 and 9).

Here, again Bent's rule appears to be operating. The presence of a very electronegative fluorine atom forces the anionic carbon to be pyramidal so the fluorine can be bonded to a high *p* character orbital. The decrease of the C-C bond order and of the change in C-C bond length with increasing fluorine substitution in the acetonitrile anion (Table 7) shows that the fluorine disrupts the π conjugation between the anionic center and the substituent. However, the stabilization effect exerted by the fluorine atom bonded to the pyramidal carbanionic center may replace the stabilization lost by disrupting the π resonance. This disruption may account for the smaller change of the acidity observed in acetonitrile

Table 12. Geometry and Bond Orders in Fluoroacetaldehydes

	bond	neutral	anion	diff
(a) Geometry Changes				
CH ₃ CHO	C-O	1.227	1.285	+0.058
	C-C	1.502	1.387	-0.115
CH ₂ FCHO	C-O	1.221	1.285	+0.064
	C-C	1.509	1.371	-0.138
	C-F	1.389	1.429	+0.040
CHF ₂ CHO	C-O	1.222	1.296	+0.074
	C-C	1.519	1.362	-0.157
	C-F	1.377	1.374(1.392) ^a	-0.003(+0.015)
(b) Bond Orders				
CH ₃ CHO	C-O	1.401	1.191	
	C-C	1.009	1.642	
CH ₂ FCHO	C-O	1.415	1.179	
	C-C	0.969	1.641	
	C-F	0.774	0.765	
CHF ₂ CHO	C-O	1.416	1.155	
	C-C	0.882	1.585	
	C-F	0.712	0.723(0.717) ^a	

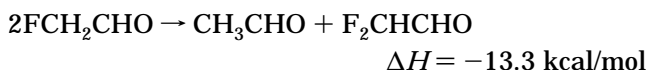
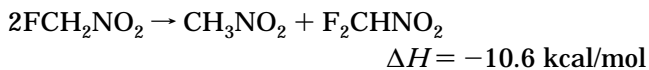
^a Fluorine anti to oxygen.**Table 13. Charges in Fluoroacetaldehydes**

	atom	neutral	anion	diff
CH ₃ CHO	O	-1.122	-1.303	-0.179
	H	0.049	-0.063	-0.111
	C	0.994	0.786	-0.208
	C	-0.115	-0.388	-0.273
	H	0.063	-0.007	-0.070
	H	0.063	-0.025	-0.083
CH ₂ FCHO	H	0.073		
	O	-1.089	-1.288	-0.199
	H	0.059	-0.049	-0.108
	C	1.013	0.837	-0.176
	C	0.496	0.169	-0.327
	F	-0.648	-0.693	-0.045
CHF ₂ CHO	H	0.084	0.026	-0.058
	O	-1.080	-1.285	-0.205
	H	0.103	-0.013	-0.116
	C	1.038	0.901	-0.137
	C	1.113	0.768	-0.345
	F	-0.648	-0.679	-0.031
F	-0.648	-0.685	-0.038	

compared to methyl isocyanide. In this later compound the resonance effect is small as shown by the small C-N bond orders, and thus, there is little loss of acidity due to disruption of resonance. Hence, the net effect of the multiple fluorine substitution is a larger enhancement of the acidity via the inductive effect.

6. Effect of Fluorine on Nitromethane and Acetaldehyde

In the cases of nitromethane and acetaldehyde, mono- and disubstitution can also be compared. Here, the changes in geometry and atomic charges are given in Tables 12-15. The isodesmic reactions that show the effects of fluorine substitution on the parent compounds are as follows:



Here again, the stabilization by multiple fluorine substitution in the neutral compounds is similar to that

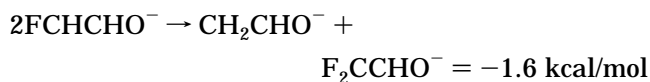
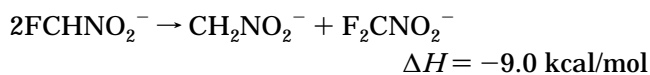
Table 14. Geometry and Bond Orders in Fluoronitromethanes

	bond	neutral	anion	diff
(a) Geometry Changes				
CH ₃ NO ₂	N-O	1.244	1.293	+0.049
	C-N	1.490	1.348	-0.142
CH ₂ FNO ₂	N-O	1.240	1.288	+0.048
	C-N	1.509	1.354	-0.145
	C-F	1.366	1.381	+0.015
CHF ₂ NO ₂	N-O	1.241	1.259	+0.048
	C-N	1.514	1.473	-0.041
	C-F	1.348	1.412	+0.064
(b) Bond Orders				
CH ₃ NO ₂	N-O	1.834	1.464	
	C-N	0.836	1.585	
	C-F	0.771	0.726	
CH ₂ FNO ₂	N-O	1.822(1.864)	1.473(1.498)	
	C-N	0.803	1.525	
	C-F	0.771	0.723	
CHF ₂ NO ₂	N-O	1.839(1.858)	1.758	
	C-N	0.744	0.935	
	C-F	0.695	0.704	

Table 15. Charges in Fluoronitromethanes

	atom	neutral	anion	diff
CH ₃ NO ₂	O	-0.450	-0.700	-0.250
	O	-0.450	-0.700	-0.250
	N	0.378	0.076	-0.302
	C	0.208	0.222	0.013
	H	0.102	0.052	-0.049
	H	0.106	0.052	-0.054
CH ₂ FNO ₂	O	-0.401	-0.688	-0.287
	O	-0.451	-0.649	-0.198
	N	0.414	0.083	-0.331
	C	0.825	0.844	0.019
	F	-0.648	-0.680	-0.032
	H	0.129	0.090	-0.040
CHF ₂ NO ₂	H	0.129		
	O	-0.420	-0.547	-0.127
	O	-0.388	-0.547	-0.159
	N	0.426	0.337	-0.089
	C	1.503	1.121	-0.382
	F	-0.644	-0.680	-0.036
	F	-0.644	-0.680	-0.036
	H	0.170		

in the fluoromethanes and the fluorinated isocyano and cyanomethanes. The corresponding reactions for the anions give the following differences in energy:



In the case of the anion, fluorine substitution shows significantly different energy changes. For example, in both anions the relative magnitude of the stabilization effect between parent compounds and anions has been inverted. In the case of nitromethane a small differential effect is observed, whereas in acetaldehyde the neutral molecule is stabilized significantly more than its corresponding anion. The *Z* isomer of the fluoroacetaldehyde anion was found to be 0.5 kcal/mol more stable than the *E* isomer.

Unlike the anion of nitromethane, the anions of the fluorinated nitromethanes show pyramidalization that disrupts the π interaction between the anionic carbon and the nitro group that is largely responsible for the greater

acidity of nitromethane compared to methane. As may be seen in the changes in bond lengths and in the bond orders of the anions, the effect of fluorine substitution is particularly large on going from the monofluoro to the difluoro anions. The slight increase in acidity of the fluorinated nitromethanes suggests that part of the π stabilizing interaction is replaced by the incremental geminal stabilization effect exerted by the fluorine atoms.

Acetaldehyde is unique in that neither the parent anion nor the fluorinated anions show pyramidalization. In the neutral molecule, the fluorine atom is bonded to an sp^3 carbon, which provides the high p character orbital preferred by this atom, while in the anion the strong π interaction between the anionic carbon and the acetyl group forces the fluorine atoms to be part of the π system. This may be seen in the relatively constant increases in C-C bond lengths and C-C bond orders on going to the anions (Table 12).

The greater pyramidalization observed with the nitro compounds may indicate that in addition to its π accepting ability, the nitro group also can exert an inductive effect. This later feature is less important in the acetyl group, which is closer to a pure π acceptor substituent than the nitro group.

7. Charge Transfer

Upon fluorine substitution of the parent molecules, the fluorines consistently take the same amount of charge (0.64 e) regardless the type of substituent present. On ionization of those molecules, the charge on the fluorine atoms increases only by about 0.04. The fluorine atoms appear not to accept much of the charge made available by the ionization. This limited charge-accepting capacity of fluorine has been found to be related to its high electronegativity.¹² Despite this apparent charge saturation of the fluorine atoms, the total charge in the substituents decreases with the fluorine substitution (Table 15). This depletion of charge is always larger than the charge gained by the fluorine atoms. Thus, the presence of fluorine does not appear to affect the anion by withdrawing substantial amounts of charge from the anionic center but instead it appears to induce a high p character hybridization at the anionic center. This allows the carbanion to put the negative charge in an orbital with high s character, leading to stabilization of the negative charge. This mechanism is quite efficient in the anions of methyl isocyanide and acetonitrile and those of the fluoromethanes. But it loses efficiency in the presence the acetyl group, as with the anion of acetaldehyde where the fluorine has to compete with the acetyl group for the p -character. This competition also occurs with the nitromethane anion, but here the inductive effect exerted by the nitro group helps to induce an sp hybridization at the anionic center, minimizing the importance of the π -system.

Conclusions

The effect of α -fluorine atoms on the stability of anions arises from a compromise between its inductive electron-withdrawing ability and the repulsion between its electron pair and that on the carbanionic center. The stabilizing inductive effect predominates in carbanions

(12) Politzer, P.; Heheey, J. E.; Murray, J. S.; Grodzicki, M. *J. Mol. Struct.* **1992**, *259*, 99.

with pyramidal anionic centers such as the fluoromethanes and fluorinated acetonitrile and methyl isocyanide. On the other hand, the destabilizing repulsion between adjacent electron pairs dominates in planar sp^2 hybridized carbanions, as in the case of acetaldehyde where the second fluorine substitution leads to a decrease in acidity.

The acidity increasing influence of fluorine in the compounds studied here appears to be a consequence of the competition for the p character at the anionic center between the α -fluorine atoms and the substituent. The result of this competition depends strongly on the con-

formation of the anionic center. The inductive effect of fluorine seems to predominate over the weaker π -acceptor substituents such as isocyano and cyano, and it is overcome by the π -accepting ability of the acetyl group. In the case of the nitro group, its additional inductive effect cooperates with that of fluorine to induce pyramidalization at the anionic center, leading to increased acidity.

Calculations

The ab initio calculations were carried out using Gaussian-95.¹³ The atomic charges were calculated using AIM96,¹⁴ and the bond orders were calculated using BONDER.⁵

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