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A MOLECULAR ORBITAL EXAMINATION (CNDO/2) OF THE IMPORTANCE OF FLUORINE HYPERCONJUGATION

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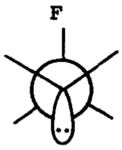
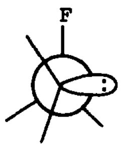
Fluorine hyperconjugation has been cited as a factor in the stabilization of fluoro anions (1,2). For example, in the 2-fluoroethyl anion we can draw the resonance forms:

An alternative explanation holds that the anion is stabilized primarily by inductive effects.

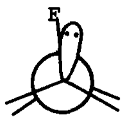
The availability of semi-empirical all-valence electron methods, such as the CNDO/2 method, makes it possible to evaluate the relative importance of the two mechanisms of stabilization (3). Calculations employing CNDO/2 were performed on a number of geometries of fluoroethane, fluoroethyl anion, trifluoroethane, trifluoroethyl anion, ethane, and ethyl anion and cation. All angles were assumed to be tetrahedral. The bond distances used were: C-C, 1.54 Å; C-H, 1.09 Å; C-F, 1.39 Å. The results are presented in Table I.



anti



perpendicular



syn

Table I. Total Energy (CNDO/2) for Various Systems

Compound	Energy (eV)[a] syn	perpendicular	anti
ethane	0.0947	0.0471	(0.0000)[b]
anion	27.3809	27.3486	27.3167
cation	38.3467	38.3323	38.3185
fluoroethane	0.0867	0.0431	(0.0000)[c]
anion	26.5872	26.6887	26.5793
trifluoroethane	0.0758	0.0380	(0.0000)[d]
anion	25.3483	25.3187	25.2891
methane	(0.0000)[e]		
anion	28.2979[f]		

[a] For each system the anti-form of the parent is taken as the zero of energy. A more positive number indicates less stability.

[b] -511.6887 eV. [c] -1245.6181 eV. [d] -2714.4083 eV.

[e] -275.1322 eV. [f] Hartree-Fock calculation gives 19.6 eV (5).

The energy change between a hydrocarbon and its anion can be taken as a measure of the stability of the anion. Thus, on the CNDO energy scale fluoroethyl anions are about 0.7 eV more stable than the corresponding ethyl anions. The difference between the syn- or anti-fluoroethyl anion and the perpendicular isomer, which would be expected not to conjugate, can be interpreted as measuring the amount of hyperconjugation. This difference is 0.11 eV, or ∿ 15% of the total energy stabilization by fluorine. Other criteria suggest that the magnitude of this percentage indicates a small role for fluorine hyperconjugation. For example, the calculations indicate that fluorine carries a net formal charge of -0.35, -0.37, and -0.37 in the perpendicular, syn- and anti-fluoroethyl anions, respectively. For comparison, hydrogen carries a net charge of -0.10, -0.13, and -0.13; and +0.17, +0.24, and +0.25 in the corresponding unsubstituted ethyl anions and cations. Thus fluorine does not appear to delocalize charge by conjugation even though the CNDO/2 calculations are known to overemphasize charge delocalization from carbanion lone pairs (4).

Perhaps the most revealing information is gained from an examination of the CNDO bond order parameters (Table II). If fluorine hyperconjugation were important for fluoroethyl anion we might expect a large increase relative to fluoroethane in the π-bonding between the carbon atoms. In fact, for the *syn* and *anti* conformations, which are most favorable for π-bonding, a small increase (0.12) in bond order is noted in moving from fluoroethane to the fluoroethyl anion. It is significant that the magnitude of this increase is similar to that (0.10) observed in the case of ethane-ethyl anion and far less than the case (0.27) of ethane-ethyl cation where hyperconjugation is thought to be important. It appears that fluorine stabilizes negative charge by hyperconjugation little better than hydrogen.

Table II. Bond Orders (CNDO/2) for Various Conformational Systems

Compound	syn	perpendicular	anti
ethane	0.1662	0.0021	0.1705
anion	0.2656	0.0003	------
cation	0.4359	0.0026	------
fluoroethane	0.1636	0.0012	0.1653
anion	0.2864	0.0012	0.2830

[a] Pi bond order between appropriate p-orbitals on adjacent carbon atoms.

Energetic considerations also reenforce the above conclusions. Consider the results obtained for 2,2,2-trifluoroethyl anion (Table I). This anion is more stable than ethyl anion by ∿ 2.0 eV or about three times the amount by which fluoroethyl anion is more stable than ethyl anion. The effect of added fluorines on anion stability is thus approximately additive. However, the energy difference between conformers in trifluoroethyl anion has been reduced relative to fluoroethyl anion and the relative order of stability, *anti* > *perpendicular* > *syn*, has changed. This behavior is readily explained by noting that the stability of a given conformer of trifluoroethyl anion is equal, to good approximation, to the sum of the stabilities of the three relevant conformations of monofluoroethyl anion (6). Thus even if the enhanced stability of the *syn* isomer of fluoroethyl anion is attributed to hyperconjugation, such stabilization is lost in the trifluoroethyl anion due to unfavorable 120° conformational interactions (6). The observed large and additive effect of fluorines on anion stability must be due to some other mechanism besides fluorine hyperconjugation. Recent reactivity studies indicate that inductive effects are fully adequate to rationalize the stabilities of fluoro anions (7). We thus conclude that anionic hyperconjugation is a minor factor in the stabilization of fluoro anions of the above type.

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References

1. J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.* **72**, 408 (1950).
2. W. A. Sheppard, *J. Am. Chem. Soc.* **87**, 2410 (1965).
3. (a) J. A. Pople and G. A. Segal, *J. Chem. Phys.* **44**, 3289 (1966);
   (b) A version of QCPE program #100 was used.
4. A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, J. R. Wright, P. H. Owens and D. M. E. Reuben, *Proc. Israel Acad. Sci. and Hum.*, in press.
5. M. Krauss, Compendium of *ab initio* Calculations of Molecular Energies and Properties, Technical Note 438, United States Department of Commerce, National Bureau of Standards, 1967.
6. The energies calculated for the 30°, 60°, 120°, and 150° conformers of fluoroethyl anion are, respectively, 26.5859, 26.6176, 26.6959, and 26.6318 eV. The *syn*-isomer is considered to be the 0° conformer.
7. A. Streitwieser, Jr., and D. Holtz, *J. Am. Chem. Soc.* **89**, 692 (1967), and results presented at the Fifth International Conference on Fluorine Chemistry, Moscow, U.S.S.R., July 22, 1969; A. Streitwieser, Jr., A. P. Marchand and A. H. Pudjaatmaka, *J. Am. Chem. Soc.* **89**, 693 (1967).