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AB INITIO ELECTRON DENSITY ANALYSIS OF β-FLUOROETHYL ANION: THE NON-IMPORTANCE OF ANIONIC FLUORINE HYPERCONJUGATION†

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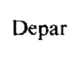
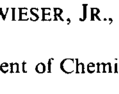
Abstract—Integration of the electron density functions derived from SCF LCAO-MO calculations of β-fluoroethyl anion provide integrated spatial electron populations (ISEP) around specific regions such as the fluorine atom. Comparison of two conformations of a planar carbanion in which the C-F bond is either alligned with the carbanion lone pair or perpendicular to it shows only a very small difference in fluorine population and demonstrates that the traditional fluorine anionic hyperconjugation mechanism is essentially insignificant. The important difference is that of polarization of electrons rather than charge transfer. Similar conclusions derive from other kinds of comparisons.

Anionic hyperconjugation, particularly as concerns C–F bonds remains a controversial subject. In resonance language it may be defined as a significant contribution of a "no-bond" resonance structure with comparable charge transfer to fluorine; an example is the hyperconjugation structure 1b for β-fluoroethyl anion, 1.



1a



1b

In MO language the effect can be defined in terms of significant mixing of a lone-pair orbital with the σ^* orbital of a C–F bond as in Fig. 1. Such mixing should provide a stabilization of the lone pair. Moreover, by reference to the orbital diagram in Fig. 2 we see that such interaction is equivalent to the no-bond resonance in **1**; that is, mixing in additional σ^* character into the lone pair orbital has the effect of increasing π- or double-bond character between the carbons and of decreasing the C–F bonding. Moreover, charge-transfer to fluorine also results.

C–F no-bond resonance or hyperconjugation was first invoked as a factor important in reactivity by Roberts *et al.* in 1950.[1] The suggestion found immediate and widespread acceptance and has since been invoked frequently to explain various physical and chemical phenomena. In assessing the importance of the effect the problem has always been to dissociate hyperconjugation from purely inductive, or more properly, field effects associated with the electronegative fluorine and its attendant bond dipole. In two reviews Holtz[2,3] has presented much of the evidence in favor of fluorine anionic hyperconjugation and has compared it with results expected from inductive effects; he concluded that anionic hyperconjugation was not a significant factor in chemistry.[4]

The type of experimental argument used to support the concept is typified by acidity measurements of fluorocarbon C–H bonds. In 1964, Andreades published his kinetic acidity measurements of various fluorocarbons containing a single hydrogen.[5] Hydrogen isotope exchange rates in methanolic sodium methoxide depended strikingly on the number of β-fluorines; he found the following relative rate sequence $CF_3H:R_FCF_2H:(CF_3)_2CFH:(CF_3)_3CH$ to be $1:6:2 \times 10^5:10^9$, and considered this dependence on the number of β-F atoms to be too high to be accountable solely as an inductive effect. Shortly thereafter, Tatlow and Stephens and their research group at the University of Birmingham synthesized a number of highly fluorinated bicyclic compounds of the type **2**, and found the bridgehead hydrogens to be readily metallated.[6] The importance of these compounds is that the enforced conformational effects at the bridgehead preclude important hyperconjugation but allow for normal inductive field effects; that is, hyperconjugation as in **3** should be less important than in acyclic systems such as those studied by Andreades.

These qualitative results were quantified by kinetic and equilibrium acidity studies at Berkeley.[7] The acidities were found to be comparable to $(CF_3)_3CH$ and to be fully explicable by normal electrostatic effects between the carbanion center and C–F bond dipoles. Similarly, a study of the kinetic acidities of a series of 9-substituted fluorenes gave a normal correlation with inductive parameters with no deviation of the CF_3 substituent that would require an additional reactivity to be associated with hyperconjugation.[8]

More recent experimental studies have only reinforced these results. Ibbitson *et al.* have studied the dipole moments of a series of substituted trifluoromethylbenzenes.[9] The magnitude of the differences between the observed moments and those calculated by vector analysis are satisfactorily

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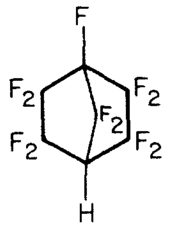
† This paper is dedicated to the memory of the late Prof. Robert B. Woodward. Although Prof. Woodward did not work directly in fluorocarbon chemistry, he pioneered the applications of physical organic principles to synthetic organic chemistry.



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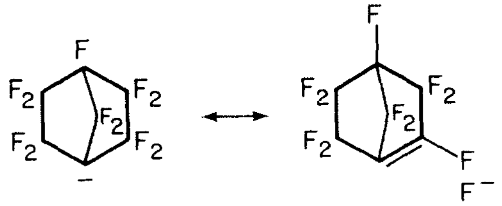

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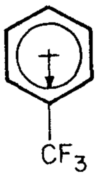


4

explained in terms of a π-electron inductive effect of the trifluoromethyl group **4**.

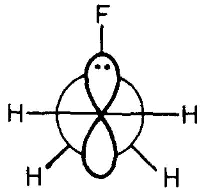
Chambers *et al.* have investigated the effects of substituted perfluoromethyl groups on the rates of nucleophilic aromatic substitution.[10] As the F atoms in the $-CF_3$ group are replaced by $-CF_3$ groups in the series, $-CF_3$, $-CF_2CF_3$, $-CF(CF_3)_2$, $C(CF_3)_3$, the extent of negative hyperconjugation should diminish and the rate constants decrease. This is demonstrably not the case, since all of the perfluoroalkylbenzenes in the series react at comparable rates with, in fact, perfluorotoluene being the least reactive. The results imply a normal inductive effect.

Theoretical considerations

Thus, the pattern of experimental results now makes the special effect of anionic fluorine hyperconjugation unnecessary. Nevertheless, theoretical results have been interpreted to require the concept. Calculated changes in C–H bond lengths adjacent to anions have been interpreted in terms of back-donation into σ^* orbitals.[11] Bingham has emphasized that the strength of C–F bonds and the large energy separation of σ and σ^* C–F orbitals may well result in small hyperconjugation effects in fluorine chemistry; however, since carbon-halogen bond strengths decrease in the order C–F > C–Cl > C–Br > C–I and σ–σ^* splitting decreases proportionately, he argues that anionic hyperconjugation should be increasingly important with the larger halogens.[12]

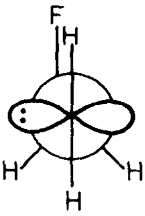
In short, the importance of anionic hyperconjugation remains controversial.[13] In part, of course, the controversy arises because of a lack of precise definition. Physical organic chemical concepts commonly deal with physical non-observables that, therefore, cannot be precisely defined. Such concepts are nevertheless useful because they frequently allow the correlation or prediction of qualitative effects of structure on reactivity. Organic compounds are so large and complex that it is essential to dissect a molecule into parts and to assess—qualitatively if not quantitatively—the contributions of different portions of the molecule to changes in reactivity behavior. Thus despite the fact that anionic fluorine hyperconjugation cannot be evaluated analytically and accurately independently of everything else that goes on in a structural change, it is, nonetheless, a significant concept that has definite implications and whose qualitative importance needs to be assessed. The problem comes in dissecting the effects of this "effect" from those of others, notably polarization. The problem arises even in theoretical calculations. In principle, it is possible to do a reasonably good quantum mechanical calculation within certain limits. Such a calculation would yield a wavefunction; the wavefunction for an MO-type calculation can generally be expressed analytically as a linear combination of basis functions. With a wavefunction we can calculate, more or less accurately, molecular properties such as the energy, dipole moment, etc, and such calculated properties can be compared, more or less satisfactorily, with experiment. But what do such calculations tell us that experiment doesn't? Inspection of page after page of computer output gives us no insight into the system unless we attempt an interpretation—again frequently with simplifying concepts that deal with physical non-observables and therefore with only qualitative significance. Such concepts clearly are useful but need to be made with care.

An example is the energy of two conformations of β-fluoroethyl anion with a planar carbanion **5a** (planar syn) and **5b** (planar perp) (X = F). In **5a** the lone pair and the C–F bond are lined up and hyperconjugation is conformationally possible; in **5b** the two units are perpendicular and hyperconjugation cannot occur. SCF-MO calculations on "standard" structures[14] with the 4-31G basis set[15] gives an energy difference of 10.8 kcal mol^{-1} (Table 1) and taken alone would suggest that hyperconjugation is a significant effect. This conclusion does not depend qualitatively on the specific structures assumed although, of course, it would be best to use energy-optimized structures. But if the effect is truly an important one it should be discernable for any reasonable structure. The use above of planar carbanions should exaggerate the effect although the true anion undoubtedly has a pyramidal structure. Some such structures based on tetrahedral carbons are **6a** (pyramidal perp), **6b**



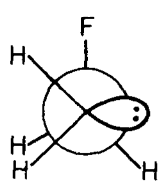
planar syn

5a



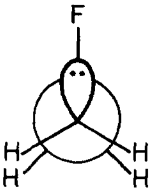
planar perp

5b



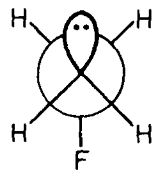
pyramidal perp

6a



pyramidal syn

6b



pyramidal anti

6c

(pyramidal syn) and **6c** (pyramidal anti). The energy difference between **6a** and **6c** is 6.8 kcal mol^{-1} (STO-3G) but this difference includes a significant torsional effect.

Pople *et al.*[16] have analyzed computed rotational barriers in terms of a Fourier series, eqn (1).

$$V = V_1 \cos\theta + V_2 \cos 2\theta + V_3 \cos 3\theta. \qquad (1)$$

The V_1 term is associated with Coulombic charge interactions and the V_3 term is a torsional term. The V_2 term was considered to derive from back-donation or hyperconjugation. The rotational barrier of pyramidal β-fluoroethyl anion has recently been calculated more thoroughly by Schleyer *et al.* who find the value of V_2 (4-31G) to be 7.5 kcal mol^{-1}.[17,18] This value is an order of magnitude higher than can be accounted for on a simple Coulombic interaction of the carbanionic negative charge with a C–F bond dipole.[19,20] However, the angular dependence of the effect is also consistent with a charge-induced polarization of the appropriate σ-bond. Such polarization is expected to have many of the same consequences as hyperconjugation such as, for example, structural changes.

Nevertheless, there is one clear distinction between polarization effects and hyperconjugation. Structure **1b** clearly implies *charge-transfer to fluorine*; that is, we expect the F in an appropriately oriented β-fluoroethyl anion to be more negatively charged than that of an orthogonal analogue. We now consider the problem of charges of atoms in molecules.

Atomic charges

The concept of the charge of an atom in a molecule has been an important one in chemistry. It has heuristic value and is useful in correlating diverse facts and phenomena. Yet, such atomic charges are not physical observables and, consequently, have no precise definition. The most widespread and generally used definition based on the LCAO-MO method is the Mulliken Population Analysis.[21] Each MO is a linear combination of basis functions centered on atoms and the Mulliken Population Analysis is actually a basis function population. Unfortunately, the Mulliken scheme has important weaknesses. These were recognized by Mulliken[22] and have been further elaborated by many authors.[23,40] The problem is illustrated in Fig. 3. A diffuse function centered on one atom is used to help describe the electron distribution near a second nucleus, but part of the electrons involved are assigned to the first center because the diffuse function is centered there. Consequently, the

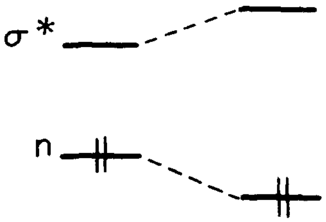


Fig. 1. Stabilization of a lone pair (n) orbital by interaction with a σ^* MO.

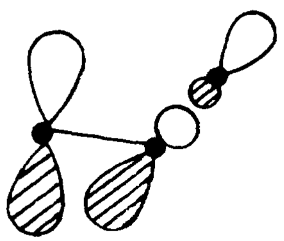


Fig. 2. Approximate orbital picture of the interaction of a lone pair p-orbital with a σ^* C–X orbital.

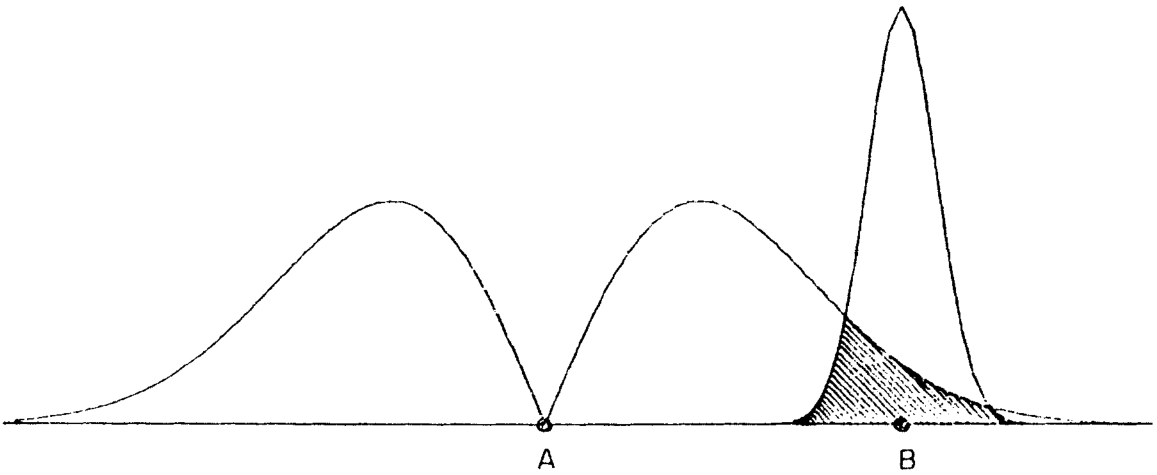


Fig. 3. Part of the electron population near atom B is assigned by the Mulliken Population method to A because a diffuse function required to describe the electron distribution at B is centered mathematically on A.

Mulliken Population is basis-set dependent. Several variations of the Mulliken scheme have been proposed but these also have similar weaknesses and are generally also basis set dependent.

An alternative is to make use of electron density functions for integrated spatial electron populations. The electron density, ρ_k, is defined for each MO, ϕ_k, by eqn (2). The total density, ρ, is a physical observable and is given for the MO method as the sum over occupied MOs, eqn 3 where $c_{i,j}$'s are coefficients of the n basis functions, $\chi_{i,j}$'s in MO ϕ_k in which N_k is the occupation number of MO ρ_k. Integration of the

$$\rho_k(x,y,z) = \phi_k^2\ (x,y,z) = \sum_{i=1}^{n}\sum_{j=1}^{n} c_i C_j \chi_i(x,y,z)\chi_j(x,y,z) \tag{2}$$

$$\rho(x,y,z) = \sum N_k \rho_k \tag{3}$$

electron density function over a region of interest gives the integrated electron population for that spatial region. The next problem is to choose boundaries for assignment of such integrated spatial electron populations (ISEP) to individual atoms. The choice of such boundaries is necessarily *ad hoc*.

Bader has made effective use of boundaries defined by limiting gradients of ρ around atoms;[41] these "virial boundaries" are uniquely defined and have some important mathematical properties. Unfortunately, these virial boundaries frequently do not correspond even closely to empirical "covalent radii" and the associated "atomic charges" differ from chemical expectations. However, when the virial boundary results from an electron density function that approaches zero in a region between atoms, the matter is far less ambiguous. This situation results, for example, when two atoms or ions are not covalently bound.[40,42] We will make use of this principle by focusing attention on difference populations rather than on individual structures.

Electron projection function

The electron density function is a four-dimensional function and as such is impossible to visualize without some restrictions. Most often, the function is displayed for a given plane of interest in a molecule either in contour or perspective plot format. Such plots work best when all or most of the atoms of a molecule lie on one plane but even for such systems this plane is often the nodal plane of π-electrons; that is, for non-linear systems one cannot compare σ and π electron density distributions with the same plane.

An alternative is to integrate the electron density function along one or more coordinates. In the planar density function of Brown and Shull,[43] the integration is along two coordinates; in effect, the electron density is projected on a line. The result provides a simple and useful display for diatomic molecules and others that are adequately represented by a straight line.[42,44,45]

For systems adequately represented by a plane we have found it convenient to modify the linear function of Brown and Shull by integrating along a single coordinate (y) perpendicular to a plane of choice (the xz plane) (eqn 4). In this "Electron Projection Function", P_{xz},[46] all of the planes of ρ perpendicular to the y-axis may be considered to be collapsed onto the xz plane.

$$P(x,z) = \int_{-\infty}^{\infty} \rho(x,y,z)dy. \tag{4}$$

In this manner σ and π electrons can be visualized in the same coordinate frame. Of course, information is lost in going from ρ to P but perception is heightened and pattern recognition becomes more feasible. The program PROJ accomplishes these integrations for a grid superimposed on the molecule[47] and the results are plotted in contour or perspective plot format; examples of both are shown below.

Hyperconjugation in β-fluoroethyl anion

The electron projection function was calculated for different conformations of β-fluoroethyl anion. The $F{-}C_\beta{-}C_\alpha$ atoms define the xz plane and identical

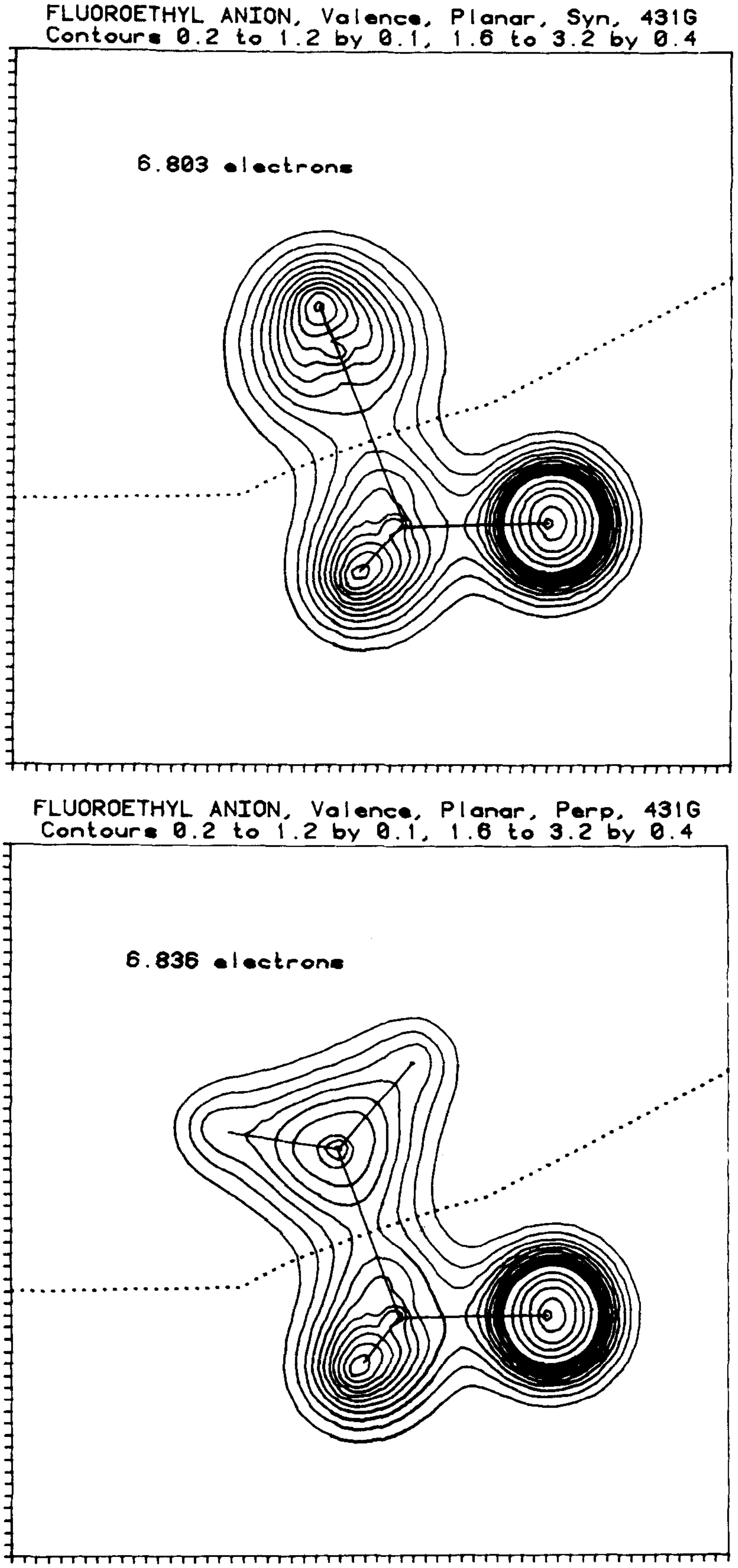


Fig. 4. Contour plots of the valence electrons of **5a** and **5b**. The dotted line is an integration boundary for the upper CH_2^- group and is identical in both figures. The $-CH_2F$ group is also identical in the two halves with the F located at the lower right.

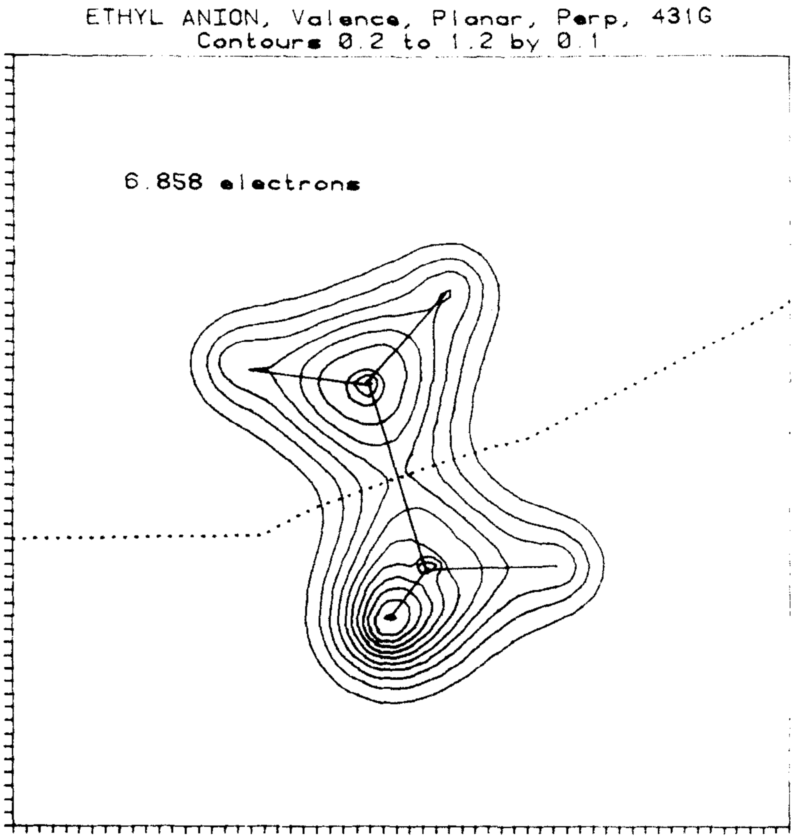


Fig. 5. Ethyl anion: Valence projection plot for planar perp conformation. The dotted line is the same integration boundary used in Fig. 4.

coordinates for these atoms were used in order to facilitate the interpretation of difference plots. For the planar carbanion the "planar syn" structure **5a** has the $C_\alpha H_2$ group perpendicular to the xz plane and the lone pair in the plane where it is best able to hyperconjugate with the C–F bond. Contour plots of the projection function, P_{xz}, for **5a** and **5b** are shown in Fig. 4. These plots pertain to valence electrons only; inclusion of core electrons makes the function more difficult to represent in this format. The dotted lines in the two parts of Fig. 4 are identical and correspond approximately to a "virial boundary".[41] Numerical integration of the upper parts, the $-CH_2^-$ portion, gives the number of valence electrons shown. The results show that the syn-CH_2^-, which is in position to hyperconjugate, has lost 0.033 electrons relative to the perp-isomer, and taken alone would suggest the operation of hyperconjugation. These results may be compared with the population of the $-CH_2^-$ group of Et anion with the same geometry and using the same integration boundary. The planar perp conformation shown in Fig. 5 has an integrated population of 6.858 electrons, 0.03–0.06 electrons more than either of the fluoroethyl conformations. As expected, the population of $-CH_2^-$ group is not sensitive to the Me orientation. A comparable treatment for the planar syn conformation gives a carbanion population of 6.862 electrons, actually slightly more than the perp conformation.

Far more revealing are the difference functions $\Delta P = P(\mathbf{5a}) - P(\mathbf{5b})$ as shown in Fig. 6. Both contour and perspective representations are shown in this plot together with the superposition of the two structures. The large feature corresponds to the rotated CH_2 group in which atoms have moved. Indeed, the pattern in this region shows that the relative populations of the $-CH_2^-$ group in the two conformations will be sensitive to the precise boundary chosen—the integration boundary of Fig. 4 cuts through significant positive and negative contours.

The crucial region is that near fluorine where nuclei remain the same in both structures. We see immediately that the fluorine region is clearly defined—it is an isolated feature surrounded by regions where the ΔP function approaches zero. As such, the fluorine region shows a "difference virial boundary" in the Bader sense and differs importantly in this sense from the $-CH_2^-$ region. This region shows a depression together with a mound characteristic of *polarization*, a shift of electrons from one side of the fluorine atom to the other. This feature is especially clear in the contour plot of Fig. 7 in which negative contours are indicated as dashed lines. Integration of the region around the F (dotted circle on Fig. 7) shows an excess ISEP of 0.0272e for the hyperconjugating F. The larger integration region shows an additional diffuse 0.013 electrons. These numbers may again be compared with those for Et

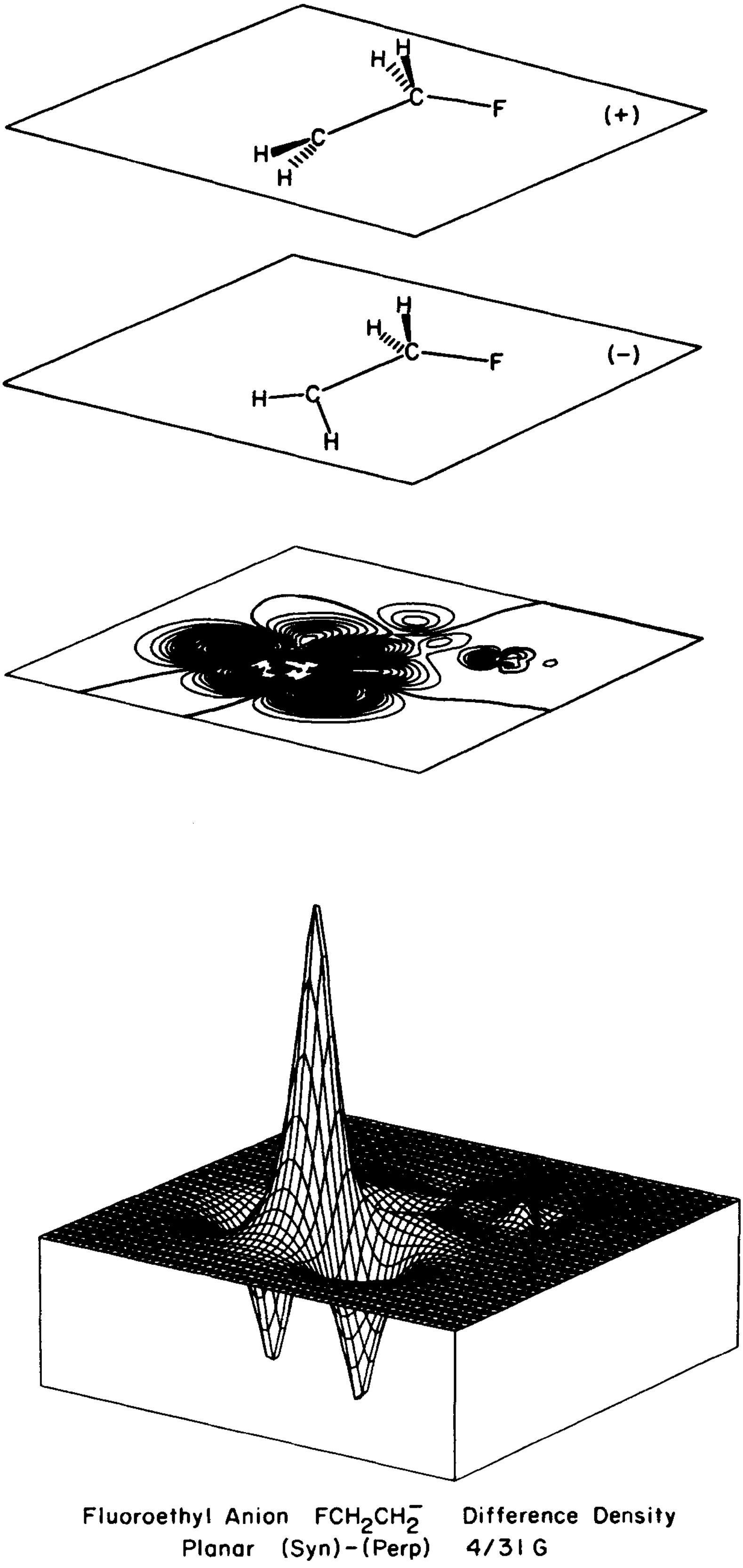


Fig. 6. Electron projection difference plots for two conformations of planar β-fluoroethyl anion, P(**5a**)–P(**5b**) (4-31G basis set).

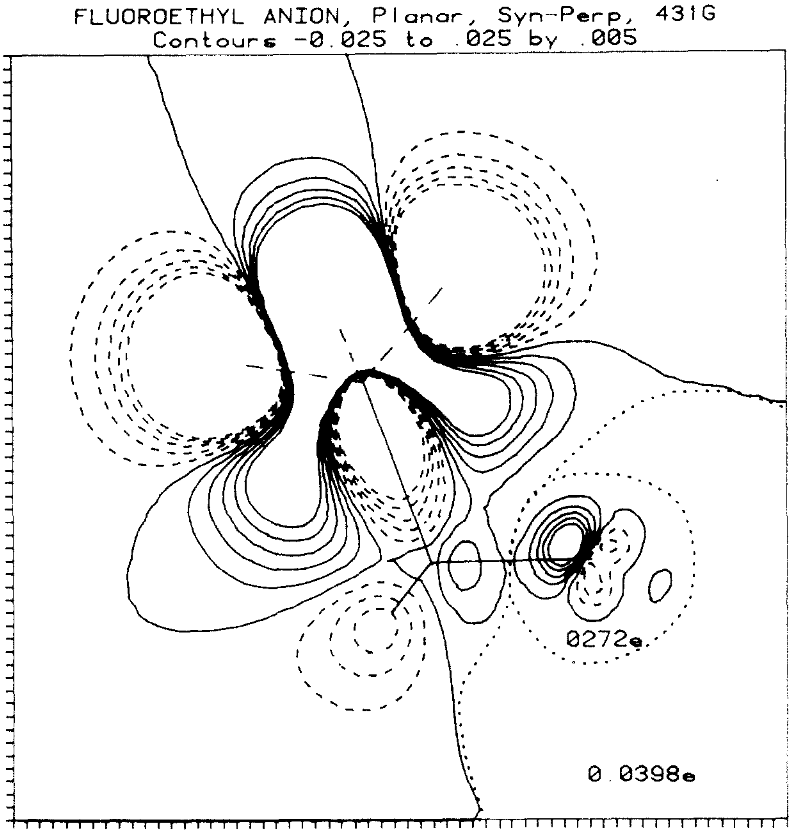


Fig. 7. Contour plot of ΔP, P(**5a**)–P(**5b**). ISEP differences are shown for two different integration regions indicated as dotted lines. The C–H bonds rotated in the two conformations are shown as straight dashed lines.

anion in a comparable treatment. Fig. 8 is arranged to compare with Fig. 6. We note the presence of a mound showing electron excess for a hyperconjugating hydrogen but no polarization. The corresponding contour plot is shown in Fig. 9. Integration boundaries comparable to those in Fig. 7 give comparable values for ISEP changes. That is, *according to the criterion of charge transfer a* C–H *bond is as effective in anionic hyperconjugation as* C–F!

Moreover, this conclusion would appear to be rather firmly established. Our integrations are reliable to about 0.001e. Our experience with a number of different systems show generally that changes in basis set would be expected to alter the specific numbers somewhat, but they are unlikely to produce such large changes as to alter the conclusion (for example, ref. 42).

The polarization phenomenon in Figs. 6a–d and 7 provides the real key to what is happening in these systems. Such polarization does not show up in typical Mulliken population calculations and is frequently ignored as a significant interaction mechanism in physical organic chemistry. Such polarization at atoms also remains unrevealed in all schemes involving complete integration of electron densities within spheres or similar definitions of net atomic charge. One of the important virtues of the ΔP plots in either contour or perspective format is that such polarization is qualitatively discernable as a characteristic pattern. Moreover, integration of the positive and negative parts is readily accomplished. In Fig. 6 we find that 0.005e have transferred from the back of the fluorine to the side towards the carbanion carbon. Moreover, we note, perhaps unexpectedly, that such polarization is in the direction that puts the additional electron population on the side *towards* the in-plane lone pair, as if the carbanion carbon nucleus is effectively less shielded by its lone pair electrons than by bonded electrons. In this connection we may note also that lone pair electrons generally have smaller optimum Slater exponents and are more diffuse than bonded electrons.

Finally, we emphasize that although the above results were calculated for planar anions with no structural optimization they are not expected to change significantly with reasonable structural modifications. An effect significant at one geometry is not expected to change dramatically with a small geometrical change; most effects behave in a continuous manner. Furthermore, hyperconjugation should be enhanced for a planar carbanion compared to a pyramidal one. Nevertheless, we shall show below that equivalent results obtain also for pyramidal systems.

Roles of inner and outer orbitals

The 4-31G basis set uses two orbitals to describe each traditional valence orbital, a linear combination of three gaussian functions with relatively high exponents for the inner (e.g. $p_z(i)$) part and a single more diffuse gaussian function for the outer (e.g. $p_z(o)$)

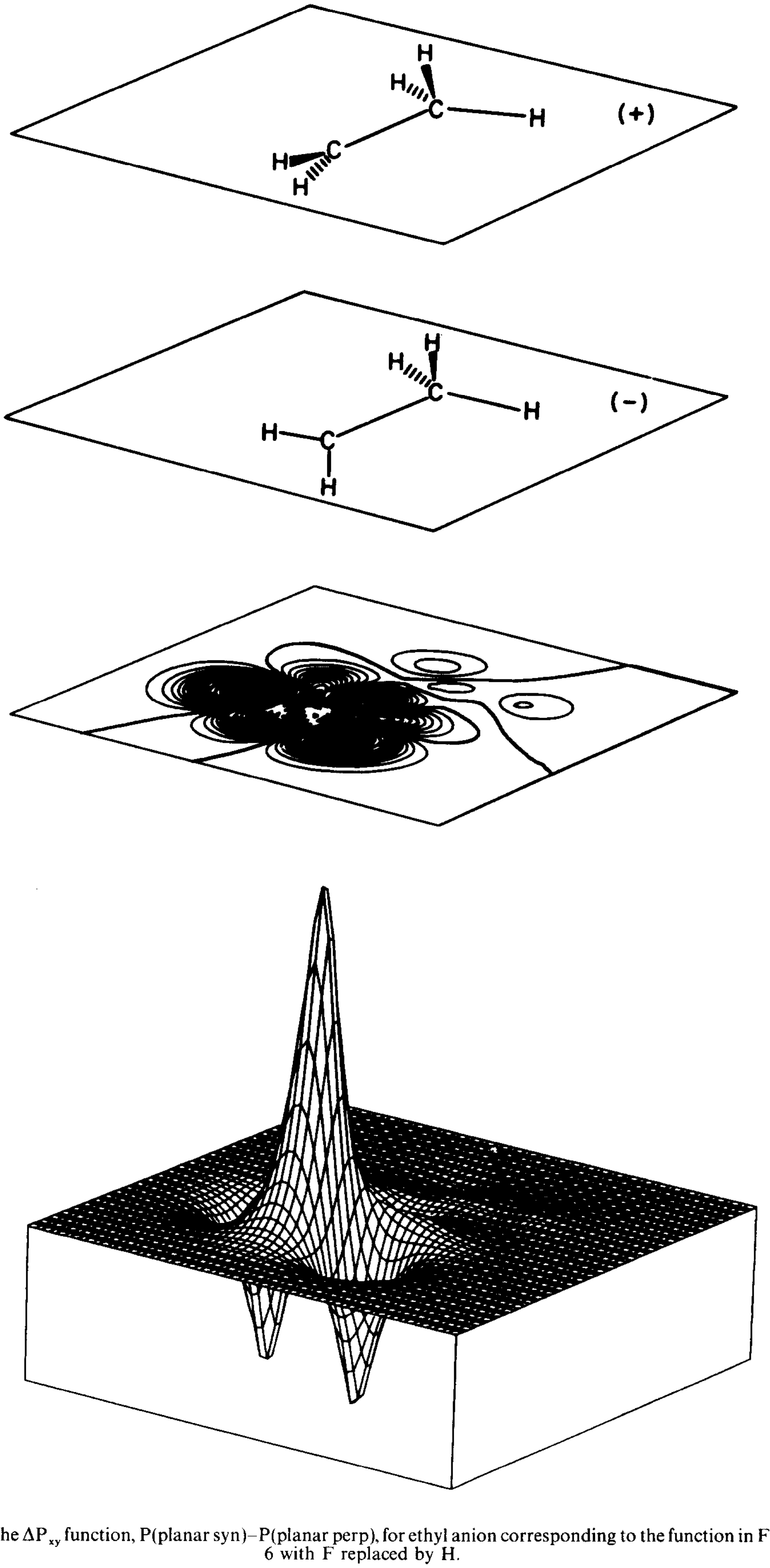


Fig. 8. The ΔP_{xy} function, P(planar syn)–P(planar perp), for ethyl anion corresponding to the function in Fig. 6 with F replaced by H.

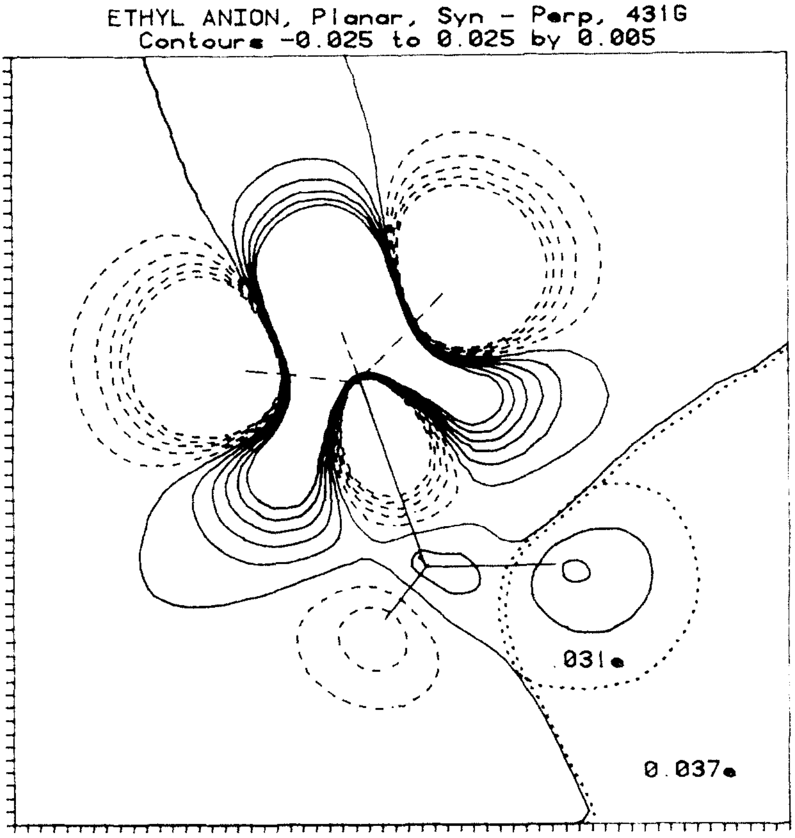


Fig. 9. Contour plot of ΔP for ethyl anion, P(syn)−P(perp) corresponding to Fig. 9. Difference ISEP values are shown for two integration regions bounded by dotted lines. The C–H bonds rotated in the two conformations are shown as straight dashed lines.

part. In individual MOs the inner and outer parts are separately optimized to give the lowest energy and, of course, it is that additional flexibility that makes the 4-31G basis set so much better than a minimum basis set such as STO-3G. The relative contributions of inner and outer parts of orbitals can be quite instructive but have generally been ignored as a source of heuristic information. For example, in bonding MOs the contribution of inner parts is generally more important than outer; that is, coefficients for a given valence orbital generally have the same sign but with |c(i)| > |c(o)|. On the other hand, in relatively low-lying antibonding or virtual orbitals, generally |c(o)| > |c(i)| but again with the same signs. This pattern is readily understood on the basis that outer orbitals are effectively less electronegative than inner; hence, in a bonding MO the more electronegative orbitals have larger coefficients but in antibonding MOs the reverse is true in order to maintain mutual orthogonality of orbitals. An example is shown for the HOMO of planar syn ethyl anion in Table 2. This MO in the 4-31G approximation is antibonding (positive energy, $\varepsilon = 0.0604$ au) and, accordingly, |c(o)| > |c(i)| for all atoms. This MO is primarily the carbanion lone pair and the ratio of inner and outer parts provides for the diffuseness of this lone pair. Note also that the signs of the orbitals are such that the Me hydrogens are antibonding with respect to the carbanion lone pair.

The corresponding HOMO of planar syn β-fluoroethyl anion shows some important contrasts (Table 3). Although for the carbanion lone pair, c(o) > c(i), the ratios are not nearly so great as for Et anion. More important for the fluorine p_z orbital we find a sign reversal that provides the mathematical mechanism for polarization. The net result is not nearly as obvious as what one would have expected from a simple interaction of lone pair and σ^* as implied in Figs. 1 and 2. In fact, *a simple HOMO–LUMO argument does not suffice in this case.* Even in a first approximation we must include the effects of the corresponding σ orbital. That is, we can consider the interaction of the lone pair first with σ; this is the effect most important in normal carbonium ion hyperconjugation where only the lowest orbital considered is occupied. Next we can allow interaction with σ^* as in Fig. 10. The resulting pattern is substantially more complex than that of Fig. 2 but even so, the effects of other orbitals cannot be neglected.

We note in this connection that in their study of methyl substituent effects in conjugated systems Libit and Hoffman[48] used a second order perturbation analysis; such an analysis does involve all of the molecular orbitals.

Deprotonation of ethane and fluoroethane

Finally, we examine the electronic changes that accompany deprotonation of ethane and fluoroethane. Ethane and ethyl anion are isoelectronic. In Fig. 11 we display the ΔP function for P(ethyl anion)−P(ethane) in contour format. The C–H bond

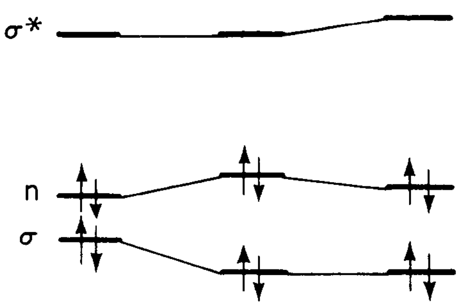


Fig. 10. Showing the approximate effects of allowing a lone pair orbital (n) the interact first with σ, then with the corresponding σ* MO.

being broken is shown as a dashed line. The bunched negative contours at the proton being lost at the upper left show the movement of electrons towards the carbon on ionization. This region within the zero contour integrates to 0.47 e. Removal of the proton is accompanied by successive increases and decreases in electron population as shown by alternating regions of positive and negative contours. The positive contours show regions that have greater electron population in the carbanion than in the hydrocarbon. Such a region is that of the trans periplanar Me hydrogen; this region is about 0.1 e richer in ethyl anion than in ethane. The *pattern* of Fig. 11 shows that this result stems more from alternations of polarization than from direct charge transfer.

Fig. 12 displays a comparable difference plot for ethyl fluoride and the fluoroethyl anion, **6c**, derived by removing a proton with no other structural change. Again, keeping identical geometries facilitates the interpretation of difference plots. Both systems are again isoelectronic so that the integral over the entire figure vanishes. The bunched contours at the acidic proton now integrate to 0.49 e, a difference of only 0.02 e from ethyl case. Indeed, the entire figure resembles the ethyl case closely except at fluorine where we again discern the familiar pattern of polarization. The direction of polarization is aimed at the C_α nucleus and again suggests that the lone pair electrons at the rear of C_α in the carbanion provide less shielding of the carbon nucleus than in the hydrocarbon. The total region around the fluorine has 0.08 electrons more in the carbanion than in ethyl fluoride, a number again similar to the ethyl case.

The comparison is made still more dramatic by a difference plot, ΔΔP, $(P(FCH_2CH_2^-)-P(FCH_2CH_3)-(P(CH_3CH_2^-)-P(CH_3CH_3))$, in Fig. 13. In effect this figure is Fig. 11 subtracted from Fig. 12. The shallow contours over most of the figure demonstrate graphically that deprotonation of ethane and fluoroethane cause almost identical electronic changes except for the characteristic polarization change at fluorine.

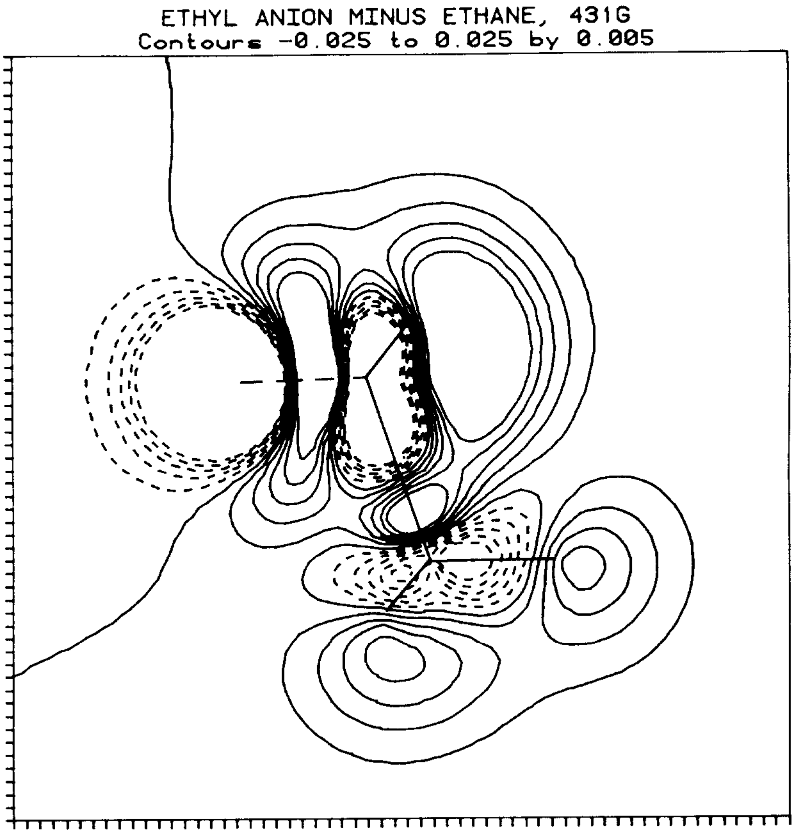


Fig. 11. The ΔP function for deprotonation of ethyl anion in a staggered conformation $(P(CH_3CH_2^-)-P(CH_3CH_3))$. The C–H bond being broken is shown as a straight dashed line. Dashed contours are negative.

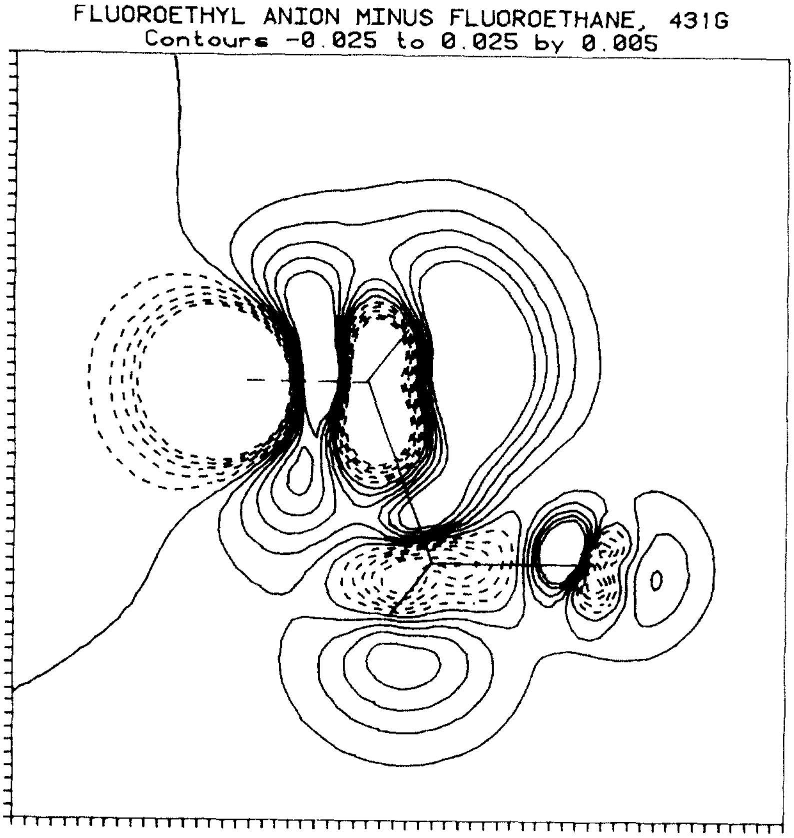


Fig. 12. ΔP function for deprotonation of fluoroethane with the same geometry as Fig. 12, the $P(FCH_2CH_2^-) - P(FCH_2CH_3)$. The fluorine is at the lower right.

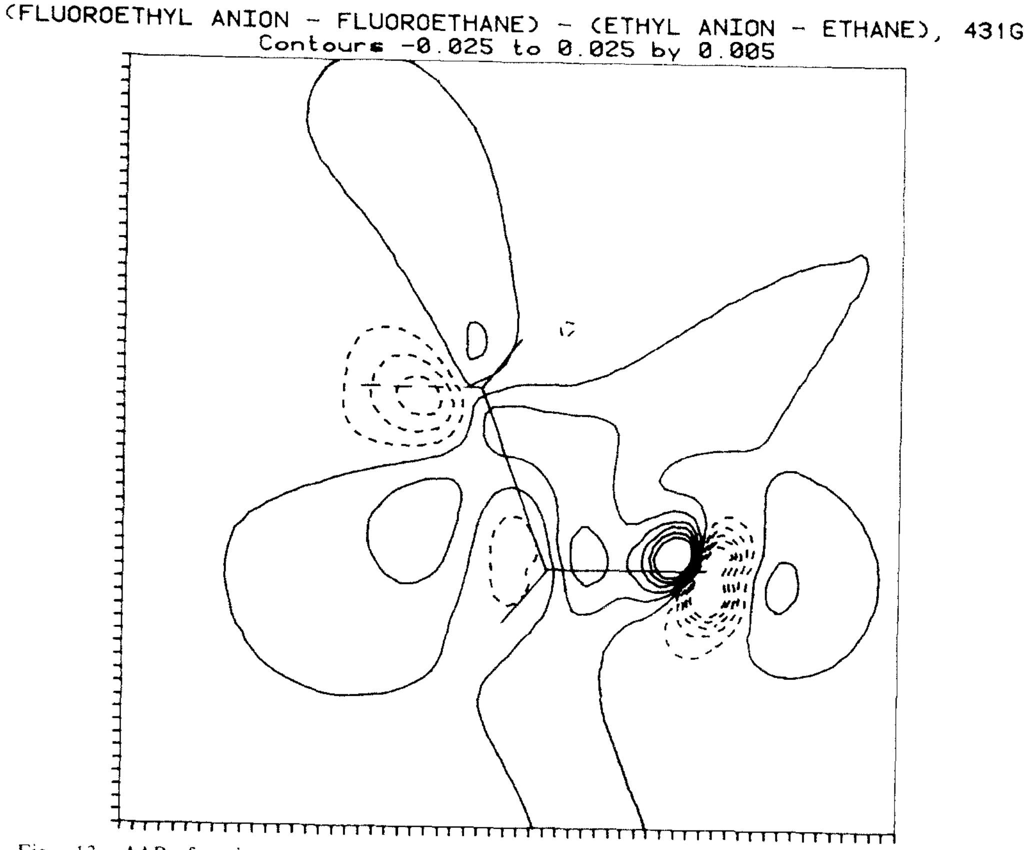


Fig. 13. ΔΔP function comparing deprotonation of fluoroethane with that of ethane, $[P(FCH_2CH_2^-) - P(FCH_2CH_3)] - [P(CH_3CH_2^-) - P(CH_3CH_3)]$.

The positive contours to the left of this fluorine integrate to 0.026 e; the negative contours to the right integrate to −0.018 e.

SUMMARY

We conclude that *charge transfer* from a carbanion lone pair to a fluorine atom in conjugating position plays no significant role; that is, the conventional concept of fluorine hyperconjugation is not significant in organic chemistry. Polarization is a much more significant phenomenon and needs to be given greater recognition as a physical organic effect. This effect does not show up in conventional Mulliken populations but is readily discernable by characteristic patterns in integrated electron density functions. Polarization may be responsible for many of the properties previously associated with hyperconjugation. However, we also emphasize that the present results apply specifically to fluorine. Anionic hyperconjugation to other halogens with weaker C–X bonds may still be significant. We are presently applying our approach to β-chloroethyl anion.

Calculations. MO calculations were run at the University of California Computer Center using the Gaussian 70 series of programs.[49] Perspective plots (Figs. 6 and 8) were done at the Computer Center using SDL graphics software.[50] The later contour plots at the Lawrence Berkeley Laboratory made use of the graphics program MOG written primarily by J. Sender. The integrations were accomplished on a Tektronix 4051 system, and most of the plotting was done on a Tektronix 4662 plotter.

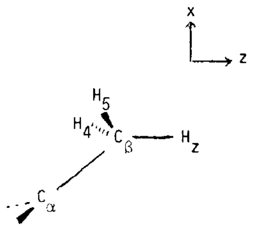
Table 1. *Ab initio* calculated energies

Compound[a]	STO-3G[b]	4/31 G[a,b]
CH_3CH_2F		
staggered	-175.752143 (0.0)	-177.841538 (0.0)
eclipsed	-175.747709 (2.8)	-177.835763 (3.6)
$^-CH_2CH_2F$		
planar syn	-174.859991 (16.0)	-177.123855 (6.7)
planar perp.	-174.846078 (24.7)	-177.106648 (17.5)
pyr. syn	-174.881251 (2.6)	-177.127077 (4.7)
pyr. perp.	-174.874610 (6.8)	-177.118855 (9.9)
pyr. anti	-174.885472 (0.0)	-177.134558 (0.0)
CH_3CH_3		
staggered	-78.305499 (0.0)	-79.114847 (0.0)
eclipsed	-78.300195 (3.3)	
$^-CH_2CH_3$		
planar syn	-77.385260 (19.1)	-78.362386 (8.4)
planar perp.	-77.385225 (19.1)	-78.362337 (8.4)
pyr. syn	-77.411177 (2.9)	
pyr. perp.	-77.413461 (1.4)	
pyr. anti	-77.415753 (0.0)	-78.375698 (0.0)

(a) Planar and pyramidal (pyr.) refer to the geometry of the CH_2^- group; syn, perpendicular (perp.), and anti refer to the angle between the carbonion lone pair and the C-F bond (0°, 90°, and 180°, resp.).

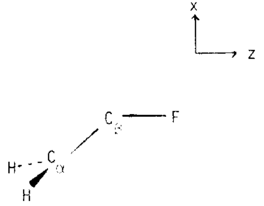
(b) Energies are in atomic units (1 a.u. = 627.49 Kcal/mole); entries in parentheses are relative energies in Kcal/mole^{-1}.

Table 2. HOMO coefficients for planar syn ethyl anion



Atom	Orbital	4-31G (i)	Coefficient (o)
H_2	1s	-0.12	-0.25
H_4,H_5	1s		.13
Cα	$2p_x$	.15	.21
	$2p_z$	.44	.62

Table 3. HOMO coefficients for planar syn β-fluoroethyl anion, **5a**



Atom	Orbital	4-31G (i)	Coefficient (o)
F	$2p_z$	0.12	-0.18
	2s		.16
C_β	$2p_z$		.16
C_α	$2p_x$	.15	.18
	$2p_z$	.44	.58

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