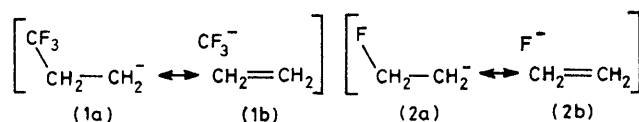# Negative Fluorine Hyperconjugation.   A Theoretical Re-examination

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Summary   Molecular orbital ab initio calculations show that the small changes in hydrocarbon acidities or in the rates of nucleophilic substitution reactions, which are found when a β-F is substituted by a β-CF_3 group, do not reflect absence of fluorine hyperconjugation, but result from the stronger inductive effect of the CF_3 group relative to F, which compensates for its poorer hyperconjugation.


Negative fluorine hyperconjugation (FHC) has been the subject of controversy for many years.[1]   An authoritative review has claimed that most of the effects attributed to FHC could be explained otherwise.[1a]   Hyperconjugation (HC) is maximized in charged species.   The effect of a β-fluorine on the stabilities of carbanions is therefore of special significance.   One of the central arguments of the opponents of the FHC hypothesis is that substitution of β-fluorine by a

β-CF_3 group fails to diminish the effect attributed to FHC, although 'no-bond resonance' involving the C–CF_3 bond, i.e. (1a)$\rightleftharpoons$(1b), is expected to be much less important than for a C–F bond, i.e. (2a)$\rightleftharpoons$(2b).[1a]

$$\left[\begin{matrix} CF_3 \\ \diagdown \\ CH_2\text{—}CH_2^- \end{matrix} \longleftrightarrow \begin{matrix} CF_3^- \\ \\ CH_2\text{=}CH_2 \end{matrix}\right] \left[\begin{matrix} F \\ \diagdown \\ CH_2\text{—}CH_2^- \end{matrix} \longleftrightarrow \begin{matrix} F^- \\ \\ CH_2\text{=}CH_2 \end{matrix}\right]$$

(1a)   (1b)   (2a)   (2b)

For example, ammonia reacts with $C_6F_5\cdot CF_3$, $C_6F_5\cdot CF_2CF_3$, $C_6F_5\cdot CF(CF_3)_2$ and $C_6F_5\cdot C(CF_3)_3$ at comparable rates, probably via (3), despite the successive replacement of F by CF_3.[2]   The comparable acidities of the bridgehead compounds (4) and (5) and the unconstrained (6) are also presented as strong evidence against FHC, because contributions

analogous to (2b) are extremely unlikely ('Bredt's rule') in (4) and (5).[1a,3] However, Tatlow and co-workers have re-measured recently the acidities of these fluorinated hydro-carbons and found that acidity decreases in the order (6) ~(5) > (4).[4] Tatlow's report[4] calls for a reinterpretation of the experimental data and reopens the old FHC controversy.

(3) X = F or CF$_3$ (4)

(5)   (6)
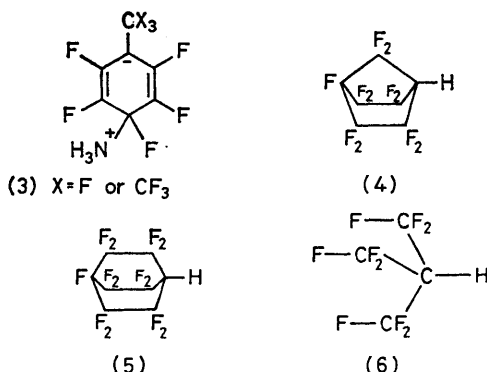
We present here MO calculations which strongly support the FHC hypothesis. We find that β-F and β-CF$_3$ substituents stabilize an adjacent carbanionic centre to a similar extent. Furthermore, hyperconjugation is an important stabilizing mechanism for both substituents. The smaller anionic hyperconjugative stabilization provided by the C–CF$_3$ bond (relative to C–F) is fully compensated by its higher inductive effect. The small changes which are often observed in comparisons of β-F and β-CF$_3$ substituents cannot be attributed therefore to the absence of FHC, as is often claimed in the literature.[1-3]

We have carried out molecular orbital ab initio calculations for FCH$_2$CH$_2^-$ and for CF$_3$CH$_2$CH$_2^-$,† with the STO-3G[5a] and the 4-31G[5b] basis sets.[6] Two extreme conformations (7a) [or (8a)] and (7b) [or (8b)] were calculated for each carbanion.

(7a) X = F   (7b) X = F

(8a) X = CF$_3$ (8b) X = CF$_3$
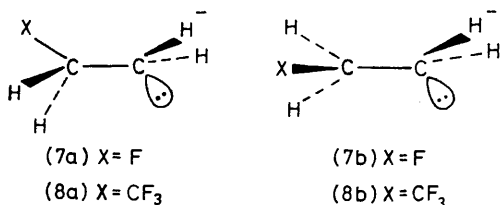
Hyperconjugation (HC) requires proper alignment of the interacting orbitals.[7] HC is maximized in (7a) and (8a), where the 2p(C$^-$) orbital and the orbitals of the C–X bond (i.e. σ_{C-X} and σ^*_{C-X}) are antiperiplanar, and minimized in

(7b) and (8b) where these orbitals are perpendicular and have zero overlap.[7] [The syn conformations of (7) and (8) (i.e. where the lone-pair CCX dihedral angle = 0°) are less stable than (7a) and (8a) by 13·4 and 11·4 kJ mol^{-1} (STO-3G) respectively.] The rotation barriers (7a)→(7b) and (8a)→(8b) measure therefore the hyperconjugation ability (relative to hydrogen) of the C–F and the C–CF$_3$ bonds respectively.[7,8] At 4-31G, the (7a)→(7b) barrier is 46·9 kJ mol^{-1}. Surprisingly, a relatively high barrier of 33·5 kJ mol^{-1} (4-31G) is found also for (8) [similar rotation barriers have been reported[8] for (7) and (8) with a planar carbanionic centre]. The assumption that these high rotation barriers are due to HC is supported by the Mulliken overlap populations.[9] Thus, the CC total overlaps (STO-3G) in (7a) and in (8a) (0·758 and 0·728) are higher than in (7b) and (8b) (0·723 and 0·708) respectively, pointing to increased CC double-bond character in (7a) and (8a) as suggested by the resonance structures (1b) and (2b). The C–X bonds on the other hand are weakened by HC [e.g. the C–CF$_3$ overlap is 0·638 in (8a), compared with 0·674 in (8b)]. Charge transfer from the 2p(C$^-$) orbital to the CF$_3$ group is also more extensive in (8a) (0·185 electrons) than in (8b) (0·147 electrons). Furthermore, partial geometry optimizations result in shorter CC but longer C–CF$_3$ (or C–F) bond lengths in (8a) [or (7a)] compared with (8b) [or (7b)]. In contrast with previous studies which assumed that resonance contributions such as (1b) are unimportant,[1-3] we find that the C–CF$_3$ bond exhibits strong HC.‡

Relative acidities or the stabilities of carbanionic intermediates are determined by the total electronic effect of the substituent. This effect, which is calculated in equation (1), includes inductive and hyperconjugative contributions.

$$CH_3CH_2^- + XCH_2CH_3 \rightarrow CH_3CH_3 + XCH_2CH_2^- \quad (7a) \text{ or} \quad (8a) \quad (1)$$
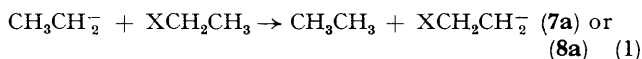
X = F, ΔE = 72·8 (STO-3G), 100·4 (4-31G) kJ mol^{-1}
X = CF$_3$, ΔE = 82·0 (STO-3G), 108·1 (4-31G) kJ mol^{-1}

The calculations§ show that β-fluorine and β-CF$_3$ substituents stabilize the adjacent carbanionic centre to a similar extent, and similar results are obtained if (7a) and (8a) are assumed to possess a planar carbanionic centre as in (3). The acidities of the β-hydrogens in CF$_3$CH$_2$CH$_3$ and in FCH$_2$CH$_3$ differ by only 7·7 kJ mol^{-1} (4-31G). The poorer HC ability of CF$_3$ (33·5 kJ mol^{-1}) relative to F (46·9 kJ mol^{-1}) is compensated by its stronger inductive effect (74·6 and 53·5 kJ mol^{-1} respectively at 4-31G). We believe that these conclusions will hold when higher levels of theory are used. It was shown recently that the relative energies of anions can be reproduced accurately even with the relatively simple levels of theory used here.[10] The similar rates of addition of NH$_3$ to C$_6$F$_5$·CF$_3$, C$_6$F$_5$·CF$_2$-CF$_3$, C$_6$F$_5$·CF(CF$_3$)$_2$, and C$_6$F$_5$·C(CF$_3$)$_3$ reflect the comparable stabilities of the corresponding intermediates (3).[2]

† Standard geometries were used except for C$^-$–H = 1·065 and C–C$^-$ = 1·487 Å taken from the optimized geometry of CH$_3$CH$_2^-$. The carbanionic centre was assumed to be tetrahedral. With X = CF$_3$ the FCCC dihedral angle = 180°.

‡ The use of Mulliken overlap populations was recently criticized by A. Streitwieser (for a summary see: C. Berke, Ph.D. Thesis, University of California, Berkeley, 1978). These authors have constructed difference density projection plots for (7a) and (7b) and concluded that HC does not play a significant role in the stabilization of anions by fluorine.

§ The calculated total energies are (in Hartrees): STO-3G: CH$_3$CH$_2^-$, −77·40871; (7a), −174·88311; (8a), −408·40389; 4-31G: CH$_3$CH$_2^-$, −78·36910; (7a), −177·13411; (8a), −413·60381. Standard geometries were used for the hydrocarbons. The total energies are: STO-3G: C$_2$H$_6$, −78·30549; C$_2$H$_5$F, −175·75212; C$_3$H$_5$F$_3$, −409·26941; 4-31G: C$_2$H$_6$, −79·11484; C$_2$H$_5$F, −177·84154; C$_3$H$_5$F$_3$, −414·30835.

The small effect observed[2] when a β-C–F bond is replaced by a β-C–CF$_3$ is in excellent agreement with the results of equation (1). The nearly identical dipole moment increments for CF$_3$ and for CF(CF$_3$)$_2$ in *para*-substituted dimethyl-anilines[1a] can be rationalized similarly. The measured acidities of (4), (5), and (6)[3,4] are also consistent with our computational results.¶ The acidities of (6) and (5) are comparable because the corresponding anions [(6)$^-$ and (5)$^-$] are stabilized to a similar degree. In (6)$^-$ the 2p(C$^-$) orbital is antiperiplanar to three C–F bonds compared with three C–CF$_2$ bonds in (5)$^-$ [equation (1)]. In (4)$^-$ only two C–CF$_2$ bonds are aligned antiperiplanar to the 2p(C$^-$) orbital so that (4) is the less acidic.[4] Finally, we emphasize that the calculations which rationalize these data point to strong

negative hyperconjugation for both β-C–F and β-C–CF$_3$ bonds. [Even if HC is not important as claimed‡ our calculations show that the same effects which are responsible for the barrier in (7) determine the barrier height also in (8) in contrast with previous assumptions.][1–3]

The magnitude of FHC depends on the cosine of the angle (θ) between the lone-pair and the C–F bond.[8a] A study of the acidity of suitably constrained fluorohydrocarbons where θ is varied systematically (in a manner analogous to that used in establishing that HC determines the magnitude of the β-deuterium isotope effect in carbenium ion reactions)[11] may therefore resolve the FHC controversy.

¶ CF$_3$CH$_2$CH$_3$ and FCH$_2$CH$_3$ are of course only crude models for (4)—(6). We neglect several effects such as solvation, different number of fluorines, different degrees of pyramidalization at the carbanionic centre, *etc.* (refs. 1a, 3) so that only an approximate agreement with experiment can be expected. Note also that our calculations apply to the isolated molecule in the gas phase and extrapolations to solution must be treated with caution.

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[6] After the submission of this paper we became aware of a related 4-31G study of (7) and (8) by J. G. Stamper and R. Taylor, *J. Chem. Res. (S)*, 1980, 128. The calculations reported in this paper are in good agreement with our results; small differences are due to the choice of different geometries. Stamper and Taylor also interpret their results as supporting F and CF$_3$ negative HC.

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