Tetrahedron Vol. 41, No. 3, pp. 499 to 506, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00

ANIONIC HYPERCONJUGATION

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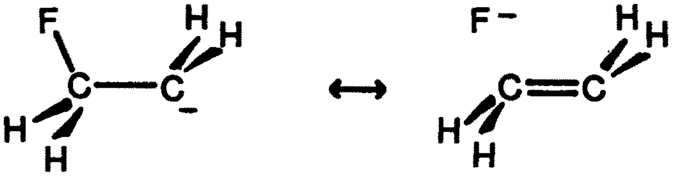
(*Received in USA* 16 *August* 1984)

ABSTRACT:

Although hyperconjugation involving alkyl groups to a carbocation is a well-established concept, the analogous charge delocalization generated in anions by electronegative substitution has long been a subject of controversy. We have investigated this phenomenon for the β-hydroxyethyl and β-trifluoroethyl anions using ab initio electronic structure calculations. Split valence basis sets augmented by diffuse functions were used with fully optimized geometries. Three dimensional molecular orbital plots clearly show an in-plane HOMO-LUMO mixing of a C-X σ antibonding orbital with the carbon lone pair which yields hyperconjugative π bonding in the anti conformation. Deformation density maps further demonstrate that this delocalization leads to the development of a π component as well as a previously unrecognized sigma enhancement. These results support and extend the work of Apeloig and that of Schleyer and Kos, but are in opposition to the induction hypothesis of Streitwieser and Holtz. The recent experimental determination of the acidity of $(CF_3)_3CH$ by Tatlow et al. and their interpretation in terms of fluorine hyperconjugation are also in accord with this work.

INTRODUCTION

Anionic hyperconjugation was originally proposed by J. D. Roberts in 1950 as an explanation for trifluoromethyl substituent effects.[1] Since then, the concept has been used to explain stabilization of carbanions as well as patterns of aromatic substitution. The original valence bond picture as described by Roberts involves a "no-bond resonance" structure. In the archetypical case, β-fluoroethyl anion, such a structure is written as:



Alternative explanations of carbanion stabilization by β-fluorine have relied on inductive and field effects. In 1963, Clark et al. distinguished between the electron-withdrawing σ inductive effect of fluorine and the effects of the repulsion between filled p orbitals on fluorine and the α carbon.[2] The latter effect results in the destabilization of carbanions α to fluorine. In his 1971 reviews[3,4] Holtz employs this balance of σ and π inductive efforts to explain reactivity in fluorinated aliphatic systems, while using a π-induction model to account for the influence of fluoroalkyl substituents on aromatic rings. The latter scheme suggests that the dipolar fluoroalkyl substituent polarizes the π aromatic electrons via a through space interaction. The limitations of this proposal have also been discussed.[3] The stability of the carbanions $C_6H_5XC(CF_3)_2^-$ have been determined by Klabunde and Burton.[5] Trends in acidities in the meta series were attributed to polarization effects similar to Holtz's π-induction scheme. Polarizability was considered to be less important for the para series where "+R donation", i.e. the destabilizing back donation of p-orbital density to the anionic center, was the overwhelming effect. As evidence suggested that the carbanion center was pyramidal, hyperconjugation (which is most effective when the anionic center is planar) was not regarded as a significant factor. The authors cite the slight differences between the acidity of the fluoro and trifluoromethyl substituted compounds in further support of the insignificance of hyperconjugation in these systems.

In a later study, Klabunde and Burton compared the acidities of the aliphatic systems HCF_3, $HCHXCX_2CF_3$, and $HCX(CF_3)_2$.[6] Again, the dominant effects were considered to be polarization and +R destabilization. It seems clear, however, that no conclusions about fluorine hyperconjugation, as opposed to induction, can be drawn from this work since all species having β-F substitutents also had either $-CF_3$ or -F groups α to the anion center.

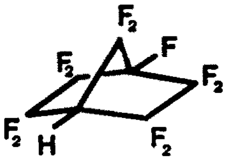
A more powerful method of testing the importance of the two effects was discussed by Holtz[3] and has received much attention over the past decade. Bridgehead hydrogen acidities on 1H-perfluorobicyclo[2.2.1]heptane and 1H-perfluorobicyclo[2.2.2] octane cannot be influenced by fluorine restrictions on the bridgehead carbon violate Bredt's rule. In contrast, $(CF_3)_3CH$ is subject to both inductive and hyperconjugative effects.

Equilibrium and kinetic acidities of fluorinated bicycloalkanes were measured by Streitwieser et al. and used to estimate pK values of related halogenated acids including that of $(CF_3)_3CH$.[7] Classical field effects were estimated by the Kirkwood-Westheimer model. The predicted acidities appeared to be in adequate agreement with those experimentally determined for the bicyclic systems and the estimated value for $(CH_3)_3CH$. Based upon these results Streitwieser asserted that hyperconjugation does not noticeably stabilize $(CF_3)_3C^-$. His estimated pK of $(CF_3)_3CH$ was obtained assuming that the corresponding carbanion is localized, though if hyperconjugation were occurring this would not be the case.

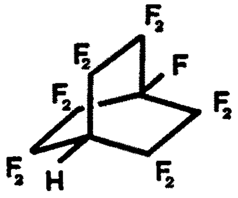
These conclusions have recently been examined by Sleigh, Stevens and Tatlow.[8] The variety of values obtained for the acidity of $(CF_3)_3CH$ led them to perform a direct competition experiment on I, II, and III.

$(CF_3)_3CH$

I



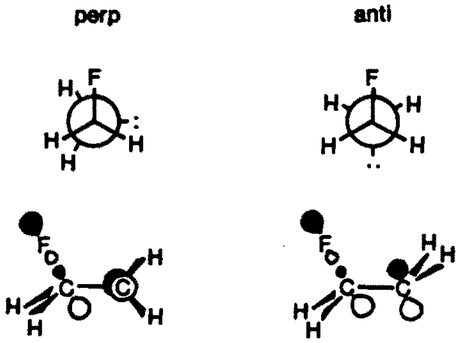
II



III

The acidity of tristrifluoromethyl methane was found to be "exceptional", thus the authors conclude that fluorine hyperconjugation must be considered as a possible explanation for their findings.

It is only in the last five years that ab initio molecular orbital studies have been done for systems relevant to the problem of anionic hyperconjugation. Apeloig[9] has compared energies for the syn, antiperiplanar, and perpendicular conformations of β-F and β-CF_3 ethyl anion. Geometries with the C-F or C-CF_3 σ* and the C lone pair orbitals coplanar allow hyperconjugation, while symmetry forbids it if the orbitals are perpendicular, as shown below:



At the 4-31G basis set level, large stabilization energies are found for both F& CF_3 substituents in the anti geometry; while syn conformers were slightly less stable than the corresponding anti. Using partially optimized geometries Apeloig has shown that C-F and C–CF_3 bonds lengthen while C–C bonds shorten in the anti configuration. He found that the stabilization produced by β-fluorine's stronger hyperconjugation approximately equaled the greater inductive stabilization with the CF_3 substituent. Apeloig has used this result to explain the small changes found in the literature for the replacement of β-fluorine by β-trifluoromethyl.

Streitwieser et al.[10] used integrated spatial electron populations and electron projection function plots to compare fluoroethyl anion configurations as well as those for the control system of ethyl anion. Their contour plots, from calculations using the STO-2G and 4-31G basis sets, were interpreted as showing only a polarization effect on the β-fluorine, with negligible charge transfer. Geometries for each conformer were not optimized, however, and the rigid rotor approximation was used throughout.

Schleyer and Kos, on the other hand, state that anionic hyperconjugation has significant energetic and geometrical consequences.[11] Using the augmented split valence basis sets 3-21G+ and 4-31G+, along with fully optimized geometries, these authors have investigated the structures of an extensive set of molecules for which hyperconjugation is expected to be important. Comparison of geometrical features clearly demonstrates the importance of this effect. Calculated energies and rotational potentials also confirm the stabilizing nature of anionic hyperconjugation. However, it is not surprising that the Mulliken population analysis charges which they tabulate do not consistently show the expected increase in charge on the carbanion substituents. To avoid this well-known problem and to gain a deeper insight into the bonding in hyperconjugated anions, molecular orbital and charge density difference plots are employed in the present work.

METHODS

Fully optimized 3-21G+ geometries for antiperiplanar and perpendicular conformations of β-trifluoroethyl and $4\text{-}31G^+$ geometries for β-hydroxyethyl anions were taken directly from the work of Schleyer et al. The augmented basis sets insure an adequate description of diffuse anionic centers.[12]

Three dimensional molecular orbitals at a contour level of $0.10e^-/au^3$ were obtained using the Jorgensen MO plotting program.[13] Deformation density (total charge density minus the sum of spherical atoms) contour maps were generated at the $3\text{-}21G^+$ level. Visual comparison of the anti and perpendicular forms, rather than a computed difference between them, were employed because of differences in the optimized geometries of the structures.

RESULTS AND DISCUSSION

Bonding of both the classic fluorine hyperconjugation and the more general anionic hyperconjugation have been treated. The structure of the anti conformer of the β-hydroxyethyl anion (Table I) is strongly indicative of hyperconjugation. The C-C bond is shortened considerably relative to that in the perpendicular conformer and the CO distance lengthened. The anti conformation is stabilized by more than 13 kcal mol^{-1} relative to the perpendicular structure. In contrast, the CC bond distance in the β-trifluoroethyl anion is not altered upon rotation from the anti to the perpendicular conformation nor is the anti structure significantly more stable than the perpendicular. Lengthening of the CF bond is, however, observed. Though the differences between the two conformers of β-trifluoroethyl anion are expected to be less pronounced than those for the β-hydroxy case, the almost complete lack of change in the former system is surprising. An analysis of the bonding in these systems reveals the origin of this finding and the explanation further strengthens the case for anionic hyperconjugation.

The deformation densities of the anti and perpendicular conformer of β-hydroxyl anion in the plane containing the lone pair and carbon-carbon bond are compared in Figure 1. Note the localized lone pair region in the perpendicular structure. By contrast in the other conformer, the charge density increases in the vicinity of the lone pair extends across the CC bond toward the opposite

TABLE I STRUCTURES OF β-HYDROXYETHYL AND β-TRIFLUOROETHYL ANIONS.

Molecule	r(CC)	r(CX)
perp-CH_2CH_2OH	1.525	1.473
anti-CH_2CH_2OH	1.448	1.572
perp-CH_2CF_3	1.389	1.399
anti-CH_2CF_3	1.389	1.499

Figure 1. Charge density difference contour maps of the C-C lone pair plane of antiperiplanar (a) and perpendicular (b) conformers of β-hydroxyethyl anion. Solid lines indicate density increase while dashed lines indicate contours of density loss. Note the delocalization of the anion lone pair into the CC bonding region in (a).

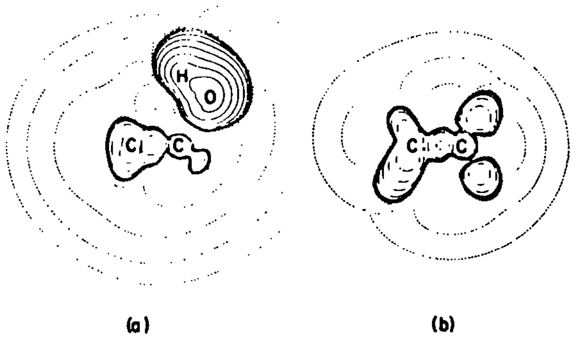
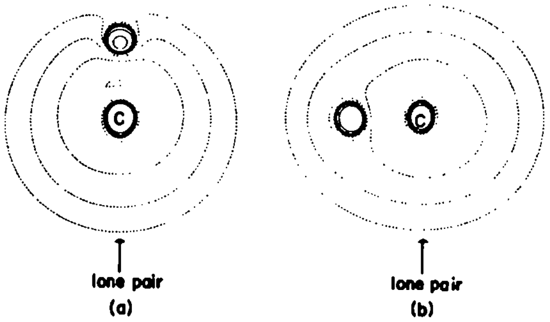


Figure 2. Charge density difference contour maps of a plane perpendicular to the CC bond at its midpoint for (a) the antiperiplanar and (b) perpendicular conformers of β-hydroxyethyl anion. Increase in electron density is seen both in the direction of the lone pair and in that perpendicular to it in (a) indicating both π and σ enhancement.



carbon. This delocalization can also be seen in Figure 2 which compares the charge density differences in a cross section of the CC bond taken at its midpoint. Hyperconjugation is a π effect, as the MO plot in Figure 3 illustrates. It is also interesting to note a CC σ bond density increase in the plane normal to the lone pair relative to the perpendicular structure (Figure 4). Sigma bonding is enhanced by the significantly shorter CC distance (by .1 Å) in the antiperiplanar (hyperconjugating) anion. Figure 5, on the other hand, shows no difference in the σ region of the β-trifl oroethyl anion; however in this system the CC bond length does not decrease. It is clear that hyperconjugated systems in which bond shortening occurs can be further stabilized by sigma enhancement.

Unlike the Mulliken population analysis, the deformation density maps reveal the expected increase in charge about the OH substituent. Comparison of this region in Figure 1a and Figure 4b shows both the enhancement of electron density above the oxygen and a larger region of charge loss between the oxygen and carbon.

The orbital interaction leading to hyperconjugation in the β-trifluoroethyl anion is clearly illustrated in Figure 6, the HOMO of the anti conformer of β-trifluoroethyl anion. The CH_2^- lone pair orbital mixes with the CF σ^* orbital in a stablizing fashion, delocalizing electron density over both carbon centers and weakening the CF interaction. Rotating the CF_3 group by 90° severely decreases the efficiency of this overlap though it cannot be completely negated. Figure 7, the HOMO of the perpendicular conformer, shows the absence of lone pair interaction with the CF σ^*. Note, however, that the lone pair is not completely localized in this conformation due to stabilization by the π^* orbital of the CF_3 fragment. This competing mechanism for lone pair delocalization onto the adjacent carbon atom in these systems rationalizes the otherwise puzzling lack of difference in the CC bond distance between conformers. Bond shortening is occurring in both conformers. Figure 8 compares the π plane, i.e., the plane containing the CC bond and the lone pair. Delocalization in the anti conformer (Fig. 8a) does not appear grossly different from that in the perpendicular structure (Fig. 8b), as might be expected when both the σ^* and π^* interaction are operative. Perpendicular slices through the C-C bond (Figure 9) further demonstrate the enhancement in both conformers.

Hyperconjugation can, however, be differentiated from the π^* CF_3 effects in the region of the CF bond. Comparing Figure 5a with Figure 8b shows an enhanced lone pair region around the fluorine in the former structure similar to that observed for the β-hydroxyethyl anion. A decrease in density between the carbon and fluorine is apparent in both planes, but is somewhat more pronounced in the anti conformer. Density around the tops of the lone pair is, in fact, removed by the hyperconjugating fluorine.

SUMMARY

1. Hyperconjugation, not induction, is shown to be the dominant mode of stabilization in anionic systems in which an electronegative β-substituent is trans to the lone pair. Our calculations support Roberts' original proposition and the explanation given by Tatlow and coworkers for their experimental results. The results of the present work are in accord with those of Apeloig, and Schleyer and Kos and do not support the conclusions by Streitwieser and Holtz.

2. The π nature of the effect is revealed in molecular orbital plots of the HOMO which clearly show the incipient CC double bond. Enhancement of the sigma bond is also present in hyperconjugated systems; this is a previously unrecognized consequence of hyperconjugation. Both the β-hydroxyethyl and β-trifluoroethyl anions are hyperconjugated in the anti conformation. Charge density difference contour maps illustrate the delocalization of the lone pair and the increase in charge on the substituent. The corresponding maps for the perpendicular conformers do not show comparable effects.

3. The difference between the conformation in which hyperconjugation is possible and that for which it is not are more pronounced in the β-hydroxyethyl anion than in the trifluroethyl due to a competing stabilization mechanism in the latter. Analysis of the electronic structure of these anions has demonstrated the importance of hyperconjugative stabilization in organic systems.

Figure 3. The HOMO of $(OH)CH_2CH_2^-$. Note the delocalization of the p orbital on the anion center of the antiperiplanar conformation.

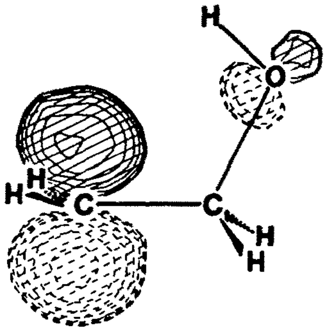
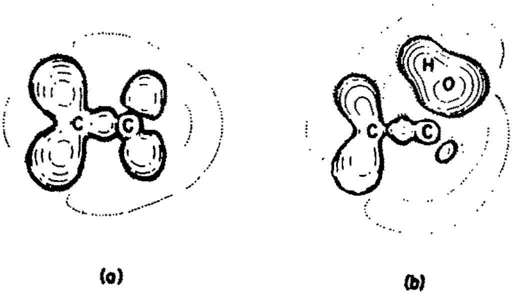
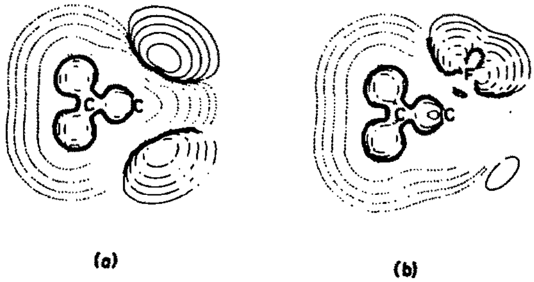


Figure 4. Charge density difference contour maps of the plane perpendicular to the CC lone pair plane in (a) the antiperiplanar and (b) perpendicular conformers of β-hydroxyethyl anion. The enhancement of the σ bonding region in (a) relative to (b) is clear.



(a) (b)

Figure 5. Charge density difference contour maps of the plane perpendicular to the CC lone pair plane in (a) the antiperiplanar and (b) perpendicular conformers of β-trifluoroethyl anion. In contrast to Figure 4, neither structure is enhanced in the σ bonding region relative to the other.



(a) (b)

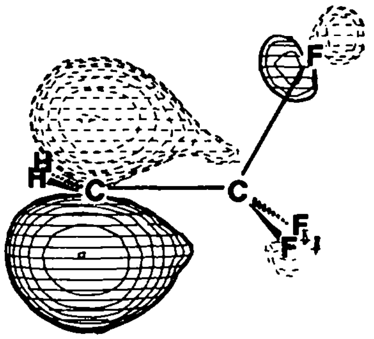


Figure 6. (right) The HOMO of antiperiplanar $CF_3CH_2^-$. Note the interaction between the σ* and lone pair fragments.

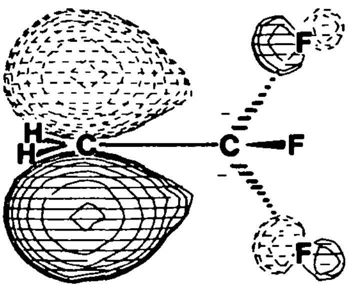


Figure 7. (left) The HOMO of perpendicular $CF_3CH_2^-$. Note the lone pair is not stabilized by σ* on CF it is by π* on the CF_2.

Figure 8. Charge density difference contour maps of the CC-lone pair in β-trifluoroethyl anion. Delocalization of the lone pair region occurs in both the (a) antiperiplanar and (b) perpendicular conformers.

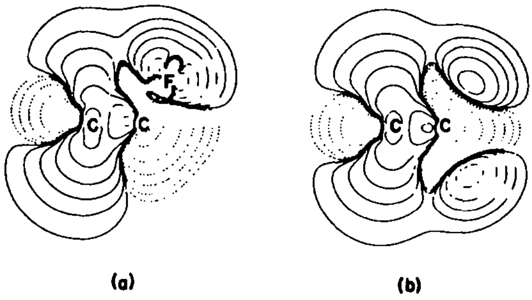
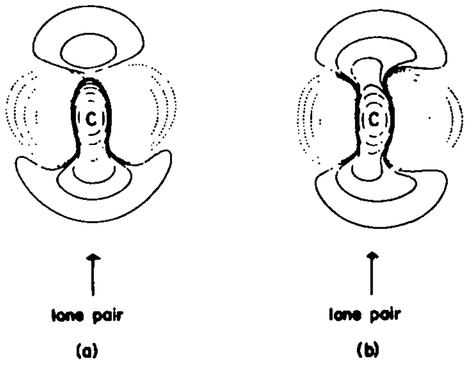


Figure 9. Charge density difference contour maps in the plane perpendicular to the CC bond in (a) the antiperiplanar and (b) perpendicular conformers of β-trifluoroethyl anion.



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