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THE IMPORTANCE OF NEGATIVE (ANIONIC) HYPERCONJUGATION

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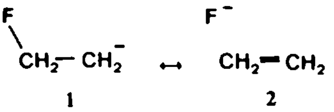
Abstract—The consequences of negative (anionic) hyperconjugation (interactions of orbitals of π-symmetry of saturated groups with filled p orbitals) upon geometries, energies, and charge distributions are calculated for anions and related neutral systems using the *ab initio* split valence basis sets, 3-21+G and 4-31+G, which are augmented by a set of diffuse s and p functions on the non-hydrogen atoms. The β-fluorethyl anion, which has often been used for analysis, is not a minimum on the potential energy surface. Essentially complete transfer of negative charge to fluorine leads to rupture of the C–F bond and formation of a hydrogen bonded F^- ethylene complex, **10**, during geometry optimisation. The effects of fluorine negative hyperconjugation, assessed by using the trifluorethyl anion, are in accord with the implications of the "no-bond" formalism for negative hyperconjugation; the C–C bond is shortened by 0.10 Å and the C–F bond antiparallel to the carbanion lone pair is elongated by 0.13 Å compared to trifluoroethane. Similarly large geometrical differences are found when β-amino-and β-hydroxyethyl anion are compared with ethylamine and ethanol. The total anion stabilisation energies are quite large. The inductive contributors, evaluated using conformations in which the carbanion lone pair cannot interact hyperconjugationally with the C–X bond, are 11.3, 10.3 and 5.3 kcal mol^{-1} for F, OH and NH_2 in β-ethyl anions. The hyperconjugative contributions to the total effect are of similar magnitude. The potential rotational energy surfaces of fluoromethyl amine and aminomethanol also demonstrate the importance of negative hyperconjugation in neutral systems (anomeric effect). Unsaturated olefinic systems, e.g. the 2-fluorovinyl and 2,2-difluorovinyl anions, also show the expected C–F bond lengthening and C=C bond shortening. The planar inversion barrier of the 2,2-difluorovinyl anion (11.9 kcal mol^{-1}; 3-21+G//3-21+G) is lowered from that of the vinyl anion due to hyperconjugative stabilisation of the transition state. Fluorine negative hyperconjugation is also illustrated in the stabilisation of the rotational transition states of species like $F_2BCH_2^-$ and $F_2AlCH_2^-$. Negative (anionic) hyperconjugation and the anomeric effect are the same phenomena from a qualitative molecular orbital viewpoint. Both are well established, important, and uncontroversial.

We wish to end once and for all the "controversy" concerning negative (anionic) hyperconjugation. This important effect has energetic and geometrical consequences of general significance. In particular, we wish to rebut a recent paper[1] dealing with the β-fluoroethyl anion system **1**.



$F{-}CH_2{-}CH_2^- \longleftrightarrow F^-\ CH_2{=}CH_2$

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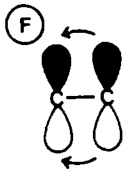

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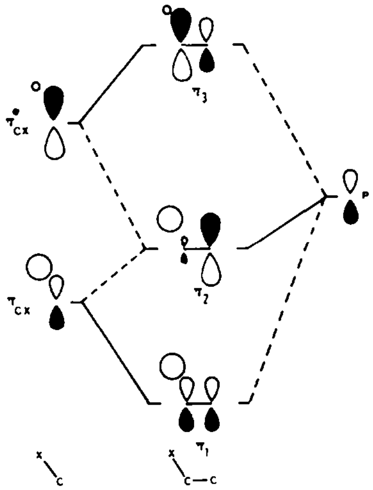
DEFINITION OF HYPERCONJUGATION

Hyperconjugation was introduced by Mulliken to describe the "conjugation" of CH_3 with other groups containing double or triple bonds.[2] Hyperconjugation involves the interaction of orbitals[3] of π symmetry (antisymmetric with regard to a defining plane) present *both* in unsaturated and in *saturated* groups. CH_3, CH_2 and CF_3, although considered to be σ systems, possess orbitals of π symmetry[3,4] which can interact with p-orbitals on adjacent atoms.[5]

The Scheme[6] illustrates the interaction of a p-orbital (right side) with C–X bonding (designated π_{CX})[4,5] and antibonding orbitals (π_{CX}*). Three new orbitals (π_1, π_2 *and* π_3, center) result. If the original p orbital is vacant (as in a carbocation), only π_1 will be occupied and stabilisation will normally result.

The concept of negative hyperconjugation, discussed in terms of "no bond resonance", was first introduced by Roberts in 1950 to help explain the electrical effects of the trifluoromethyl group.[7,8] Representations like **2** were used at that time. The equivalent MO formulation (Scheme) involves interaction of the filled anion lone pair orbital (p) with the filled π_{CX} and the vacant π_{CX}* orbital. Thus, both π_1 and π_2 are now occupied, and the net effect, stabilising or destabilising, depends primarily on the degree to which the π_{CX}* orbital is involved.



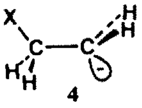
Scheme 1.

When X is an electronegative element or group (like F), this involvement is large and considerable stabilisation can be expected.[6] When X is H, the π_{CH}*-p interaction is weak and the destabilising four electron π_{CH}–p interaction may dominate. Thus, the ethyl anion is less stable than the methyl anion,[9] but when more electronegative atoms are involved, methyl groups can stabilise anions hyperconjugatively.[10]

Both **2** and the MO representation (summarized by **3**) imply a torsional angle (θ) dependence with the carbanion orbital. Hyperconjugation of the C–F bond should be at a maximum when $\theta = 0°$ (180°) and fall to zero when $\theta = 90°$. Hyperconjugation of the CH bonds, e.g. of a CH_2F group, are minor by comparison.

Inductive effects, also expected to be large due to the exceptional electronegativity of fluorine, should not show significant rotational variation.

Much of the controversy has resulted from difficulties in differentiating quantitatively between inductive and hyperconjugative contributions.[8] As suggested by Hoffmann *et al.*[11] this can be calculated by comparing the energies of β-substituted ethyl anions in different assumed conformations with standard bond lengths and angles. Thus, in **4** both hyperconjugative and inductive effects involving X can operate, but in **5**, due to the 90° dihedral angle between the carbanion long pair orbital and the C–X bond, only the inductive effects of X are present.



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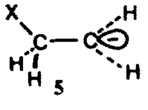

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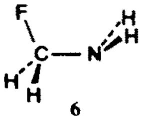
Thus, the energy differences between **4** and **5** measure the hyperconjugative contribution for each substituent, X. All subsequent calculations,[1,12,13] have confirmed the original conclusion:[11] the energy differences between **4** and **5** are large, being on the order of 8–15 kcal/mol for electronegative substituents like F, OH and NH_2. The total stabilization by the substituent can be evaluated by eqn (1). With the substituent in the most favorable conformation **4** (allowing C–X hyperconjugation), larger values (e.g. 10–20 kcal/mol) result. The energies corresponding to conformation **5** provide an assessment of the inductive effect. For F and OH, the inductive contribution is calculated to be of comparable magnitude to the additional effect attributed to hyperconjugation[11]

$$CH_3CH_2^- + XCH_2CH_3 \rightarrow C_2H_6 + XCH_2CH_2^- \quad (1)$$

$$CH_3NH_2 + FCH_3 \rightarrow CH_4 + FCH_2NH_2. \quad (2)$$

Negative hyperconjugation is important in neutral systems as well;[6] e.g. the anomeric effect has been studied intensively.[14–16] Results with FCH_2NH_2 are both representative and particularly pertinent; this amine is isoelectronic with $FCH_2CH_2^-$ and should serve as a particularly good model. Initial *ab initio* studies by Pople *et al.* on standard geometries[15] have been extended,[14b,5] but only by the optimisation of bond lengths (standard bond angles were assumed). While the total interaction between NH_2 and F groups, given by eqn (2), was 6 kcal mol^{-1} (4-31G), the conformation **6** permitting hyperconjugation (corresponding to **4**) was 8.5 kcal/mol more stable than **7** (corresponding to **5**).



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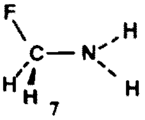

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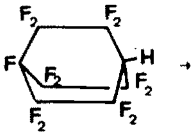
All bond length differences in **6** and **7**[16] are those expected on the basis of hyperconjugation: **6** has a longer C–F bond and a shorter C–N distance; the C–H bond is longer in **7**. Similar geometrical and energetic effects are found in numerous theoretical investigations of systems with two (or more) electronegative groups attached to the same carbon.[14–16]

Recent theoretical papers[17,18] have provided convincing explanations for facts which have long provided the major arguments against anionic hyperconjugation:[1,8] perfluorinated cage molecules like **8** are quite acidic despite the unfavorable torsional angels of the fluorines adjacent to the bridgehead.



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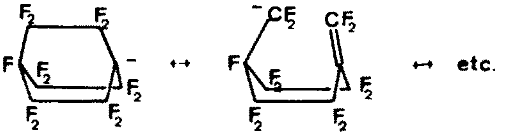

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Likewise, replacement of β-F by β-CF_3 groups does not result in decreased acidity.[1,8] Taylor[17] and Apeloig[18] have now calculated that hyperconjugation involving β-CF_3 groups, i.e. X = CF_3 in **4**, is nearly as large as that involving β-F; the inductive contribution of β-CF_3 is greater than β-F. Thus, hyperconjugation shown in **9** contributes significantly to the enhanced acidity of such systems.

Have all doubts concerning anion hyperconjugation been stilled? Unfortunately not. Streitwieser, Berke, Schriver, Grier and Collins (SBSGC)[1] have re-examined the β-fluoroethyl anion system **1** theoretically. Although large energy differences were found between conformations like **4**-F and **5**-F, this was *not* ascribed to hyperconjugation (which implies to them a partial transfer of electrons to fluorine) but rather to *polarisation* (which implies only a redistribution of electrons). SBSGC concluded, "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".

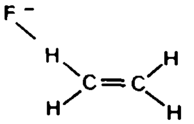
We could hardly disagree more. The *definition* of hyperconjugation[3] involves orbital interactions, not charge transfer. Both charge transfer as well as polarisation are possible consequences of hyperconjugation, which will have geometrical and energetic manifestations as well. Libit and Hoffmann have stressed that the relatively weak hyperconjugative interaction between the methyl group and the π double bond orbitals in propene results mainly in *polarisation* rather than in *charge transfer.*[19] Streitwieser's group attempts to differentiate between these two mechanisms,[1] but both are to be associated with hyperconjugation.

We also disagree with SBSGC's claim that charge transfer is not important in the β-fluoroethyl anion **1**. In fact, charge transfer to fluorine in **1** is *essentially complete* provided the system is released from artificial geometrical constraints! All of the calculations on anions discussed above[1,12] have been carried out on standard or assumed geometrical models. That is, bond lengths and bond angles were fixed; only the torsional angles were varied, e.g. in **4** and **5**. In the case of X = F this is completely artificial: *no minimum corresponding to a β-fluoroethyl anion exists on the potential energy surface.* Instead, as pointed out by Back *et al.*[13] 4-31G geometry optimization of **4** does not give a minimum, but leads to steady C–F bond elongation without evidence of a barrier! In the extreme, complete dissociation into F^- and ethylene (eqn 3) would occur. Using the lowest $FCH_2CH_2^-$ 4-31G energy reported by SBSGC, dissociation is indicated to be *exothermic* by 22.3 kcal/mol, eqn (3)!

$$FCH_2CH_2^- \rightarrow H_2C{=}CH_2 + F^- \quad \Delta E = -22.3\ \text{kcal/mol.} \quad (4\text{-}31G) \qquad (3)$$

The manifestations of hyperconjugation include not only energy stabilisation and charge transfer, but also bond elongation. Thus, the C–X bond in **4** should be longer than that in **5**. By artificially restricting these bonds to have the same length, SBSGC prejudiced the results of their integrated spacial electron population analysis. We question the validity of such analyses when they are carried out on arbitrary points on potential energy surfaces. When "polarisation" is conformationally dependent, it may also be a characteristic of hyperconjugation, as it may then result from orbital interactions.[19]

The β-fluoroethyl anion is fundamentally unsuitable as a model system for a more sophististicated investigation of anionic hyperconjugation. As will be discussed below, the hydrogen bonded complex **10** is the only $C_2H_4F^-$ potential minimum we have found. Instead, β-substituted ethyl anion systems are needed which do not "fall apart" upon optimization. A particularly pertinent example, $CF_3CH_2^-$ **11** has been reported by Pross *et al.*[20] Comparison of the 4-31G geometries of **11** with the neutral counterparts **12** reveals the marked lengthening in the anion of the β–CF bond (1.487 Å) which is ideally oriented for hyperconjugation (i.e. in the anion lone pair plane). The other two fluorine atoms in **11** have a 60° dihedral angle to the carbanion lone pair; these C–F bonds (1.396 Å) are lengthened only slightly relative to the neutral model (**12**, C–F 1.361 Å). The prediction of hyperconjugation theory, that the C–C bond will be shortened, is also verified: C–C = 1.391 Å in **11** but 1.485 Å in **12**. There is a wealth of geometrical information in the same paper, e.g. C–H bonds anti planar to the lone pair are lengthened, which is fully in accord with hyperconjugation theory.[20]



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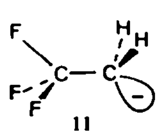

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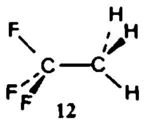

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One major worry remains, however. The levels of *ab initio* theory which have been used in all earlier investigations of anionic hyperconjugation may be inadequate in describing energetic and geometric relationships of negatively charged species. Thus, we have shown recently[9,21] that the minimal STO-3G basis set gives errors in the 110–230 kcal/mol^{-1} range when calculated proton affinities (PA) are compared with experimental values. Similarly, the PA errors at the 4-31G basis set level are around 30 kcal mol^{-1}; no improvement is achieved by inclusion of polarization functions (d orbitals) in the basis set or by correcting for electron correlation effects. Instead, diffuse orbital-augmented basis sets are needed to reproduce experimental proton affinities adequately. Hence, we have now employed the 4–31 + G[9] and 3–21 + G[21] basis sets to reexamine the question of anionic hyperconjugation. Since no potential energy minimum corresponding to the β-fluoroethyl anion exists at this level, we have examined β-substituted ethyl anion systems which do not "fall apart" on geometry optimization. The electronegative substituents, X = OH and NH_2 in **4** and **5**, serve well for this purpose. We have also studied **11** and **12** at 3–21 + G; the overall features of the earlier 4–31G examination[20] are confirmed. For completeness, FCH_2NH_2 and $HOCH_2NH_2$ were reexamined, the geometries of **6** and **7** were fully optimized (3-21G) and the rotational barriers determined.

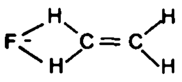
METHODS AND RESULTS

The Gaussian 76 series of programs was employed. Geometry optimizations were carried out using Davidon–Fletcher-Powell multiparameters searches[22] and analytically evaluated gradients[23] using the 3-21G basis set[24] for the neutral species and, for the anions, the 3-21 + G[21] and 4-31 + G[9] basis sets. These are the 3-21G[24] and 4-31G[25] bases which are augmented by a set of diffuse functions on all heavy (nonhydrogen) atoms.

Results are designated, e.g. 3-21 + G//3-21 + G (the "//" means "at the geometry of"). Electron correlation corrections were examined at the second order Møller-Plesset (MP2) level.[26] Absolute energies (in hartrees) and relative energies (in kcal/mol) of anions, neutral molecules, and reference species are given in Table 1. Optimized geometries and atomic charges (bold figures), following Mulliken's method,[27] are given in Fig. 1.

RESULTS AND DISCUSSION

β-Fluoroethyl anion. As discussed above, no potential minimum corresponding to a β-fluoroethyl anion was found on the 3-21 + G potential energy surface. When **4** (X = F) was used as the starting geometry and C_s symmetry imposed, geometry optimization led automatically to the planar, C_{2v} complex **13**.



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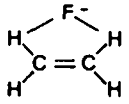

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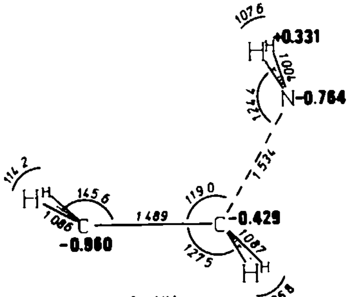
No barrier was encountered. An alternative geometry in which F^- is complexed by two vicinal hydrogens **14** was calculated by imposing C_{2v} symmetry. However, neither **13** nor **14** are minima on the potential energy surface. This distinction belongs to **10** which can be regarded as a hydrogen bonded complex between ethylene and F^-. The indicated association energy (see eqn (4)) is remarkably large. Calculated association energies of F^- with acetylene eqn (5) and with methane eqn (6) provide a comparison (all at 3-21 + G//3-21 + G).

$$C_2H_4 + F^- \rightarrow C_2H_4F^-(C_s, \mathbf{10}) \quad \Delta E = -9.1\ \text{kcal mol}^{-1} \qquad (4)$$

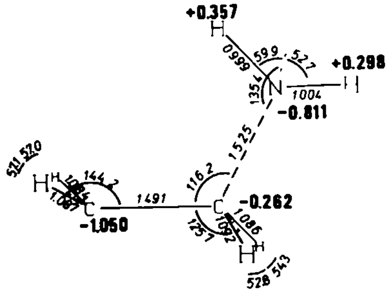
$$HC{\equiv}CH + F^- \rightarrow HC{\equiv}CHF^-(C_{\infty v}) \quad \Delta E = -20.1\ \text{kcal mol}^{-1} \qquad (5)$$

$$CH_4 + F^- \rightarrow CH_4F^-(C_{3v}) \quad \Delta E = -4.7\ \text{kcal mol}^{-1} \qquad (6)$$

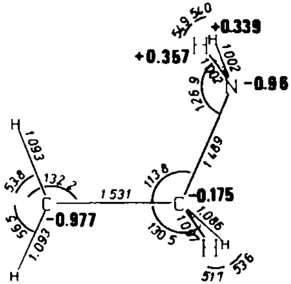
By imposing a 90° dihedral angle between the F–C bond and the carbanion lone pair (i.e. the plane bisecting the HCH^- angle) a structure corresponding to **5**–F can be obtained after geometry optimization. Even though this is considerably higher in energy than **10** or even **4**–F



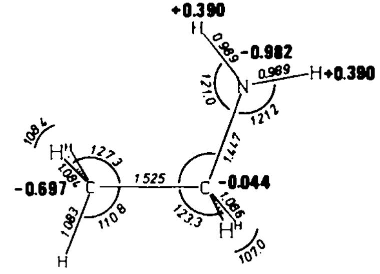
6a–NH$_2$

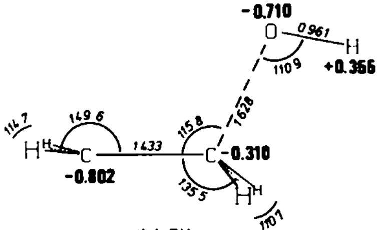


4b–NH$_2$

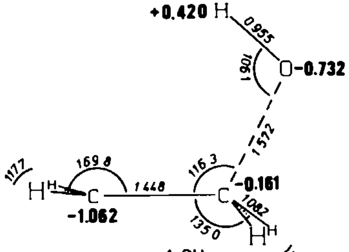


5–NH$_2$

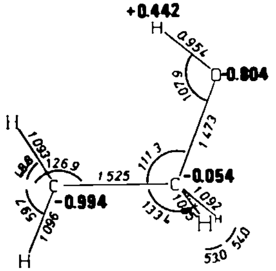




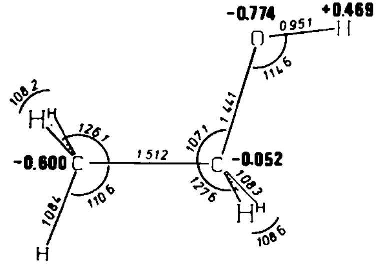
anti-4–OH

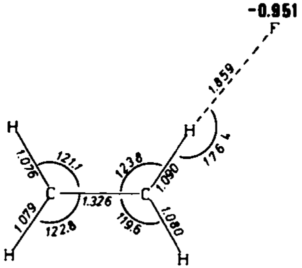


syn-4–OH



5–OH





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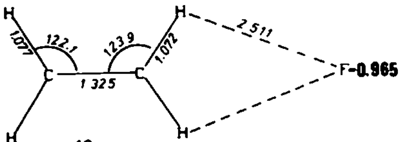

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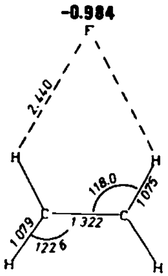

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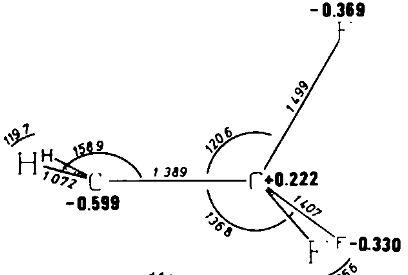

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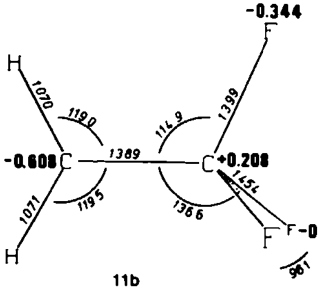

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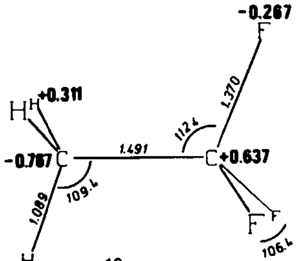

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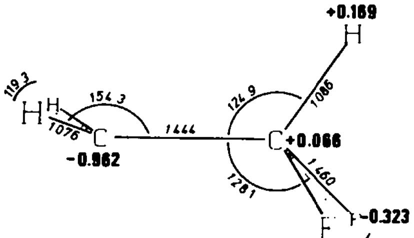

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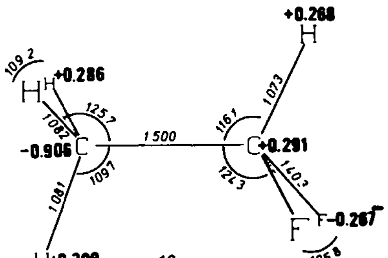

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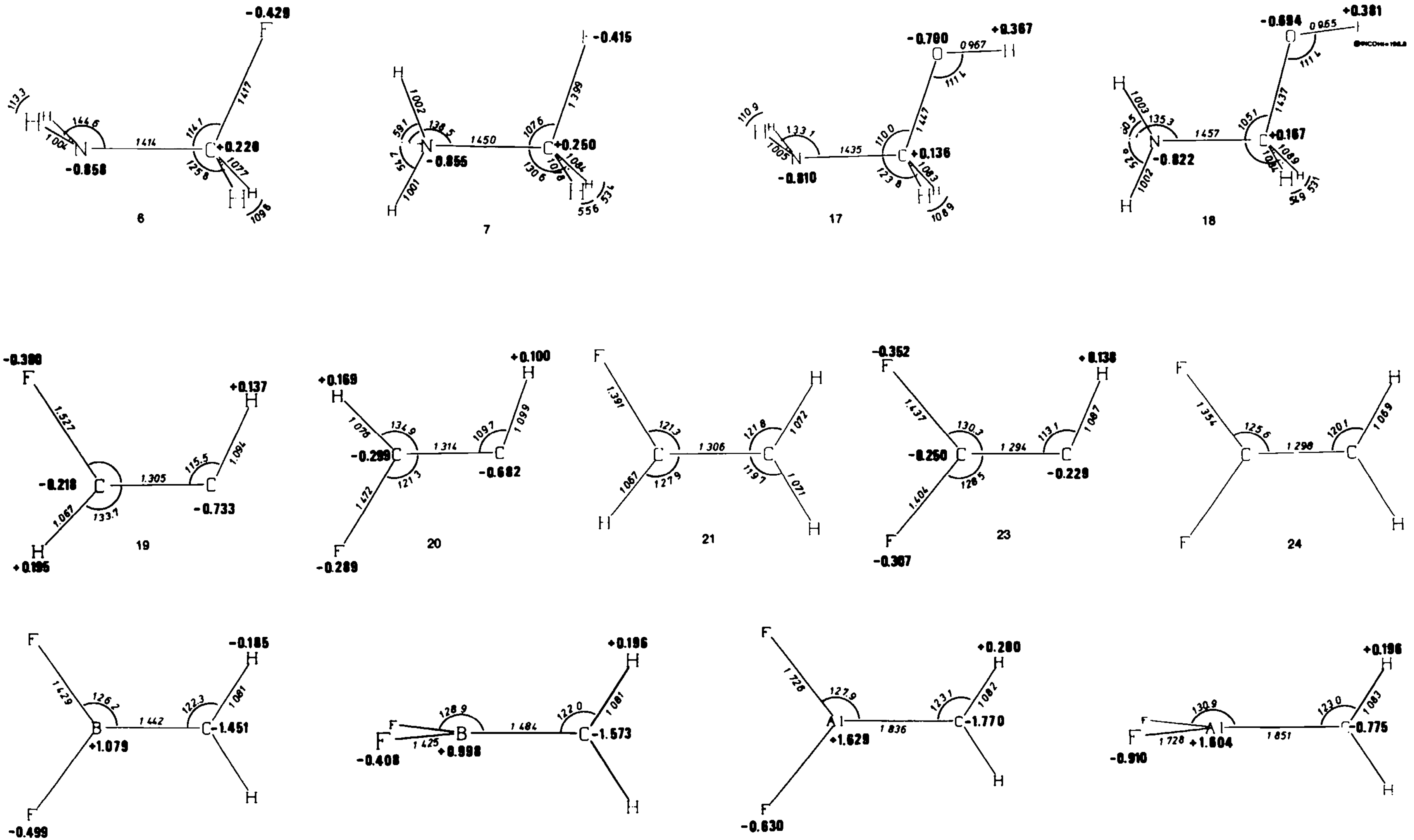


Fig. 1. Geometries: bond lengths (Å), angles (5). Atomic charges (bold figures): obtained from Mulliken population analyses.

Table 1. Absolute energies (hartrees) and relative energies (kcal mol^{-1}) of anions and neutral molecules (3-21 + G//3-21 + G if not otherwise indicated)

Molecule		Point Group	Total Energy	Relative Energy
$FCH_2CH_2^-$	4	C_s	-177.18135[a]	0.0
	5	C_1	-177.16513[a,b]	10.2
$H_2C{=}VH_2\cdots F^-$	10	C_1	-176.55612	0.0
	13	C_{2v}	-176.55214	2.5
	14	C_{2v}	-176.55119	3.1
$F_3CCH_2^-$	11a	C_s	-373.25287	0.0
	11b	C_s	-373.25168	0.8
F_3CCH_3	12	C_{3v}	-373.86735	
$HOCH_2CH_2$	syn-4–OH	C_s	-153.20219[c]	0.0
	anti-4–OH	C_s	-153.18961[c]	7.9
	5–OH	C_1	-153.18114[c]	13.2
$HOCH_2CH_3$		C_s	-153.86455[c]	
$H_2NHCH_2CH_2$	4a–NH_2	C_s	-133.37723[c]	0.0
	4b–NH_2	C_1	-133.37436[c]	1.8
	5–NH_2	C_1	-133.36694[c]	6.5
	5′–NH_2	C_1	-133.36408[c]	8.3
$H_2NCH_2CH_3$			-134.05824	
$HF_2CCH_2^-$	4	C_s	-274.86186	
HF_2CCH_2	16	C_s	-275.50769	
H_2NCH_2F	6	C_s	-193.01473[d]	0.0
	7	C_1	-192.99978[d]	9.4
H_2NCH_2OH	17	C_s	-169.12311[d]	0.0
	18	C_1	-169.11269[d]	6.6
$FHC{=}CH^-$	19	C_s	-175.32205[e]	0.0
	20	C_s	-175.31665[f]	3.4
$FHC{=}CH_2$	21	C_s	-175.95676[g]	
$F_2C{=}CH^-$	22	C_s	-273.68348	0.0
	23	C_{2v}	-273.66455	11.9
$F_2C{=}CH_2$	24	C_{2v}	-274.30066	
H_2BCH_2	planar	C_{2v}	-64.48143	0.0
	perpendicular	C_s	-64.39579	53.8
F_2BCH_2	planar	C_{2v}	-261.36875	0.0
	perpendicular	C_{2v}	-261.31546	33.4
H_2AlCH_2	planar	C_{2v}	-280.51535	0.0
	perpendicular	C_{2v}	-280.47612	24.6
F_2AlCH_2	planar	C_{2v}	-447.44689	0.0
	perpendicular	C_{2v}	-447.42476	13.9
CH_4		T_d	-39.97871	
$H_2C{=}CH_2$		D_{2h}	-77.60792	
$HC{=}CH$		D_h	-76.40476	
F^-			-98.93366	
$CH_4\cdots F^-$		C_s	-138.91985	
$HC{=}CH\cdots F^-$		C_h	-175.37048	
H_2BCH_3		C_s	-65.08200	
F_2BCH_3		C_s	-261.95664	
H_2AlCH_2		C_s	-281.13456	
F_2AlCH_3		C_s	-478.04694	
FCH_2CH[h]		C_1	-213.61223	0.0
FCH_2OH[i]		C_s	-213.60192	6.5

[a] 4-31+G//STD. [b] 4-31+G//4-31+G: -177.17576 au. [c] 4-31+G//4-31+G. [d] 3-21G//3-21G. [e] MP2/3-21+G//3-21+G: -175.64659.

[f] MP2/321+G//3-21+G: -175.63795. [g] MP2/3-21+G//3-21+G: -176.26638. [h] FCOH = 60.8°. 4-31G//4-31G, T. Clark and Y. Apeloig, manuscript in preparation

[i] FCOH = 180°

(standard geometry), 5-F does not dissociate because this would lead to F^- and perpendicular ethylene (much higher in energy than the planar form) within the constraint of C_s symmetry. However, 5-F does not represent a true minimum on the potential energy surface. It can be regarded as a maximum energy form for a hypothetical rotation around the C–C bond. Table 1 summarizes the $C_2H_4F^-$ energies although it should be noted that these refer to basically different systems.

The 2,2,2-trifluoroethyl anion. The examination of $CF_3CH_2^-$ is much more meaningful since F^- is not split off on geometry optimization. Dissociation into difluoroethylene and the fluoride anion is indicated to be endothermic eqn (7).

$$CF_3CH_2^- \rightarrow CF_2{=}CH_2 + F^- \quad \Delta E = +11.6\,\text{kcal mol}^{-1} \quad (3\text{-}21+G//3\text{-}21+G). \quad (7)$$

We have calculated two C_s conformations (Fig. 1). **11a** is the energy minimum form; **11b** is the fixed point on the potential energy surface corresponding to planar inversion at the carbanion center. The energy difference between the two conformations, 0.8 kcal mol^{-1}, is small. The lone pair–C–F dihedral angles are 180° (0°) and *ca.* 60° in **11a**, and *ca.* 30° and 90° in **11b**. As the geometries in Fig. 1 indicate, the calculated C–F bond lengths correspond very well with the expectation that hyperconjugation should be a maximum at 180° (0°) and a minimum at 90° (Table 2). As found in the earlier 4-31G study, the C–C bond is shortened significantly in the anions (1.389 Å vs 1.491 Å in CH_3CF_3), and the hyperconjugationally interacting C–F bonds elongated relative to the values in CF_3CH_3 (Table 2). Thus, "no bond resonance" formulations like **1** are satisfactory descriptions of the geometry changes due to hyperconjugation.

Figure 1 also shows the atomic charges (bold figures) obtained from Mulliken population analyses. Increased charge transfer is observed to those fluorine atoms which interact hyperconjugationally with the carbanion, but the 90° F is exceptional. This is due to the involvement of other orbitals, which are also responsible for the very small FCF angle of 96.1° involving the hyperconjugating fluorines. All C–F bond lengths in the anions are longer than those in the neutral CH_3CF_3.

The calculated proton affinity of $CF_3CH_2^-$ (**11a**), 385 kcal mol^{-1} (3-21 + G), indicates considerable total stabilization (40 kcal mol^{-1} relative to CH_3^-) by the trifluoromethyl group. (The experimental PA of $CF_3CH_2^-$ is 376 ± 6 kcal mol^{-1}).[28]

The contribution of the hyperconjugating fluorine atom (180° in **11a**) to anion stabilization can be assessed by using the difluoroethyl anion (**15**), with a 180° H-lone pair dihedral angle, as a model

$$HCF_2CH^- + CF_3CH_3 \rightarrow F_3CCH_2^- + HCF_2CH_3 \quad \Delta E = 19.8\,\text{kcal mol}^{-1} \quad (3\text{-}21+G//3\text{-}21+G). \quad (8)$$

Table 2. Lone pair-C-F bond dihedral angles, C-F bond lengths and atomic charges of fluorines in 11a and 11b

Dihedral angle lone pair-C-F bond	Bond length C-F	Charge on F
180° (0°)	1.499	-0.369
ca. 30°	1.454	-0.341
ca. 60°	1.407	-0.330
90°	1.399	-0.344
CH_3CF_3	1.370	-0.267

According to eqn (8), the third fluorine, anticoplanar to the carbanion lone pair, contributes 20 kcal mol—one half—of the total stabilization energy of the CF_3 group in the 2,2,2-trifluoroethyl anion.

The β-hydroxy and β-aminoethyl anions. Unlike the β-fluoroethyl anion, $HOCH_2CH_2^-$ and $H_2NCH_2CH_2^-$ (examined in different conformations, syn and anti 4-OH, and 4a-NH_2 and 4b-NH_2 (Fig. 1)) do not fall apart on geometry optimization. Only 4a-NH_2 and 4b-NH_2 are stable thermodynamically towards dissociation (compare eqns (9) and (10)); however, syn and anti-4-OH (constrained to C_s symmetry) are local minima (a barrier is involved although the dissociation is exothermic).

$$HOCH_2CH_2^-(\text{syn 4-OH}) \rightarrow H_2C{=}CH_2 + OH^- \quad \Delta E = -9.9\,\text{kcal mol}^{-1} \quad (4\text{-}31+G//4\text{-}31+G) \quad (9)$$

$$NH_2CH_2CH_2^-(\text{4a-}NH_2) \rightarrow H_2C{=}CH_2 + NH_2^- \quad \Delta E = 3.3\,\text{kcal mol}^{-1}) \quad (4\text{-}31+G//4\text{-}31+G). \quad (10)$$

Structures 5-OH and 5-NH_2 were investigated by imposing a 90° dihedral angle between the carbanion lone pair and the C–X bond; all other parameters were allowed to optimize fully. The perpendicular forms are found to be 13.2 and 6.5 kcal mol^{-1} *less stable*, respectively, than syn-4-OH and 4a-NH_2. These energies are attributed to negative hyperconjugation. In the perpendicular forms, where C–X hyperconjugation is not present, the inductive stabilisations are indicated to be 10.3 and 5.3 kcal mol^{-1}, respectively, for OH and NH_2 substituents. Relative to the ethyl anion, the total stabilisation in 4a-NH_2 is 11.8 kcal mol^{-1} and in syn-4-OH 23.5 kcal mol^{-1} (4-31 + G//4-31 + G, eqn (1), X = NH_2 and OH).

The structural consequences of hyperconjugation are also clear from the geometries shown in Fig. 1. The C–X bonds are significantly longer in **4** than in **5** (by nearly 0.1 Å for X = OH, and 0.05 Å for X = NH_2). The C–X bond lengths in **5** are not very different from those in the neutral molecules, ethanol and ethylamine, calculated at the same theoretical level. In addition, the C–C bonds are substantially shorter (0.04–0.08 Å) in **4**, where negative hyperconjugation is taking place, than in **5** or in the neutral molecules! The influence of hyperconjugation can also be discerned in the C–H bond lengths anti to the carbanion lone pair; these are longer in **5** (favorable for C–H hyperconjugation) than in **4** or the neutral molecules.

The Mulliken populations (Fig. 1) are again not in agreement with the simple expectations of hyperconjugation. The higher energy conformation, anti-4-OH, was included to demonstrate the strong influence of electrostatic effects on atomic charges. The charge distribution (Fig. 1) in syn-4-OH and anti-4-OH depends strongly on the orientation of the OH group. Charge

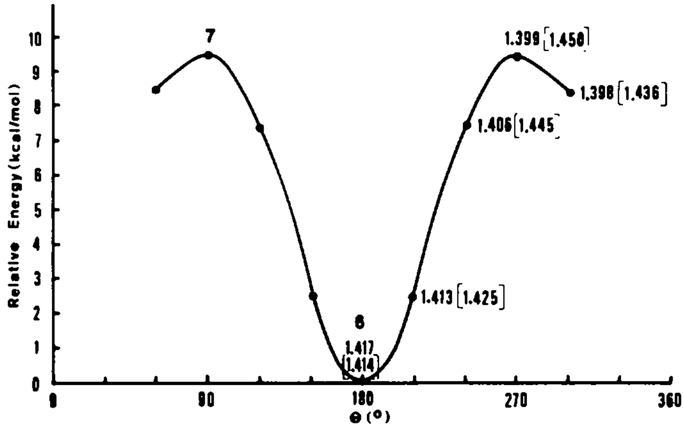


Fig. 2. Rotational potential energy surface for fluoromethylamine (3-21G//3-21G), and C–F [C–N] bond lengths (Å).

transfer from the carbanion to the substituent X is not greatest in the hyperconjugation-favorable conformation **4**. The lone pairs on nitrogen and oxygen also are involved in a complex interplay of interactions which complicate analysis.

We conclude that geometrical details, rather than electron density differences, may be more reliable indications of hyperconjugation in the anions.

Fluoromethylamine and aminomethanol. Complete optimization of fluoromethylamine and aminomethanol[16b] support earlier findings of the importance of negative hyperconjugation (anomeric) effects in neutral molecules.[14–16] The C–N rotational potential energy surface of fluoromethylamine was calculated at 30° torsional intervals by optimizing each conformation. The 180° form **6**, in which the C–F bond and the nitrogen lone pair interact hyperconjugatively, is the global minimum (Fig. 2). A maximum (rotational transition state) is obtained for the perpendicular conformation (**7**). The 30° and 330° conformations are unstable towards nitrogen inversion, which results in the discontinuity of the rotational potential energy surface. The geometrical details (Fig. 1) also show the effect of negative hyperconjugation with an elongated carbon-fluorine bond and a shortened carbon–nitrogen bond in **6** compared to the **7**. The Mulliken populations indicate the normal expectations of an increased charge on fluorine in **6** (Fig. 1).

The total interaction energy between the NH_2 and F groups in **6** eqn (2) using optimized geometries is 6.6 kcal mol^{-1} in fluoromethylamine, fluoromethanol, and 12 also indicate considerable interaction between the OH and F, as well as between the NH_2 and OH groups.

$$CH_3F + HOCH_3 \rightarrow CH_4 + FCH_2OH \quad \Delta E = -13.7\,\text{kcal/mol} \quad (4\text{-}31//4\text{-}31G) \tag{11}$$

$$CH_3NH_2 + HOCH_3 \rightarrow CH_4 + HOCH_2NH_2 \quad \Delta E = -12.7\,\text{kcal/mol} \quad (3\text{-}21G//3\text{-}21G). \tag{12}$$

These total interaction energies can be disected into inductive and hyperconjugative contributions. The latter is given by the rotational barrier; i.e. 9.4, 6.5 and 6.6 kcal/mol in fluoromethylamine, fluoromethanol, and aminomethanol respectively. As shown in Table 3, the inductive and hyperconjugational effect were found to be of similar magnitude for these compounds.

The structures and Mulliken populations in Fig. 1 show the familiar changes corresponding to the "no bond" resonance. Unlike the situation in the anions, the charges in the neutral systems are in accord with simple expectations based on hyperconjugation.

Olefinic systems

Negative hyperconjugation also is present in olefinic systems. Two local minima corresponding to the *trans* (**19**) and the *cis* (**20**) β-fluorovinyl anions, were located on the $C_2H_2F^-$ potential energy surface. However, both are thermodynamically unstable relative to fully dissociated acetylene and F^- (by 10.3 (**19**) and 13.7 (**20**) kcal mol^{-1}). The acetylene-F^- hydrogen bonded complex, eqn (5), 20.1 kcal mol^{-1} more stable than the separated fragments, was obtained during a search for the β-fluorovinyl anion inversion barrier.

The structures of **19** and **20** are also in accord with hyperconjugation: extreme elongation of the C–F bond and a short C–C bond is observed (especially in **19** (Fig. 1) where the fluorine negative hyperconjugation is maximized). The 2,2-difluorovinyl anion (**22**) structure is similar.

The calculated proton affinities of $FHC{=}CH^-$ (**19**), 389 kcal mol^{-1} (MP2/3-21 + G//3-21 + G) and of $F_2C{=}CH^-$ (**22**), 387 kcal mol^{-1} (3-21 + G//3-21 + G), compared to the proton affinity of the vinyl anion, 418 kcal/mol (MP2/4-31 + G//4-31G),[9] reflect large stabilizations by fluorine. The inversion barrier of the vinyl anion (3-21 + G//3-21 + G: 30.2 kcal mol^{-1}) is reduced markedly in the 2,2-difluorovinyl anion (3-21 + G//3-21 + G: 11.9 kcal mol). Hyperconjugation stabilizes the linear transition structure preferentially.

Table 3. Hyperconjugative and inductive contribution to the total interaction energy in fluoromethylamine, fluoromethanol and aminomethanol

XCH_2Y	Interaction Energies, kcal/mol		
X,Y	Total	Hyperconjugative	Inductive
NH_2,F	17.6[a]	9.4	8.2
HO,F	13.7[b]	6.5	7.2
NH_2,OH	12.7[a]	6.6	6.1

[a] 3-21G//3-21G [b] 4-31G//4-31G

Table 4. Energy differences between planar and perpendicular conformations of ethylene and related molecules (3-21 + G//3-21 + G)

Molecules	ΔE, kcal/mol
$H_2C=CH_2$	65[a]
$H_2B=CH_2^-$	53.8
$F_2B=CH_2^-$	33.4
$H_2Al=CH_2^-$	24.6
$F_2Al=CH_2^-$	13.6

[a] Experimental value. J.E. Douglas, B.S. Rabinovich, and F.S. Looney, J.Chem.Phys., **23**, 315 (1955).

Fluorine negative hyperconjugation thus stabilizes unusual geometries. Perpendicular conformations of species isoelectronic with ethylene also can be stabilized by negative hyperconjugation, when a more electropositive element, B or Al, is involved. The $\pi_{BX_2}{}^*$ or $\pi_{AlX_2}{}^*$ orbitals are lower in energy, than $\pi_{CX_2}{}^*$ and interact more favorably hyperconjugatively with the carbanion lone pair in the perpendicular conformations.

The rotational barriers in $H_2BCH_2^-$ (53.8 kcal mol^{-1}) and in $H_2AlCH_2^-$ (24.6 kcal mol^{-1}) are smaller than in ethylene (65 kcal mol^{-1}), but this may be due to changes in the double bond energies. The additional lowering of the torsional barrier by fluorine substitution is a measure of negative hyperconjugation: these lowerings are 20.4 kcal mol^{-1} in $F_2BCH_2^-$ and 11.0 kcal mol^{-1} in $F_2AlCH_2^-$ (Table 4).

The inductive fluorine stabilisation is evaluated roughly by reactions 12 and 13, respectively, using the planar conformations. The total stabilisation energies are calculated using the perpendicular conformations. All data are at 3-21 + G//3-21 + G.

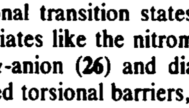
$$H_2BCH_2^- + F_2BCH_3 \rightarrow H_2BCH_3 + F_2BCH_2^- \quad (12)$$

planar conformations: $\Delta E = -8.0$ kcal mol^{-1}
perpendicular conformations: $\Delta E = -28.4$ kcal mol^{-1}

$$H_2AlCH_2 + F_2AlCH_3 \rightarrow H_2AlCH_3 + F_2AlCH_2^- \quad (13)$$

planar conformations: $\Delta E = -12.0$ kcal mol^{-1}
perpendicular conformations: $\Delta E = -23.0$ kcal mol^{-1}

Similarly, anionic hyperconjugation stabilises the rotational transition states of very common organic intermidiates like the nitromethyl anion (**25**),[9,29] the acetic acid α-anion (**26**) and dianion (**27**).[29,30] This results in reduced torsional barriers, and will be discussed in detail subsequently.



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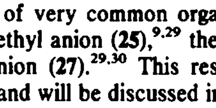

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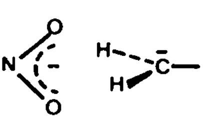

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SUMMARY

We conclude that negative (anionic) hyperconjugation is of great significance in organic chemistry. Energetically, hyperconjugation is generally as important as the inductive effects of β-electronegative substituents. Rather large hyperconjugative stabilisations, on the order of 10 kcal mol^{-1} for an optimally aligned substituent, are indicated. In such alignments, *charge transfer* from a carbanion lone pair to an electronegative group can play a significant role; polarisation may be operative in addition to or in place of charge transfer. There is a concerted set of geometrical changes which correspond to expectations based on "no bond resonance" formulations (**2**). Anomeric effects in neutral molecules, e.g. NH_2CH_2F, are similar: energetic stabilisation, conformational dependence, geometrical differences, and charge transfer. Negative hyperconjugation is *not* controversial; it is firmly established. We underscore Bingham's conclusion,[31] "anionic hyperconjugation is, indeed, a very real, general, and important concept".

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[5] Confusion in nomenclature has arisen because organic chemists generally misuse the designations "σ" and "π" to imply single and multiple bond systems. These Greek letters should be employed in their original theoretical meaning to designate orbitals which are symmetric, σ, or antisymmetric, π, with regard to a local symmetry plane.[4] The often-used description, "σ–π conjugation", is a misnomer, since systems of different symmetry cannot interact directly. "Hyperconjugation" is

preferable; it describes the same phenomenon, is more precise, and has historical precedence.

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