Ab Initio Gaussian Calculations on the CH_3 and CH_2F Anions

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Ab initio calculations with minimal basis sets of uncontracted Gaussian functions have been made on planar and pyramidal CH_3^- and CH_2F^-. As expected, both anions are more stable in the pyramidal than in the planar form; the difference in energy between the forms is greater for CH_2F^- (13.2 kcal mol^{-1}) (1 cal = 4.184 J) than for CH_3^- (1.1 kcal mol^{-1}), which is in agreement with experimental data and simple qualitative arguments. Calculations with an extended basis support the results for CFH_2^-.

THERE is strong experimental evidence [1] that simple carbanions are most stable in pyramidal conformations and it is therefore reasonable to assume that CH_3^- also prefers to be pyramidal, although there is no experimental evidence on this particular point. *Ab initio* calculations suggest this [2-5] and show that the choice of basis set has more influence on CH_3^- than on CH_3^+, and Driessler *et al.*[5] have found that the planar conformation is more sensitive than the pyramidal to this choice.

The replacement of a hydrogen in CH_3^- by fluorine would be expected to increase the stability of the pyramidal carbanion because of the inductive effect of fluorine and there is experimental evidence to support this; CF_3H is a much stronger acid [6,7] than CH_4, which reflects the greater stability of CF_3^- over CH_3^-.

In planar conformations, however, fluorine substituents can destabilize carbanions. For example, CH_2FNO_2 and CHF_2NO_2 are both weaker acids [8] than CH_3NO_2; all three anions [$^-CHFNO_2$, $^-CF_2NO_2$, and $^-CH_2NO_2$] are necessarily planar in order to take full advantage of the stabilizing NO_2-group, and the fluorine-substituents presumably destabilize the anions by repulsion between their lone pairs and the negative charge (I_π-repulsion). Further examples of the destabilizing effect of fluorine on planar carbanions are afforded by the lower acidity of *p*-fluorophenol compared to phenol,[9] and the deactivation of nucleophilic aromatic substitution by *para*-fluoro-substituents.[10] This destabilizing effect of fluorine must, of course, be present in the pyramidal conformation, and the inductive stabilization in the planar conformation; the balance between these effects seemingly lies on the side of stabilization of pyramidal forms and destabilization of planar forms. There is, in fact, experimental evidence for the presence of the destabilization effect in pyramidal fluoro-carbanions; $(CF_3)_3C^-$ is more stable [7] than CF_3^-, even though the CF_3-group is less electronegative than fluorine.

A consequence of these simple qualitative arguments is that the energy difference between planar and pyramidal conformations should be greater for CH_2F^- than for CH_3^-, with the pyramidal forms being preferred in each case. This is analogous to the situation in CH_3^+ and CH_2F^+, where qualitative arguments and *ab initio* calculations [11] agree that the energy difference between planar and pyramidal is again greater for CH_2F^+; this time, however, the planar form is favoured.

We have tested these simple ideas by carrying out *ab initio* calculations with minimal uncontracted Gaussian-type basis sets on planar and pyramidal forms of CH_3^- and CH_2F^-. Five Gaussian orbitals have been used to represent the carbon and fluorine *s*-orbitals and four for the *p*; for the hydrogen atoms, three Gaussians have been used for the *s*-orbitals. The optimized exponents for the carbon and fluorine atoms were those given by Csizmadia *et al.*[12] with the addition of one diffuse *p*-type function (exponent 0.035 for C and 0.0 885 for F, chosen by continuing the near-geomtric series in which the Csizmadia exponents fall), and for hydrogen, those of Hehre *et al.*,[13] as shown in Table 1. These are the same functions, with the addition of the diffuse *p*-type on carbon and fluorine, that we used in our calculations [11] on CH_3^+ and CH_2F^+.

TABLE 1

Basis set exponents

	1*s*, 2*s*				
C	0.302	1.53	7.77	39.6	200.0
F	0.735	3.75	19.0	96.5	488.0
H	0.158	0.584	3.207		
	2*p*				
C	0.035	0.178	0.923	4.78	
F	0.0885	0.457	2.36	12.2	

All the calculations were carried out using the program POLYATOM,[14] implemented on the University of Manchester CDC 7600 computer.

Energies have been minimized with respect to all bond lengths and angles in planar and pyramidal forms of both anions and it is to these values that the Discussion and the figures in the Tables refer. Bond lengths are probably within <0.01 Å, and angles $<0.1°$, of the 'best' values, given the basis set, for CH_3^-, and within 0.02 Å and 0.5° for CH_2F^-. The virial theorem criterion (potential energy/total energy = 2) exceeded 1.993 in all cases.

We have also carried out a few calculations on CFH_2^- with the extended basis [10*s* (contracted to 4), 6*p* (2), and 1*d* Gaussians on C and F, and 5*s* (2) and 1*p* on H] used [11] for CFH_2^+; the geometry optimization has not been carried as far because of the greater requirement for computer time. Since this basis is very different from the one given in Table 1, it provides a good check on our conclusions.

RESULTS AND DISCUSSION

We began these calculations without the most diffuse Gaussians in the set for the carbon and fluorine *p*-orbitals (exponents 0.035 and 0.0885, respectively), but since this made the highest filled orbital of CH_3^- unbound, the basis was abandoned. It is well known that, in order to get all filled orbitals bound in anions, diffuse functions must be employed.

TABLE 2

Total energies [a] and orbital energies [b]

CH_3^-			CH_2F^-		
Orbital symmetry (C_{3v})	Planar [c]	Pyramidal [d]	Orbital symmetry (C_s)	Planar [e]	Pyramidal [f]
$3a_1$	−0.0667	−0.4003	$7a'$	−0.3614	−1.5873
$1e$	−8.30	−7.70	$2a''$	−8.30	−7.10
$2a_1$	−17.09	−17.09	$6a'$	−10.65	−9.30
$1a_1$	−296.97	−296.85	$5a'$	−10.77	−10.15
			$1a''$	−11.79	−10.58
			$4a'$	−17.26	−17.22
			$3a'$	−35.43	−34.38
			$2a'$	−298.80	−298.62
			$1a'$	−705.74	−704.79
Total energy	−39.2699	−39.2716		−137.5388	−137.5599

[a] In a.u. (1 a.u. = 27.211 65 eV = 627.52 kcal mol^{-1} = 2 625.5 kJ mol^{-1}). [b] In eV. [c] C–H = 1.083 Å. [d] C–H = 1.098 Å, pyramidal angle (γ) = 15.86°. [e] C–H = 1.070, C–F = 1.460 Å; ∠ HCH = 131.6°. [f] C–H = 1.104, C–F = 1.529 Å, ∠ HCH = 107.5; γ = 24.55°.

Table 2 shows the total energies and orbital energies for the optimized bond lengths and angles of both anions. The figures for CH_3^- compare well with literature calculations using much larger basis sets [3,5] and even configuration interaction.[4] The Hartree–Fock limits for planar and pyramidal CH_3^- have been established [3] as −39.5242 and −39.5268 a.u., respectively. Our value of 1.08 kcal mol^{-1} for the inversion barrier of CH_3^- also compares well; figures between 0.9 and 5.5 kcal mol^{-1} have been reported [2-5] with values of *ca.* 1 kcal mol^{-1} being favoured by the more sophisticated [3-5] calculations. Our pyramidal angle (15.86°) is some 3° less than the values obtained in these calculations, however.

There appear to be no reported *ab initio* calculations on CH_2F^- but the agreements of literature results with ours on CH_3^- give some confidence in results with our basis sets. As expected, CFH_2^- is predicted to be pyramidal. The barrier to inversion, 13.23 kcal mol^{-1}, is much higher than with CH_3^-, wholly in agreement with the experimental observations and the qualitative arguments mentioned in the introduction; the greater pyramidal angle (24.55 compared with 15.86°) is also in accord with this. A noteworthy feature is the very long C–F bond (1.529 Å) in the pyramidal form, and this may give rise to some doubts as to the validity of our results. However, an increase in C–F length (from 1.460 to 1.529 Å), on going from the planar to the pyramidal form is paralleled in direction, if not in magnitude, by changes in the C–H lengths in both CH_2F^- (from 1.070 to 1.104 Å) and CH_3^- (1.083 to 1.098 Å). The trend in CH_3^- is in accord with literature results (1.073 to 1.093 Å [3] and 1.075 to 1.095 Å[5]).

The calculations with the extended basis [11] just mentioned were carried out mainly because of this seemingly long C–F bond. In the planar form of CFH_2^-, the optimized geometry was: C–F, 1.437; C–H, 1.072 Å; ∠HCH, 131.2°, and these figures are not very different from those given in Table 2. With the pyramidal form, however, the extended basis made the C–F bond markedly shorter, although still very much longer than is usual for C–F bonds: C–F, 1.475; C–H, 1.10 Å; ∠HCH, 105; γ (pyramidal angle), 25.4°. The difference in energies between the two forms with this basis was 19.2 kcal mol^{-1}, so our conclusions on this point still seem to be valid. The sequence of orbital symmetries was the same as with the smaller basis (Table 2), although the picture is somewhat tarnished by the highest filled orbital being unbound in the planar form, so even this large extended basis has its defects for anions.

The Koopmans' theorem ionization potential for CH_3^-, 0.40 eV, is in good agreement with reported values,[2-5] and is less than that for CH_2F^-, 1.59 eV (1.13 eV, extended basis [11]), as would be expected on qualitative grounds.

TABLE 3

Mulliken population analyses

Net charge on:	CH_3^-		CH_2F^-	
	Planar [a]	Pyramidal [a]	Planar [a]	Pyramidal [a]
C	−1.3646	−1.2345	−0.9926	−0.6318
H	+0.1215	+0.0782	+0.1465	+0.0304
F			−0.3004	−0.4290

[a] See footnotes to Table 2 for geometries.

Mulliken population analyses (Table 3) are interesting. These show that the fall in the net charge on carbon in passing from the planar to the pyramidal shape is much greater on CH_2F^- (−0.9926 to −0.6318) than in CH_3^- (−1.3646 to −1.2345), even though the total charge is less. This is again in accord with the simple argument made in the introduction: fluorine is more able to take up charge when its high electronegativity is not so offset by repulsion between its lone pairs and the filled $2p_z$ orbital on carbon, which is what, on this argument, is occurring to a greater degree in the planar than in the

TABLE 4

Coefficients of *p*-type Gaussians in highest filled [a] orbitals

	2*p* Basis set exponents [b] for:							
	Carbon				Fluorine			
Coefficients for:	0.035	0.178	0.923	4.78	0.0885	0.457	2.36	12.2
CH_3^- planar	0.388	0.564	0.321	0.067				
CH_3^- pyramidal	0.356	0.561	0.314	0.066				
CH_2F^- planar	0.391	0.640	0.359	0.075	0.200	0.207	0.139	0.031
CH_2F^- pyramidal	0.266	0.580	0.327	0.070	0.150	0.214	0.145	0.033

[a] $3a_1$ for CH_3^-, $7a'$ for CH_2F^-; see Table 2. [b] See Table 1.

pyramidal shape. These Mulliken analyses should be treated with the usual caution, however, not least because the C–F overlap populations indicate antibonding, albeit to a much lesser degree in the pyramidal (—0.0666) than in the planar (—0.2071) form. With the extended basis, the trend in the Mulliken figures for CFH_2^- was the same, although the absolute values were quite different; the C–F overlap populations in planar and pyramidal forms indicated slight bonding.

The contributions made by the most diffuse *p*-type Gaussians on carbon (exponent 0.035) and fluorine (0.0885) are most marked in the highest filled orbitals (which correspond to ' lone pair ' orbitals on carbon and fluorine in the planar forms); the coefficients are shown in Table 4. There is a notable increase in the contribution of the diffuse carbon Gaussian on passing from the pyramidal to the planar form of CH_2F^- (a similar effect occurs with the extended basis); this does not occur with CH_3^- and is therefore also in accord with the idea of I_π repulsion between the lone pair on fluorine and the filled $2p_z$ orbital on carbon. These most diffuse *p*-type Gaussians only make small contributions to the other filled orbitals.

Both types of basis used in this paper have their defects: the minimal set in the over-long and apparently antibonding nature of the C–F bonds, and the extended set in the unbound nature of the highest filled orbital of planar CFH_2^-. However, since both sets agree on the conclusions we wish to draw for CFH_2^- and CH_3^-, it seems very likely that these are valid: the general problem of treating anions in theoretical chemistry, however, remains.

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