Ab Initio Gaussian Calculations on the CH_3 and CH_2F Cations

By **James Burdon,* D. W. Davies, and Guillermo del Conde,** Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Ab initio Hartree–Fock calculations with minimal basis sets of uncontracted Gaussian functions have been made for the planar and pyramidal conformations of CH_3^+ and CH_2F^+. Both cations are more stable in the planar form and the difference in energy between the equilibrium planar form and any pyramidal form was found to be greater for CH_2F^+ than for CH_3^+; single calculations with extended basis sets lead to the same result, which is in agreement with simple qualitative arguments and is consistent with experimental data. The C–H bond lengths in the two cations are about the same and the value for CH_3^+ is in agreement with literature calculations in which extended basis sets were used. The optimum HCH angle in CH_2F^+ is larger than 120°.

Ab initio calculations have shown that CH_3^+ is planar,[1] and a potential energy surface has been obtained.[2-4]

It is interesting to consider the effect of replacing one of the hydrogen atoms of CH_3^+ by a fluorine atom to give CH_2F^+. Like most cations of this type, CH_2F^+ should be planar and the fluorine atom should stabilize the conformation by interaction between the lone pair on the fluorine atom and the vacant $2p$ orbital on the carbon. *Ab initio* calculations have been carried out by Baird and Datta[5] and by Kollmann and his co-workers[6] on *planar* CH_2F^+ and these did indeed show that fluorine substitution stabilizes the ion, probably by a π-effect, compared with planar CH_3^+. There is experimental evidence,[7] on systems for which CH_3^+ and CH_2F^+ can be regarded as models, to support the contention that α-fluorine substituents do stabilize carbenium ions in molecules where the C^+ centre is likely to be planar.

In *pyramidal* CH_2F^+, the lone pair stabilizing effect would be much less, and the electron-withdrawing inductive effect of the fluorine would be destabilizing; in the planar form this inductive effect is offset by the lone pair effect.[5,6] It is *possible* to interpret[8] the deceleration of some S_N1 reactions by α-fluorine substituents

TABLE 1

Basis set A exponents

	1*s*	2*s*				2*p*		
C	0.302	1.53	7.77	39.6	200.0	0.178	0.923	4.78
F	0.735	3.73	19.0	96.5	488.0	0.457	2.36	12.2
H	0.158	0.584	3.207					

In the extended basis set B calculations, the following additional exponents were included: C, *d*, 0.6; F, *d*, 0.6; H, *p*, 0.75.

Basis set C exponents and coefficients[a]

	C		F	
Type	Exp.	Coeff.	Exp.	Coeff.
s	9.409 00	0.426 95	23.370 5	0.421 81
	3.500 02	0.357 90	8.623 72	0.375 64
s	9 470.52	0.000 45	23 342.2	0.000 41
	1 397.56	0.003 58	3 431.25	0.003 27
	307.539	0.019 34	757.667	0.017 54
	84.541 9	0.007 36	209.192	0.070 80
	26.911 7	0.226 79	66.7261	0.213 00
s	1.068 03	0.085 02	2.691 63	0.097 10
	0.400 16	0.606 89	1.008 75	0.607 56
s	0.135 124	1.0	0.331 15	1.0
p	0.657 707	0.358 71	1.731 93	0.361 14
	1.787 29	0.182 63	4.788 19	0.192 16
	5.776 36	0.054 79	15.218 7	0.057 99
	23.365 5	0.008 75	65.659 3	0.008 80
p	0.091 063 8	0.432 76	0.620 64	0.422 68
	0.248 046	0.203 47	0.206 99	0.224 02
d	0.6	1.0	0.6	1.0

	H	
Type	Exp.	Coeff.
s	0.123 317	0.508 07
	0.453 757	0.474 49
	2.013 3	0.134 24
	13.361 5	0.019 06
s	0.079 83	1.0
p	0.75	1.0

[a] Contracted as indicated by brace.

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[1] L. Radom and J. A. Pople in ' MTP International Review of Science, Vol. 1 (Theoretical Chemistry),' ed. W. Byers Brown, Butterworths, London, 1972.

[2] R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, 1969, **50**, 1443.

[3] F. Driessler, R. Ahlrichs, U. Staemmler, and W. Kutzelnigg, *Theor. Chim. Acta*, 1973, **30**, 315.

[4] R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, 1967, **46**, 1817.

[5] N. C. Baird and R. K. Datta, *Canad. J. Chem.*, 1971, **49**, 3708.

[6] P. A. Kollmann, W. F. Trager, S. Rothenberg, and J. E. Williams, *J. Amer. Chem. Soc.*, 1973, **95**, 458.

[7] R. H. Martin and R. W. Taft, *J. Amer. Chem. Soc.*, 1966, **88**, 1353; R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965.

[8] G. Kohnstam, D. Routledge, and D. L. H. Williams, *Chem. Comm.*, 1966, 113.

as being due to a destabilizing effect of fluorine on pyramidal carbenium ions. With CH_3^+ none of these stabilizing or destabilizing effects can occur. It follows that the difference between planar and pyrimidal forms should be greater for CH_2F^+ than for CH_3^+, and it is the main purpose of this paper to show that *ab initio* Hartree–Fock calculations support this point.

TABLE 2

Total energies and orbital energies for CH_3^+

γ (°)[a]	0.0	0.0[b]	0.0[c]	3.6	5.7
$\widehat{HCH}$ (°)	120.0	120.0	120.0	119.6	119.0
Energy (a.u.)[d]	−38.986 46	−39.028 01	−39.221 74	−38.984 61	−38.981 94
γ (°)[a]	8.2	16.8	19.5	19.5[b]	19.5[c]
$\widehat{HCH}$ (°)	118.0	112.0	109.5	109.5	109.5
Energy (a.u.)[d]	−38.977 45	−38.948 69	−38.935 56	−38.977 19	−39.171 66

Orbital symmetry[e]	Orbital energies (eV)[d]									
1*e*	−25.9	−26.0	−25.1	−25.9	−25.9	−25.9	−25.6	−25.5	−25.4	−25.5
$2a_1$	−34.7	−34.8	−34.9	−34.8	−34.8	−34.9	−35.0	−35.1	−34.9	−35.0
$1a_1$	−317.1	−316.9	−318.0	−317.3	−317.2	−317.4	−317.4	−317.4	−317.1	−318.1

[a] For $\gamma = 0$ and 19.5°, CH = 1.08 Å; otherwise CH = 1.09 Å (1 a.u. = 0.529 167 Å); basis set A unless otherwise stated. [b] Basis set B. [c] Basis set C. [d] 1 a.u. = 27.211 65 eV = 627.52 kcal mol^{-1} = 2 625.5 kJ mol^{-1}. The columns (left to right) of orbital energies correspond to the increasing values of γ listed above. [e] Non-planar form.

TABLE 3

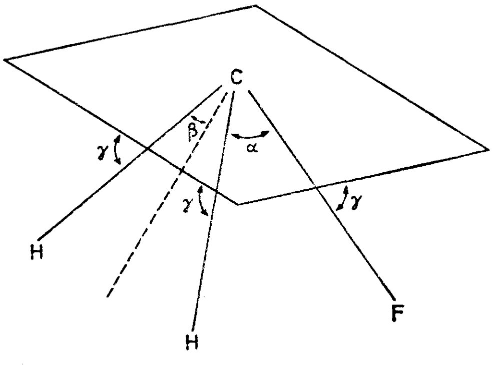
Total energies and orbital energies for CH_2F^+

γ (°)[a]	0.0	0.0[b]	0.0[c]	1.5	3.1
$\widehat{HCH}$ (°)	126.6	126.6	126.6	127.1	127.3
Energy (a.u.)[d]	−137.233 58	−137·339 37	−139.090 91	−137.232 83	−137.231 78
γ (°)[a]	5.9	16.3	19.5	19.5[b]	19.5[c]
$\widehat{HCH}$ (°)	128.0	118.0	113.0	113.0	113.0
Energy (a.u.)[d]	−137.227 92	−137.193 73	−137.177 01	−137.278 59	−138.031 30

Orbital symmetry[e]	Orbital energies (eV)[f]									
$2a''$	−25.2	−24.8	−25.1	−25.2	−25.2	−25.2	−24.8	−24.6	−23.8	−24.0
$6a'$	−28.1	−27.9	−28.1	−28.0	−28.1	−28.0	−27.7	−27.7	−27.6	−27.8
$5a'$	−29.4	−29.5	−29.5	−29.3	−29.4	−29.3	−29.3	−29.0	−29.2	−29.2
$1a''$	−30.7	−30.3	−30.4	−30.6	−30.7	−30.7	−30.4	−30.4	−29.7	−29.8
$4a'$	−35.2	−35.0	−35.2	−35.2	−35.2	−35.2	−35.2	−35.3	−34.7	−34.9
$3a'$	−55.3	−54.6	−54.9	−55.2	−55.3	−55.3	−55.0	−55.4	−54.4	−54.6
$2a'$	−320.1	−319.3	−320.5	−320.1	−320.2	−320.2	−320.2	−320.0	−319.5	−320.6
$1a'$	−724.3	−724.2	−725.6	−724.3	−724.4	−724.3	−724.1	−724.1	−724.2	−725.5

[a] For $\gamma = 0°$, CH = 1.08, CF = 1.278 Å; for $\gamma \neq 0°$, CH = 1.09, CF = 1.292 Å; basis set A unless otherwise stated. [b] Basis set B. [c] Basis set C. [d] Minimum energy (interpolated) is −137.177 21 a.u. for $\widehat{HCH}$ = 115.1°. [e] Non-planar form. [f] The columns (left to right) of orbital energies correspond to the increasing values of γ listed above.

The calculations have been mainly carried out with minimal basis sets (set A, Table 1) of uncontracted Gaussian orbitals, for both CH_3^+ and CH_2F^+, on the University of Birmingham KDF9 and 1906A computers using POLYATOM.[9] The optimised exponents for the carbon and fluorine atoms are those given by Csizmadia *et al.*,[10] and for the hydrogen atoms by Hehre *et al.*[11] These basis sets were used to minimise energies with respect to bond lengths and angles (see below). Eight further calculations were then carried out on the Atlas Laboratory IBM 370/195 computer, using extended basis sets (set B, Table 1, footnote, and set C, Table 1) and the ATMOL suite of programs; these were all carried out on geometries optimised with the minimum basis set. Set B is merely the minimum set A extended by the addition of polarisation functions for C, H, and F; set C is completely different and consists of minimum sets taken from Huzinaga[12] as contracted by Clementi and Davis[13]



Geometrical parameters for CH_2F^+

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[9] Quantum Chemistry Program Exchange, Indiana University, QCPE 47.1.

[10] I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, *Theor. Chim. Acta*, 1966, **6**, 191.

[11] W. J. Hehre, R. F. Stewart, and J. A. Pople, Faraday Soc. Symposium No. 2, 1968, p. 15.

[12] S. Huzinaga, *J. Chem. Phys.*, 1965, **43**, 1293.

[13] E. Clementi and D. R. Davis, *J. Chem. Phys.*, 1966, **45**, 2593.

(C,H) [or by following their scheme (F)] again extended by the addition of polarisation functions.

In the Figure, the geometrical parameters varied in the minimum set calculations on CH_2F^+ are shown. The CF and CH bond lengths, the $H\widehat{C}H$ angle, 2β, and the pyramidal angle γ define a given conformation. For the planar conformation $\gamma = 0°$, and for the tetrahedral, $\gamma = 19.5°$. Let α be the $H\widehat{C}F$ angle, then $\cos\alpha = \sin^2\gamma - \cos\gamma\,(\cos^2\gamma - \sin^2\beta)^{\frac{1}{2}}$.

RESULTS AND DISCUSSION

The total energies and orbital energies for CH_3^+ are shown in Table 2. They confirm that CH_3^+ is planar. The energy difference between the planar and the tetrahedral conformations is 31.9 kcal mol^{-1}. The optimised [14] CH bond lengths of 1.08 Å for $\gamma = 0°$ and 1.09 Å for $\gamma = 19.5°$ may be compared with the values 1.078 Å for $\gamma = 0°$ and 1.09 Å for $\gamma = 19.5°$ obtained by Kari and Csizmadia,[2] and the 1.082 Å for $\gamma = 0°$ obtained by Driessler *et al.*[3] The other CH bond lengths shown in Table 3 were not optimised.

The total energies and orbital energies for CH_2F^+ are shown in Table 3, and the former confirm that the ion is planar with an optimised [14] geometry of CH = 1.08 and CF = 1.278 Å, and $H\widehat{C}H = 126.6°$ (Baird and Datta [5] found CF = 1.26 Å, but they did not carry out a complete optimisation). The bond lengths obtained for $\gamma = 19.5°$ were used in the other calculations for $\gamma > 0°$ to optimise the $H\widehat{C}H$ angle.

The presence of the fluorine atom does not have any appreciable effect on the CH bond length, but the HCH angle is larger in CH_2F^+ than in CH_3^+, which suggests that H · · · H repulsion may be more important than H · · · F repulsion.

As Tyler and Sheridan [15] have pointed out, CF bond lengths show considerable variation in different molecules, from 1.38 in methyl fluoride to 1.34 in vinyl fluoride and 1.28 Å in fluoroacetylene. The value of 1.278 Å found here, and the 1.26 Å by Baird and Datta,[5] fit well into this picture.

For CH_2F^+, the energy difference between the pyramidal ($\gamma = 19.5°$) and the planar conformations is 35.5 kcal mol^{-1}, which is 3.6 kcal mol^{-1} larger than for CH_3^+. This is consistent with the qualitative arguments and experimental evidence mentioned earlier. Tables 2 and 3 also show that this energy difference is greater in CH_2F^+ than in CH_3^+ for all pyramidal conformations. The difference, 3.6 kcal mol^{-1}, is rather small, however, and it was to lend further credence to its reality that we carried out the extended basis set (B and C) calculations. These were performed for $\gamma = 0$ and 19.5° for both CH_3^+ and CH_2F^+, using in every case the optimised geometries found by the minimum set calculations. The 3.6 kcal mol^{-1} difference became 6.3 with set B and 6.0 for the very different set C. Our conclusions, then, concerning the effect of fluorine on the stabilities of planar and pyramidal carbenium ions, are therefore very probably correct.

We have carried out Mulliken population analyses on planar and pyramidal CH_3^+ and CH_2F^+ for all three basis sets used. No clear trends emerged on passing from a planar to a pyramidal form, changes in both gross and overlap populations being generally very small.

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[5/009 *Received, 3rd January,* 1975]

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[14] G. del Conde, Ph.D. Thesis, University of Birmingham, 1974.

[15] J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.*, 1963, **59**, 2661.