Calculations on Fluorine Bridged Carbocations*

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Ab initio molecular orbital calculations of the ions $C_3H_4F_3^+$ at the MP4SDQ/6-31G**//HF/6-31G* + ZPE level lead to the prediction that $CH_2FCH_2CF_2^+$ **43** is the global minimum, and that the ion $CF_3CH_2CH_2^+$ **40** can rearrange to **43** by a 1,3-fluorine migration *via* the fluorine bridged cation **42**. Calculations of the ions $C_2H_2F_3^+$ at the MP4/6-31G**//HF/6-31G* + ZPVE level lead to the prediction that $CF_3CH_2^+$ **50** will spontaneously isomerize without a barrier by 1,2-fluoride migration to $CH_2FCF_2^+$ **52**.

INTRODUCTION

The effect of fluorine as a substituent on carbocations has been a major topic of investigation in recent years.[1-5] Fluorine bonded directly to the cationic site has a π-donor effect that is quite strong because of good overlap between the vacant p-orbital on carbon and the filled p-orbitals on fluorine, with the result being resonance stabilization of the cation as depicted.[4,6]
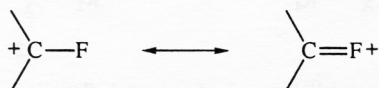

The ion CF_3^+, which should benefit from such π-conjugative stabilization, is more stable than CH_3^+ as indicated by the exothermicity of the reaction in equation (1).[6] However, attempts to directly observe CF_3^+ in strong acid were unsuccessful, although CCl_3^+ and CBr_3^+, could be observed by NMR.[7] Calculations[8,9] at the MP4/6-31G*//MP2/6-31G* level give the hydride affinities of CF_3^+, CCl_3^+, and CBr_3^+ as 55.4, 23.0, and 25.4 kcal/mol, respectively, indicating that the order of stability is $CBr_3^+ > CCl_3^+ > CF_3^+$. Thus while one fluorine can be highly stabilizing the additional fluorines are destabilizing and the net result is a less stable ion. However this con-

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* Dedicated to Professor Dionis E. Sunko on the occasion of his seventieth birthday.

parison is also affected by the stabilities of CHF_3, $CHCl_3$, and $CHBr_3$, and is not a true measure of relative carbocation stability.

$$^+CH_3 + CHF_3 \longrightarrow CH_4 + {}^+CF_3 \qquad \Delta H = -13.2 \text{ kcal/mole} \qquad (1)$$

The ^{19}F chemical shifts and the ^{13}C-^{19}F coupling constants have been used as a measure of the extent of fluorine π-donation in a series of substituted difluorobenzylic carbocations **1** as a function of the aryl substituents.[10]

1
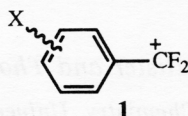
Fluorine is, however, a highly destabilizing substituent when it is β to the cationic carbon due to its strong σ-electron withdrawing ability, which arises from electronegativity and polarization effects. However, electron donation may be possible to give a neighbouring group stabilized intermediate as shown in equation (2).
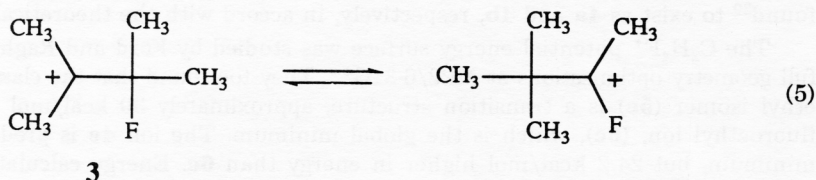
$$(2)$$
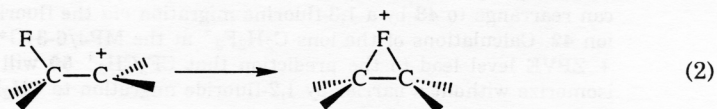
The intermediacy of cyclic halonium ions as shown in equation (3) has long been recognized for X = Cl, Br, and I.[11] However, in the case of fluorine such structures are unknown as long-lived intermediates.

$$(3)$$

2
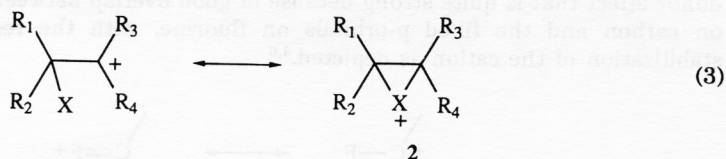
Merritt[12] showed that addition of elemental fluorine to alkenes occurred in a predominantly *cis* (*syn*) manner and proposed that the addition of F_2 occurs through a molecular complex which, upon collapse, gives products of *syn* stereochemistry (equation 4). It was concluded that the participation of a cyclic fluoronium ion (as in equation 3) is of little or no importance in these reactions.

$$F_2 + \quad \longrightarrow \quad \delta^- \cdots \mid \cdots \delta^+ \quad \longrightarrow \quad (4)$$
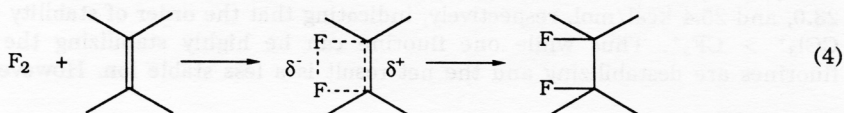
The existence of cyclic halonium ions for Cl, Br, and I in solution has been amply demonstrated by NMR studies in $HSO_3F–SbF_5–SO_2$ (magic acid) solutions at low temperatures.[11] However, these studies did not produce evidence for the existence of the analogous fluoronium ions. For example, the ion **3** was shown to exist as a rapidly equilibrating β-fluoro carbocations,[13] in which all the methyl groups were equivalent in the NMR spectra. A subsequent study[14] verified that equilibration was *via* rapid 1,2 methyl shifts with the intermediacy of an α-fluorocarbocation, as in equation (5), and not through a bridged fluoronium ion.

$$
\begin{array}{ccc}
\underset{\substack{\\ \text{CH}_3 \\[2pt] | \\ \overset{+}{\text{C}} \\ | \\ \text{CH}_3}}{} \quad \underset{\substack{\\ \text{CH}_3 \\ | \\ \text{C}-\text{CH}_3 \\ | \\ \text{F}}}{} & \rightleftharpoons & \underset{\substack{\\ \text{CH}_3 \\ | \\ \text{CH}_3-\text{C} \\ | \\ \text{CH}_3}}{} \quad \underset{\substack{\\ \text{CH}_3 \\ | \\ \overset{+}{\text{C}} \\ | \\ \text{F}}}{}
\end{array}
\qquad (5)
$$

3

Acylic halonium ions are well known in the gas phase, including examples involving fluorine. Thus $(CH_3)_2F^+$ is a prominent ion observed on gas phase protonation of CH_3F (equation 6),[15,16] and is a convenient gas phase methylating agent.[15b] However gas phase studies using radiolytic techniques did not produce any evidence for cyclic fluoronium ions.[17]

$$
CH_3F \xrightarrow[-B]{BH^+} CH_3FH^+ \xrightarrow{-HF} CH_3^+ \xrightarrow{CH_3F} (CH_3)_2F^+ \qquad (6)
$$
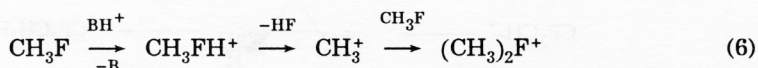
Theoretical studies have compared the bridged halonium ions **4** and the corresponding unbridged ions **5** and **6**.[18-21] Reynolds showed[18] that at the MP2/6-31G**//MP2/6-31G** level of theory, the cyclic chloroethyl ion (**4a**) is only 4.0 kcal/mol higher in energy than the 1-chloroethyl isomer (**6a**). The 2-chloroethyl cation (**5a**) is found to be much higher in energy, and is a transition state, such that any displacement along the transition vector (reaction coordinate) leads spontaneously to **4a**.

4   **5**   **6**
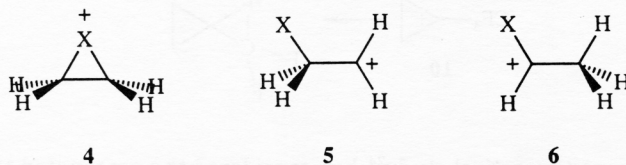
Relative Energy of ions (kcal/mol)

| X	4	5	6	Ref.
Cl (a)	4.0	31.0	0.0	18
Br (b)	0.0	30.0	1.5	19
F (c)	24.0	29.6	0.0	21

A similar study by Schaefer[19a] revealed that the cyclic bromonium ion **4b** is the global minimum on the $C_2H_4Br^+$ energy hypersurface. The 1-bromoethyl isomer (**6b**) is 1.5 kcal/mol higher in energy than **4b**. The 2-bromoethyl ion (**5b**) is 30 kcal/mol higher than **4b**, and, like **5a** was found to be the transition state for H-scrambling.

The potential energy hypersurfaces of the ions $C_2H_2Cl^+$ and $C_2H_2Br^+$ have been examined[19b] with high level *ab initio* theory, and in both cases the halogen-bridged structure and the α-halovinyl cation isomer $CH_2=C^+Hal$ are found to be stable minima.

The chloroethyl and bromoethyl cations have been isolated in solid matrices at 77 to 200 K in their most stable forms and examined by IR spectroscopy.[20] The ions were found[20] to exist as **4a** and **4b**, respectively, in accord with the theoretical predictions.

The $C_2H_4F^+$ potential energy surface was studied by Ford and Raghuveer,[21] with full geometry optimizations at MP2/6-31G**. They too found that the classical 2-fluoro-ethyl isomer (**5c**) is a transition structure, approximately 30 kcal/mol above the 1-fluoroethyl ion, (**6c**), which is the global minimum. The ion **4c** is predicted to be a minimum, but 24.2 kcal/mol higher in energy than **6c**. Energy calculations for this study were done at MP4/6-31G**.

A preliminary study[22] has shown that at the HF/6-31G*//HF/3-21G level, rearrangement of the 2,2,2-trifluoroethyl cation (**7**) to the 1,1,2-trifluoroethyl isomer (**9**) is exothermic by about 20 kcal/mol, with a calculated barrier of approximately 3 kcal/mol *via* the transition structure, **8** (equation 7).

$$CF_3CH_2^+ \longrightarrow \quad\quad\quad \longrightarrow \ ^+CF_2CH_2F \tag{7}$$

7   8   9
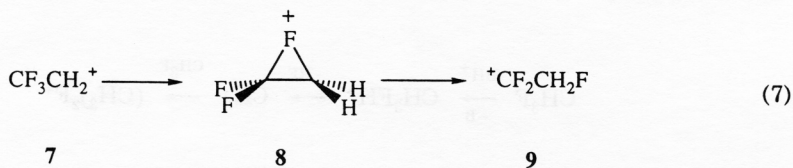
Calculations using MINDO predict that fluorine bridging will occur in trifluoro-methyl-1-cyclopropyl ions, (**10**), and also in the corresponding CF_2H and CH_2F substituted cyclopropyl cations (equation 8).[23] Higher level calculations are however needed to confirm these results.

$$CF_3 - \triangleleft^+ \longrightarrow \tag{8}$$

10
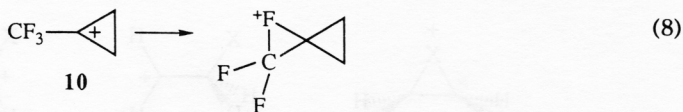
Another recent theoretical study[24] has considered the protonated trihalobenzenes such as **11** (there are 12 isomers in all) and hydrogen (but not fluorine) migrations.

11
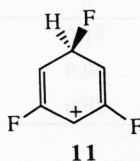
Thus it appears that some fluoronium ions might be stable relative to their open chain analogues, and that generation of suitable precursors might lead to products derived from fluorine atom migrations, *via* fluoronium ions.

EXPERIMENTAL EVIDENCE FOR FLUORONIUM IONS

Although shown to be theoretically feasible, fluorine atom migrations, *via* cyclic fluoronium ions, remained an experimental unknown until very recently.
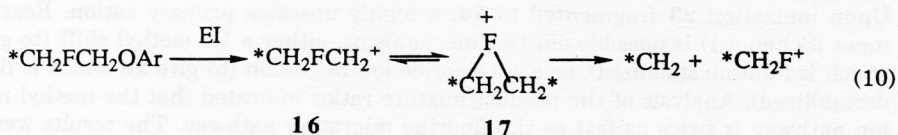
In 1990, Lemal *et al.*[25] found that warming a solution of hexafluorobenzene oxide (**12**) gave primarily hexafluorocyclohexa-2,4-dienone (**14**). He proposed a mechanism involving ring opening to give the zwitterion **13**, followed by a 1,2 fluoride shift to give **14** (equation 9).

$$\text{(9)}$$

12   **13**   **14**
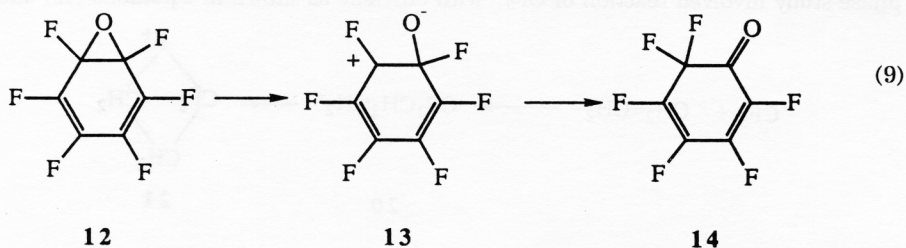
These results are consistent with earlier work by Barlow *et al*[26] who found that heating hexafluoro Dewar benzene oxide (**15**) also gave dienine **14**. It was proposed[26] that **15** rearranges to the more stable **12**, which then gives **14** by the mechanism of equation (**9**).

15
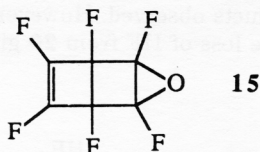
Gas phase results by Ciommer and Schwarz were suggested[27] to support fluorine migration in the fluoroethyl cation (equation 10). Starting from singly ^{13}C-labeled precursor **16**, the products of *EI* ionization showed scrambling of the ^{13}C into both fragments shown (equation 10). They reported that the scrambling of ^{13}C label could only be explained by the intermediacy of a cyclic fluoronium ion **17**.

$$*CH_2FCH_2OAr \xrightarrow{\text{EI}} *CH_2FCH_2^+ \rightleftharpoons \underset{*CH_2CH_2*}{\overset{+}{\underset{}{\bigtriangleup}}} \rightarrow *CH_2 + *CH_2F^+ \tag{10}$$

16   **17**

These results were in excellent agreement with the subsequent theoretical investigation[21] which showed that **17** was indeed predicted to be lower in energy than **16**. It has been suggested,[28] however, that these results are equally well explained by equation (11), wherein the initially formed cation losses HF to give the symmetrically bridged

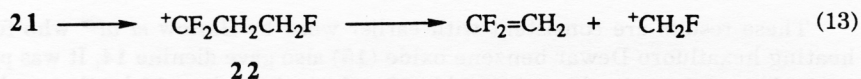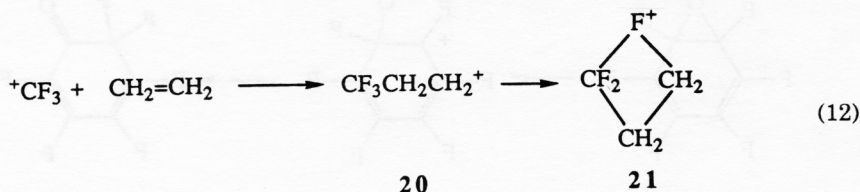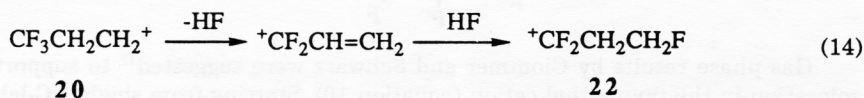vinyl cation (**18**), causing ^{13}C scrambling, then forms a molecular complex **19** with HF. Such complexes are known to correspond to minima on SCF potential energy surfaces.[29]

$$*CH_2FCH_2^+ \xrightarrow{-HF} \underset{\mathbf{18}}{*CH=CH*} \xrightarrow{HF} \underset{\mathbf{19}}{*CH=CH*} \tag{11}$$
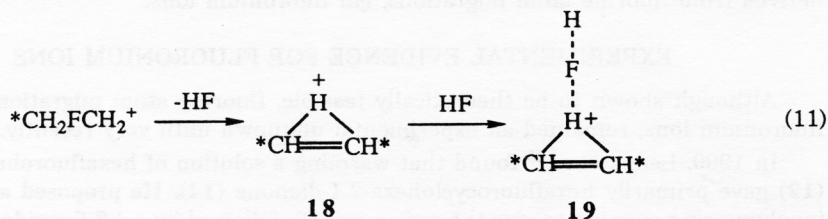
An example of 1,3 fluorine migration was proposed by Tedder *et al.*.[30] Their gas phase study involved reaction of CF_3^+ with ethylene as shown in equations (12) and (13).

$$^+CF_3 + CH_2=CH_2 \longrightarrow \underset{\mathbf{20}}{CF_3CH_2CH_2^+} \longrightarrow \underset{\mathbf{21}}{\overset{F^+}{CF_2 \quad CH_2}} \tag{12}$$

$$\mathbf{21} \longrightarrow \underset{\mathbf{22}}{^+CF_2CH_2CH_2F} \longrightarrow CF_2=CH_2 + {}^+CH_2F \tag{13}$$
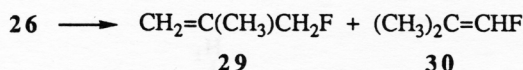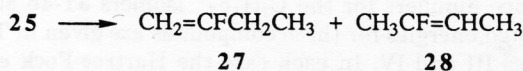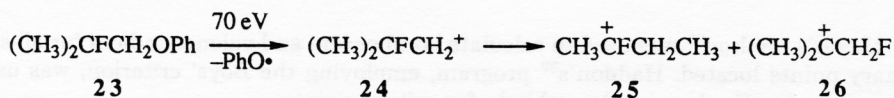
These results were interpreted as involving a 1,3 fluorine migration *via* **21**, to give **22** which fragmented to the products observed. However, these results can also be rationalized by equation (14), where loss of HF from **20** gives a stable allylic cation. Readdition of HF then gives **22**.

$$\underset{\mathbf{20}}{CF_3CH_2CH_2^+} \xrightarrow{-HF} {}^+CF_2CH=CH_2 \xrightarrow{HF} \underset{\mathbf{22}}{^+CF_2CH_2CH_2F} \tag{14}$$

Recently, good evidence for the existence of cyclic fluoronium ions was obtained from ionization of **23** using the electron bombardment flow technique,[31] which allowed isolation and characterization of the four major neutral reaction products **27-30**.[28] Upon ionization **23** fragmented to **24**, a highly unstable primary cation. Rearrangement (Scheme 1) is possible *via* two mechanisms, either a 1,2 methyl shift (to give **25** which is fluorine stabilized), or a 1,2 fluoride ion migration (to give **26** which is fluorine destabilized). Analysis of the product mixture ratios indicated that the methyl migration pathway is twice as fast as the fluorine migration pathway. The results were corroborated by extensive deuterium labeling experiments which ruled out other pathways.

Further gas phase studies,[32] of the reaction of the 2-fluoro-1-propyl cation show methyl, fluoride, and deuterium migration all occur, with a migratory aptitude of fluoride relative to methyl of 0.45, while that of deuterium relative to methyl is 1.9 (equations 15-17).

$$(CH_3)_2CFCH_2OPh \xrightarrow[-PhO^\bullet]{70\,eV} (CH_3)_2CFCH_2{}^+ \longrightarrow CH_3\overset{+}{C}FCH_2CH_3 + (CH_3)_2\overset{+}{C}CH_2F$$

$$\quad\quad\quad\quad 23 \quad\quad\quad\quad\quad\quad\quad\quad 24 \quad\quad\quad\quad\quad\quad 25 \quad\quad\quad\quad\quad 26$$

$$25 \longrightarrow CH_2{=}CFCH_2CH_3 + CH_3CF{=}CHCH_3$$

$$\quad\quad\quad\quad\quad 27 \quad\quad\quad\quad\quad\quad 28$$

$$26 \longrightarrow CH_2{=}C(CH_3)CH_2F + (CH_3)_2C{=}CHF$$

$$\quad\quad\quad\quad\quad 29 \quad\quad\quad\quad\quad\quad 30$$

Scheme 1

$$CH_3CDFCH_2{}^+ \xrightarrow{\text{D shift}} CH_3\overset{+}{C}FCH_2D \quad\quad\quad (15)$$

$$\quad\quad 31$$

$$CH_3CDFCH_2{}^+ \xrightarrow{\text{F shift}} CH_3\overset{+}{C}DCH_2F \quad\quad\quad (16)$$

$$CH_3CDFCH_2{}^+ \xrightarrow{\text{CH}_3 \text{ shift}} \overset{+}{C}DFCH_2CH_3 \quad\quad\quad (17)$$
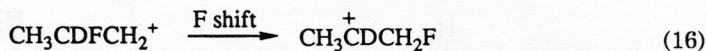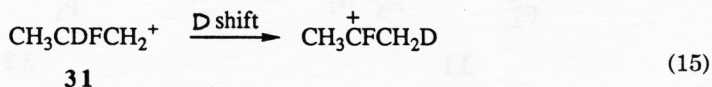
RESULTS

The first part of this work involves an analysis of the $C_3H_4F_3{}^+$ potential energy surface. The structures and stabilities of various isomeric $C_3H_4F_3{}^+$ cations are analyzed to draw conclusions as to the likelihood of fluorine migrations. The second part of this study involves fluorine migration in the trifluoroethyl cation (equation 7). This rearrangement is recalculated using 6-31G* optimized geometries and Moller-Plesset single point energies. We have recently published related work on the $C_3H_5{}^+$ and $C_3H_2F_3{}^+$ energy hypersurfaces.[33]

Ab initio calculations[34] were performed by utilizing the MONSTERGAUSS,[35a] GAUSSIAN 86,[35b] and GAUSSIAN 88[35c] series of programmes and CRAY X-MP/24,[36] Apollo DN10000 and DN3500, SUN 3-260, and Silicon Graphics IRIS 4D120 computers.

Equilibrium geometries were determined using either the Berny Optimizer[34] or the Optimally Conditioned Method,[34] and transition structures were located using the VAO5 technique.[34]

Force constants, harmonic frequencies, and zero-point vibrational energies (ZPVE) were determined at 6-31G* by numerically differentiating the analytical first derivatives of the restricted Hartree-Fock wave function. Stationary points with zero imaginary calculated frequencies (*i.e.* negative eigenvalues) are considered to be true equilibrium minima.[37] Single point energy calculations were done at the MP2, MP3, MP4 (SDQ), and MP4 (full) levels of theory. In all cases the frozen core (FC) approximation was used.[34]

Mayer's method[38] was used to calculate bond orders and valence indices for all stationary points located. Haddon's[39] program, employing the Boys' criterion, was used to compute localized molecular orbitals for critical points.

$C_3H_4F_3^+$

Cation structures and reference numbers for the $C_3H_4F_3^+$ isomers **31-46** studied appear in Figures 1 and 2. Calculated energies for these compounds are given in Tables I and II, and geometries in Tables III and IV. In each case the Hartree-Fock energy is followed by several Moller-Plesset (MP) single point energy calculations. The MP2
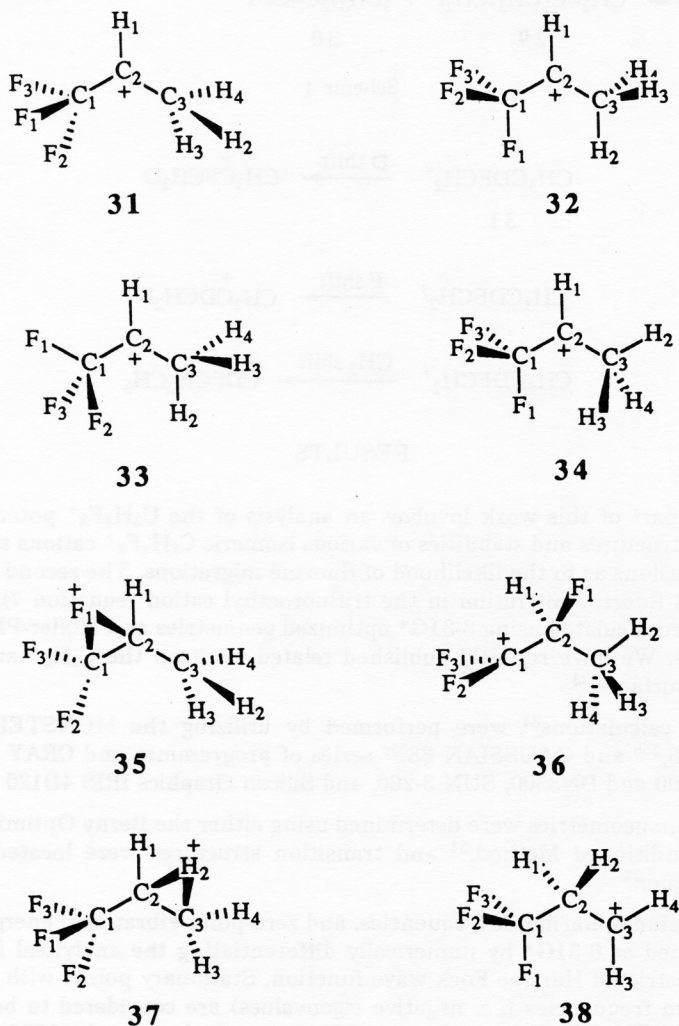
Figure 1. Structure numbers for $C_3H_4F_3^+$ cations

39

40

41

42

43

44

45

46
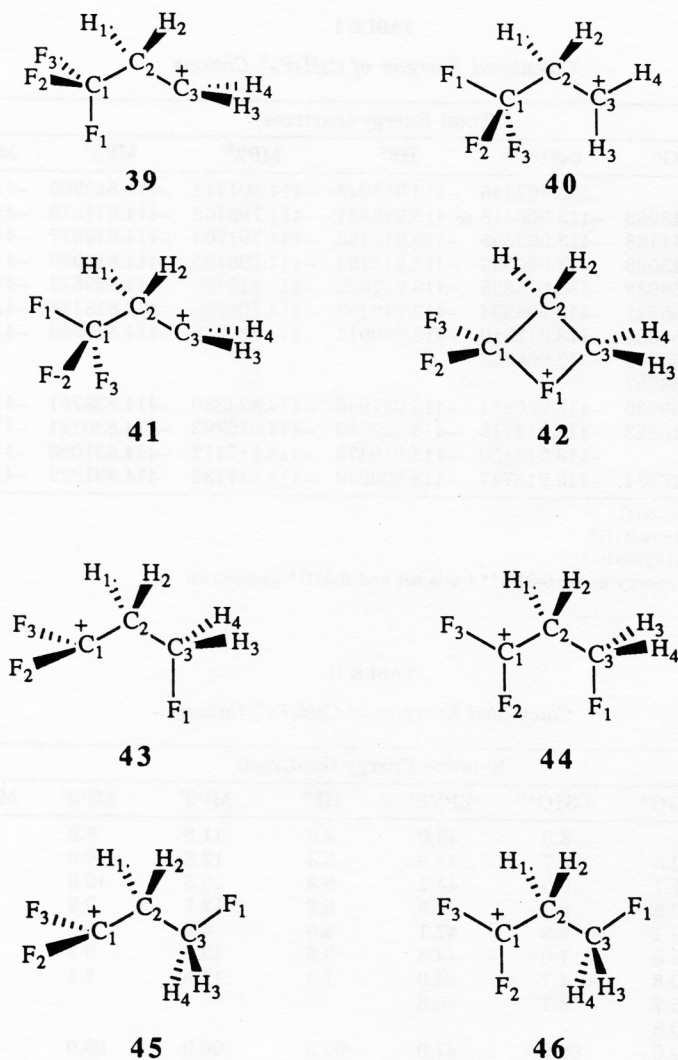
Figure 2. Structure numbers for $C_3H_4F_3^+$ cation (cont'd)

and MP3 wavefunctions are correct to full second and third orders respectively. The MP4 calculations do not include allowance for triple substitutions and are thus refered to as MP4SDQ (Single, Double, Quadruple). The 6-31G** basis set and 6-31G* optimized geometries were used for all Moller-Plesset calculations. Zero point vibrational energies were calculated at HF/6-31G*//HF/6-31G* and are given in Table II, scaled by a factor of 0.9.[34] The relative energy results shown for HF, MP2, MP3 and MP4SDQ reflect corrections made for the relative differences in zero point vibrational energies between compounds **31-46**.

TABLE I

Calculated Energies of $C_3H_4F_3{}^+$ Cations

	Total Energy (hartrees)					
Cation	3-21G[a]	6-31G*[b]	HF[c]	MP2[d]	MP3[d]	MP4SDQ[d]
31		−413.907445	−413.915048	−414.801411	−414.819980	−414.838149
32	−411.643059	−413.906418	−413.913831	−414.799162	−414.817976	−414.836284
33	−411.641188	−413.905358	−413.912763	−414.797704	−414.816677	−414.834848
34	−411.643098	−413.906362	−413.913754	−414.799195	−414.818039	−414.836278
36	−411.638938	−413.910898	−413.917882	−414.815409	−414.829512	−414.849673
38	−411.655841	−413.908994	−413.916433	−414.798266	−414.818178	−414.835201
40	−411.658634	−413.912719	−413.920011	−414.801048	−414.820989	−414.837985
41	−411.650703	−413.906353				
42	−411.658997					
43	−411.659836	−413.920211	−413.927046	−414.824330	−414.838751	−414.858757
44	−411.646323	−413.912718	−413.919783	−414.815763	−414.830721	−414.850359
45		−413.912450	−413.919473	−414.817112	−414.831050	−414.850914
46	−411.646931	−413.913727	−413.920972	−414.817132	−414.831822	−414.851440

(a) HF/3-21G/HF/3-21G
(b) HF/6-31G*//HF/6-31G*
(c) HF/6-31G**//HF/6-31G*
(d) Moller-Plesset energy using 6-31G** basis set and 6-31G* geometries

TABLE II

Calculated Energies of $C_3H_4F_3{}^+$ Cations

	Relative Energy (kcal/mol)					
Cation	3-21G[a]	6-31G*[b]	ZPVE[c]	HF[d]	MP2[e]	MP3[e]	MP4SDFQ[e]
31		8.0	45.0	4.6	11.5	8.9	10.0
32	10.5	8.7	44.9	5.3	12.8	10.0	11.1
33	11.7	9.3	44.7	5.8	13.5	10.5	11.8
34	10.5	8.7	44.8	5.2	12.7	9.9	11.0
36	13.1	5.8	47.1	5.0	4.8	5.0	4.9
38	2.5	7.0	44.8	3.5	13.3	9.8	11.7
40	0.8	4.7	44.9	1.4	11.6	8.1	10.0
41	5.7	8.7	45.6				
42	0.5						
43	00.0	00.0	47.9	00.0	00.0	00.0	00.0
44	8.5	4.7	47.5	4.2	5.0	4.6	4.9
45		4.9	47.7	4.3	4.3	4.2	4.2
46	8.1	4.1	47.4	3.3	4.0	3.9	4.1

(a) HF/3-21G//HF/3-21G
(b) HF/6-31G*//HF6-31G*
(c) Zero Point Vibrational Energy as calculated at HF/6-31G*//HF/6-31G*
(d) HF/6-31G**//HF/6-31G* + ZPVE.
(e) Moller-Plesset energy using 6-31G** basis set and 6-31G* geometries + ZPVE.

TABLE III

Calculated Bond Lengths[a] of $C_3H_4F_3^+$ Cations (6-31G*)

Bond	31	32	33	34	36	38	40	41	43	44	45	46
C_1C_2	1.533	1.534	1.537	1.533	1.503	1.537	1.522	1.562	1.479	1.474	1.463	1.465
C_2C_3	1.429	1.438	1.439	1.439	1.533	1.442	1.448	1.459	1.562	1.551	1.572	1.537
H_1C_2	1.081	1.080	1.081	1.081	1.086	1.098	1.096	1.083	1.082	1.091	1.083	1.091
H_2C_2						1.098	1.096	1.083	1.082	1.091	1.083	1.091
H_2C_3	1.117	1.078	1.078	1.078	1.082							
H_3C_3	1.081	1.098	1.097	1.097	1.082	1.079	1.080	1.079	1.076	1.078	1.080	1.080
H_4C_3	1.082	1.098	1.097	1.097	1.082	1.079	1.079	1.079	1.076	1.078	1.080	1.080
F_1C_1	1.304	1.296	1.296	1.298		1.320	1.301	1.294				
F_1C_2					1.337							
F_1C_3									1.377	1.355	1.341	1.348
F_2C_1	1.297	1.302	1.302	1.302	1.232	1.306	1.316	1.311	1.231	1.238	1.233	1.232
F_3C_1	1.299	1.302	1.302	1.302	1.225	1.306	1.316	1.311	1.231	1.225	1.233	1.234

(a) Bond lengths given in angstroms (Å).

TABLE IV

Valence Bond and Dihedral Angles for $C_3H_4F_3^+$ Cations (6-31G*)

Angle	31	32	33	34	36	38	40	41	43	44	45	46
$C_1C_2C_3$	123.9	125.5	122.2	122.9	110.1	117.1	114.0	107.2	104.5	118.1	112.0	115.8
$H_1C_2C_3$	121.3	120.3	120.5	122.8	111.7	106.7	107.4	111.4	112.5	112.6	108.5	111.4
$H_2C_2C_3$						106.7	107.4	111.4	112.5	112.6	108.5	111.4
$H_2C_3C_2$	97.6	115.0	115.0	114.4	106.6							
$H_3C_3C_2$	115.1	107.1	107.1	107.6	110.8	122.8	122.7	121.4	111.2	109.6	111.1	111.6
$H_4C_3C_2$	114.3	107.1	107.1	107.6	111.4	119.4	120.0	121.4	111.2	109.6	111.1	111.6
$F_1C_1C_2$	104.7	111.5	110.5	111.3		109.9	110.3	108.9				
$F_1C_2C_1$					105.9							
$F_1C_3C_2$									105.4	109.9	104.1	104.7
$F_2C_1C_2$	111.3	106.3	106.8	106.4	121.3	110.0	109.2	109.4	122.6	118.8	122.9	122.1
$F_3C_1C_2$	108.2	106.3	106.8	106.4	123.1	110.0	109.2	109.4	122.6	127.4	122.9	123.6
$C_1C_2C_3H_1$	176.9	180.0	180.0	180.0	-117.8	125.5	124.4	116.8	117.3	121.2	119.6	121.5
$C_1C_2C_3H_2$	90.0	00.0	00.0	180.0	180.0	-125.5	-124.4	-116.8	-117.3	-121.2	-119.6	-121.5
$F_1C_1C_2C_3$	110.0	00.0	180.0	00.0	117.5	00.0	180.0	180.0				
$F_1C_3C_2C_1$									00.0	00.0	180.0	180.0
$F_2C_1C_2C_3$		120.6	59.5	120.5	114.1	119.7	59.1	59.5	90.3	180.0	88.9	180.0
$F_3C_1C_2C_3$		-129.6	-59.5	-120.5	-64.7	-119.7	-59.1	-59.5	-90.3	00.0	-88.9	00.0
$H_3C_3C_2C_1$		125.3	125.0	54.0	61.9	00.0	00.0	88.9	117.6	119.6	62.0	61.7
$H_4C_3C_2C_1$		-125.3	-125.0	-54.0	-61.4	180.0	180.0	-88.9	-117.6	-119.6	-62.0	-61.7

$C_2H_2F_3^+$

Calculated energies for compounds **50-53** (structures shown in Figure 3) appear in Table V. Total energies are given at HF, MP2, MP3 and MP4 levels of theory. The Moller-Plesset energy calculations were done using the 6-31G** basis set and 6-31G* optimized geometries, and are correct to full fourth order. Correction for relative differences in zero point vibrational energies, as calculated at HF/6-31G*//HF/6-31G*, are included in relative energies reported for HF → MP4.

Geometries of **50-53** were fully optimized at the 6-31G* level with the only constraint being the imposition of C_3 symmetry, the validity of which was verified by vib-

rational analysis. Calculated bond lengths (in angstroms) and bond angles (in degrees) are reported in Table VI.

TABLE V

Calculated Energies of $C_2H_2F_3^+$ Cations

	Total Energy (hartrees)			
Cation	HF[a]	MP2[b]	MP3[b]	MP4[b]
50	−374.828107	−375.564050	−375.573059	−375.611130
51	−374.822941	−375.584132	−375.585939	−375.631384
52	−374.863461	−375.616311	0375.620282	−375.662405
53	−374.854409	−375.607238	−375.611081	−375.654007

(a) HF/6-31G**//HF/6-31G*
(b) Moller-Plesset energy using 6-31G** basis set and 6-31G* geometries.

	Relative Energy (kcal/mol)						
Cation	3-21G[a]	6-31G*[b]	ZPVE[c]	HF[d]	MP2[e]	MP3[e]	MP4[e]
50	16.4	22.0	26.5	20.3	30.9	27.7	30.3
51	16.5	25.3	27.2	24.2	19.0	20.4	18.3
52	00.0	00.0	28.4	00.0	00.0	00.0	00.0
53	6.0	5.5	28.6	5.9	5.9	6.0	5.5

(a) HF/3-21//HF/3-21G
(b) HF/6-31G*//HF/6-31G*
(c) Zero Point Vibrational Energy calculated at HF/6-31G*//HF/6031G*
(d) HF/6-31G**//HF/6-31G* + ZPVE.
(e) Moller-Plesset energy using 6-31G** basis set and 6-31G* geometry + ZPVE.

TABLE VI

Calculated Geometries[a] of $C_2H_2F_3^+$ Cations (6-31G)*

	Cation			
	50	51	52	53
C_1C_2	1.529	1.452	1.499	1.527
H_1C_2	1.080	1.075	1.087	1.079
F_1C_1	1.311	1.454		
F_2C_1	1.290	1.264	1.222	1.225
F_3C_1	1.290	1.264	1.229	1.225
F_1C_2		1.664	1.327	1.344
$F_1C_1C_2$	99.2	69.9		
$F_2C_1C_2$	111.2	120.7	122.8	122.2
$F_3C_1C_2$	111.2	120.7	121.0	122.2
$F_1C_2C_1$			107.7	101.8
$H_1C_2C_1$	119.7	119.2	107.5	109.3
$F_2C_1C_2F_1$	117.6	102.0	0.000	88.1
$H_1C_2C_1F_1$	87.0	90.0	121.2	118.0

(a) Bond lengths given in angstroms (Å); bond angles in degrees (°).

50

50a

51

52

53
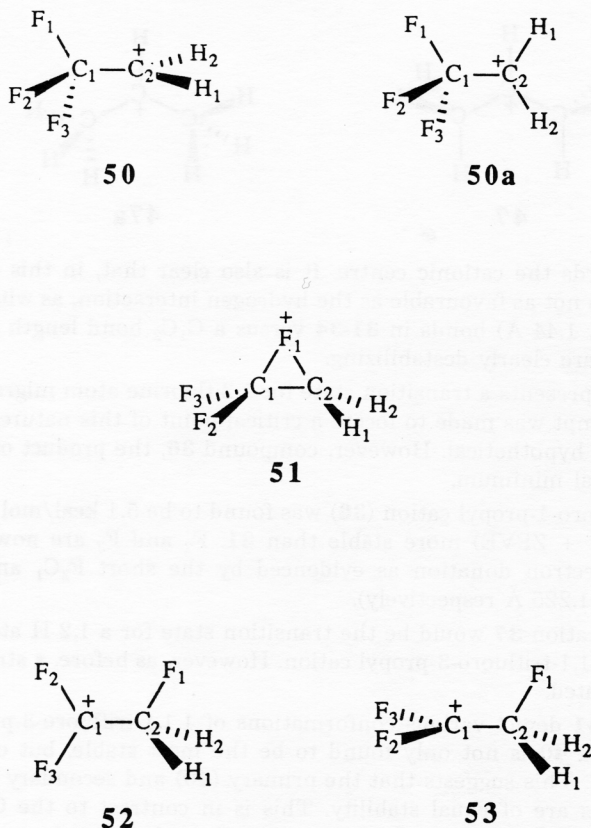
Figure 3. Structure numbers for $C_2H_2F_3^+$ cations

DISCUSSION

$C_3H_4F_3^+$

Structures **31-34** depict the various 1,1,1-trifluoro-2-propyl cations studied. It was determined that **31**, which has both the trifluoromethyl and methyl groups rotated out of plane, was the local minimum and 10.0 kcal/mol (MP4SDQ/6-31G**//HF/6-31G* + ZPVE) higher in energy than the global minimum. This is in qualitative agreement with studies[40] on the $C_3H_7^+$ potential energy surface which revealed that the classical 2-propyl cation with C_{2v} symmetry (**47**) preferred a slight twisting of methyl groups to achieve C_2 symmetry (**47a**). However, as was found in the $C_3H_7^+$ study, the various 2-propyl conformers (**31-34**) are very close in energy.

The 6-31G* optimized structures of **31-34** show little geometrical difference between conformations. A notable exception is the $H_2C_3C_2$ bond angle and H_2C_3 bond length. In cations **32-34** the H_2C_3 bond is 1.078 Å and the $H_2C_3C_2$ angle is about 115°. In **31** the H_2C_3 bond has lengthened to 1.117 Å and the $H_2C_3C_2$ angle has contracted to only 97.6°. These differences reflect the ability of cation **31** to allow σ-electron dona-

47   47a
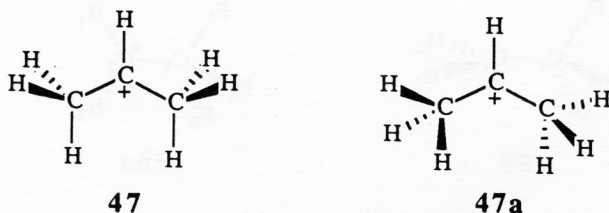
tion from H_2 towards the cationic centre. It is also clear that, in this case, fluorine electron donation is not as favourable as the hydrogen interaction, as witnessed by the short C_2C_3 (approx. 1.44 Å) bonds in **31-34** versus a C_1C_2 bond length of about 1.53 Å. The β-fluorines are clearly destabilizing.

Structure **35** represents a transition state for 1,2 fluorine atom migration from **31** to give **36**. No attempt was made to locate a critical point of this nature, so the existence of **35** remains hypothetical. However, compound **36**, the product of such a rearrangement, is a local minimum.

The 1,1,2-trifluoro-1-propyl cation (**36**) was found to be 5.1 kcal/mol (MP4SDQ/6-31G**//HF/6-31G* + ZPVE) more stable than **31**. F_2 and F_3 are now found to be stabilizing via π-electron donation as evidenced by the short F_2C_1 and F_3C_1 bond lengths (1.232 and 1.225 Å respectively).

Similar to **35**, cation **37** would be the transition state for a 1,2 H atom migration from **31** to give a 1,1,1-trifluoro-3-propyl cation. However, as before, a structure of this nature was not located.

Structures **38-41** depict various conformations of 1,1,1-trifluoro-3-propyl cations. Of these, compound **40** is not only found to be the most stable, but of comparable energy to cation **31**. This suggests that the primary (**40**) and secondary (**31**) 1,1,1-trifluoropropyl cations are of equal stability. This is in contrast to the $C_3H_7^+$ surface where the primary cation is much higher in energy than the secondary one.[40] This degeneracy is an excellent example of the highly destabilizing effect of a β-CF$_3$ group in a carbocation.[41]

Structures **38** and **40** are geometrically very similar. Structure **41** differs slightly from these. The CCC bond angle in **41** is 7–10° smaller than in **38** or **40**. One possible explanation for this is that **41** is attempting to ring close into structure **48**. This supposition is supported by the transition vectors for **41** which show C_1 and C_3 moving towards each other.

Although **48** was not investigated in this study, corresponding calculations on the hydrocarbon analogue revealed that corner protonated cyclopropanes (**49**) are in fact minima on the $C_3H_7^+$ potential energy surface.[40]

48   49
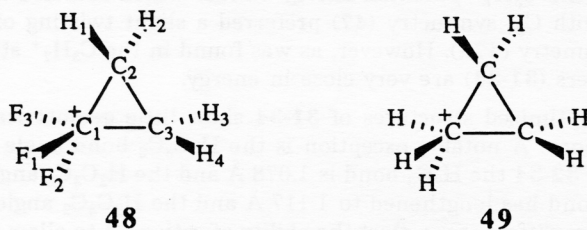
A disturbing facet of the $C_3H_4F_3^+$ study was the discovery that species **38**, **40** and **41** were all calculated to have one imaginary frequency (HF/6-31G*//HF/6-31G*) and therefore are not predicted to be true local minima. In addition, no critical point corresponding to **39** could be located. All attempts to optimize such a structure invariably led to a fluorine bridged species, depicted by **42**, which was found to have only positive eigenvalues (HF/3-21G//HF/3-21G) and is therefore an equilibrium minimum.

From this the following picture emerges: **41** is best considered as a saddle point leading to the formation of **48**; **39** does not exist, but spontaneously collapses to **42**; **38** is the transition state for rotation about the C_2C_3 bond, leading at least nominally to **39** which then gives **42** immediately; **40** would be the similar transition state for C_2C_3 rotation leading to **41**. Another possible explanation is that this surface simply can not be adequately defined at the Hartree-Fock level.
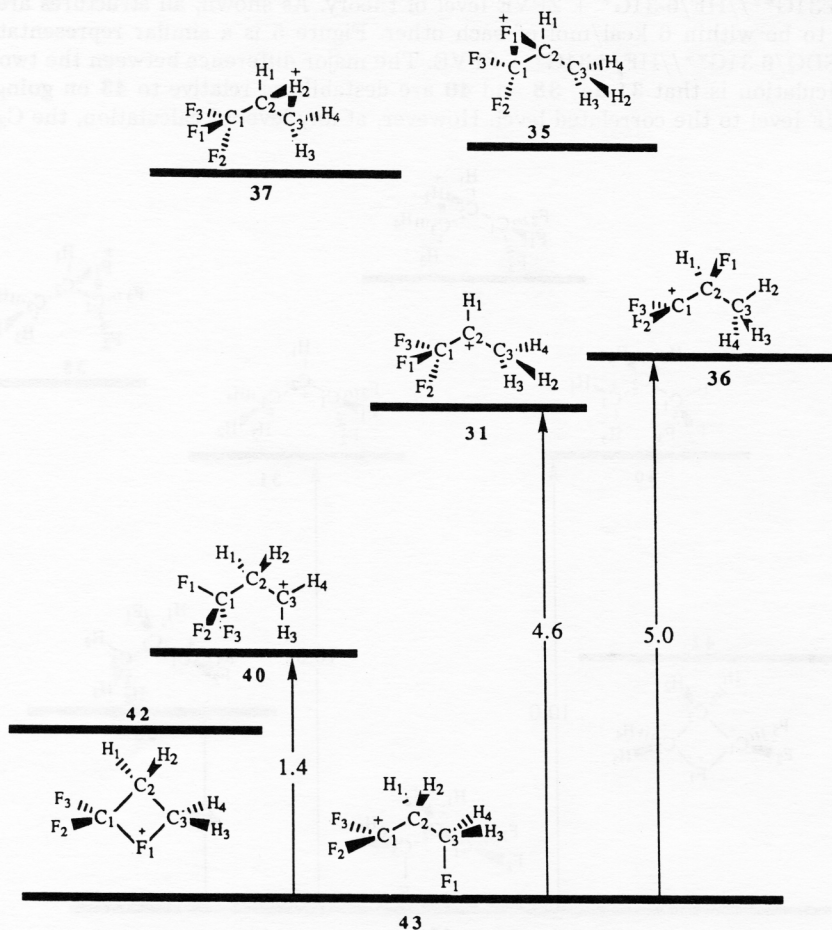

Figure 4. Calculated relative energies (kcal/mol) for $C_3H_4F_3^+$ cations at HF/6-31G**//HF/6-31G* + ZPVE.

Much of this argument depends on the existence of **42**, a fluorine bridged cation. HF/3-21G optimization gave a structure for **42**, with F_1 equidistant from C_1 and C_3 to be 2.0 kcal/mol lower in energy than **38**, and 0.2 kcal/mol more stable than **40**. Attempts to locate this structure at 6-31G* failed. Interestingly, elongation of the C_1F_1 bond smoothly leads to **43**, the global minimum, implying this region of the surface is extremely flat.

Structures **43-46** are all very similar geometrically, and represent the various 1,1,3-trifluoro-1-propyl cations studied. They contain a fairly short C_1C_2 bond of about 1.47 Å and a longer than normal C_2C_3 bond of approximately 1.56 Å. Each of **43-46** contains very short F_2C_1 and F_3C_1 bond lengths (typically 1.23 Å), indicative of significant π-donation from fluorine towards the cationic carbon.

Figure 4 is a depiction of the $C_3H_4F_3^+$ potential energy surface as calculated at the HF/6-31G**//HF/6-31G* + ZPVE level of theory. As shown, all structures are predicted to be within 6 kcal/mol of each other. Figure 5 is a similar representation at MP4SDQ/6-31G**//HF/6-31G* + ZPVE. The major difference between the two levels of calculation is that **31-34, 38** and **40** are destabilized relative to **43** on going from the HF level to the correlated level. However, at any level of calculation, the $C_3H_4F_3^+$
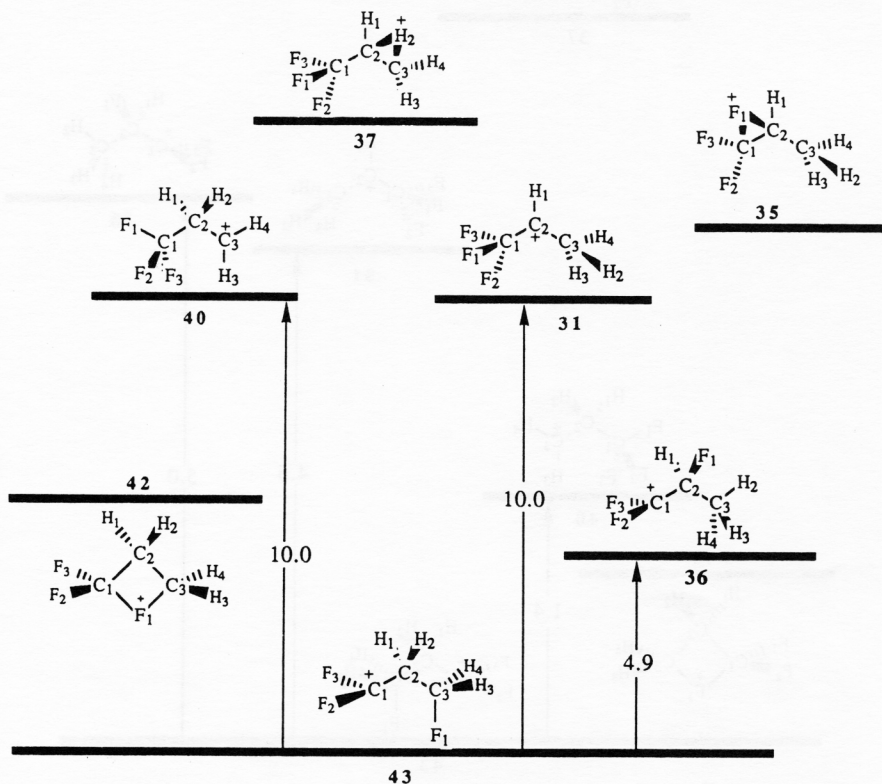

Figure 5. Calculated relative energies (kcal/mol) for $C_3H_4F_3^+$ cations at MP4SDQ/6-31G**//HF/6-31G* + ZPVE.

energy hypersurface is predicted to be very flat. It is this flatness that is causing difficulties in locating certain critical points and in determining the order of others.

Nonetheless, it seems clear that formation of a 1,1,1-trifluoro-3-propyl cation would exothermically lead to a 1,1,3-trifluoro-1-propyl cation *via* a cyclic fluoronium ion, and that such a fluoronium ion would not represent a significant barrier to migration. These calculations therefore support the interpretation of gas phase results by Tedder *et al.*[30] who claimed that addition of CF_3^+ to ethylene led to products derived from a 1,3 fluorine atom migration.

$C_2H_2F_3^+$

Previous studies[22] on the $C_2H_2F_3^+$ potential energy surface predicted a low barrier (3.1 kcal/mol at HF/6-31G*//HF/3-21G) for the 1,2 fluoride shift from cation **50** to give, at least initially, **53** which can rotate to afford the more stable **52** (Eq. 7, and Figure 3).

6-31G* optimization gives **50** to be 0.4 kcal/mol more stable than its rotational isomer **50a**. The added stabilization afforded **50** is possibly due to favourable n-electron donation from fluorine towards the vacant 2p-orbital on the adjacent carbon atom. This effect would be maximized[22] when the F_2C_1 bond is bisecting the CH_2^+ moiety (as in **50**) rather than eclipsing it (as in **50a**). The geometry of **50** is interesting in another respect. The $F_1C_1C_2$ bond angle is calculated to be a rather strained 99.2° (*versus* 111.2° for the other fluorines). This is consistent with there being a stabilizing interaction between F_1 and C_2.

Structure **51** represents the transition state for the 1,2 fluoride migration. It contains a bond breaking (F_1C_1) length of 1.454 Å, and a bond forming (F_1C_2) length of 1.664 Å. The fluorine atom is approximately half-way between C_1 and C_2, but **51** is nonetheless slightly reactant-like in geometry. Vibrational analysis at HF/6-31G*//HF/6-31G* gave one imaginary frequency, consistent with **51** being a transition state.

Cation **52** is the global minimum on this surface. It contains an $F_1C_2C_1$ bond angle of 107.7°, possibly indicating that a small interaction still exists between F_1 and the cationic carbon. However, the major source of stabilization of **52** must be π-donation from F_2 and F_3. The F_2C_1 and F_3C_1 bond lengths have substantially contracted, from 1.290 Å in **50** to 1.222 Å (F_2C_1) and 1.229 Å (F_3C_1) in **52**, suggesting significant resonance contributions from **52a** and **52b**.
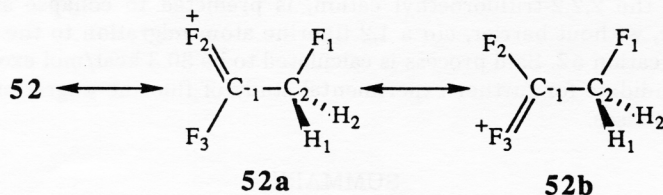
Structure **53** is the immediate product of fluorine migration. It possesses an $F_1C_2C_1$ bond angle of only 101.8° suggesting once again the tendency of fluorine to bridge.

Figure 6 shows the relative energies of these cations as calculated at HF/6-31G**//HF/6-31G* + ZPVE which is essentially the Hartree-Fock limit. At this level, **51** is predicted to be 3.9 kcal/mol higher in energy than **50**. The conversion of **50** → **52** is calculated to be exothermic by 20.3 kcal/mol.
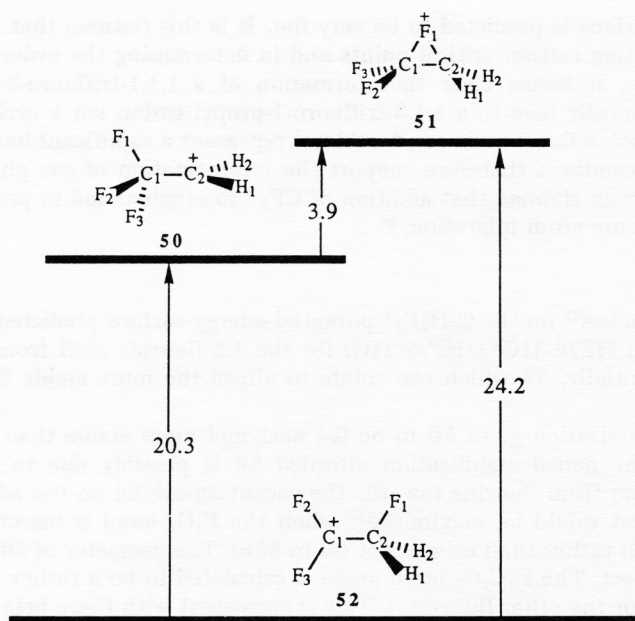
Figure 6. Calculated relative energies (kcal/mol) for C$_2$H$_2$F$_3^+$ at HF/6-31G**//HF/6-31G* + ZPVE.

This energy hypersurface is predicted to be dramatically different at MP4/6-31G**//HF/6-31G* + ZPVE (Figure 7). Cation **50** is shown to be *destabilized* by 10 kcal/mol relative to **52**, whereas structure **51** is *stabilized* by 5.9 kcal/mol, resulting in **51** now being 12 kcal/mol **more** stable than **50**. This reversal in relative stabilities must be due to the inclusion of electron correlation terms in the wavefunctions. Such calculations tend to favour nonclassical cations since they allow for a more favourable distribution of crowded electrons, and such a reversal in stabilities is well precedented.[33]

Thus **50**, the 2,2,2-trifluoroethyl cation, is predicted to collapse smoothly and spontaneously, without barrier, *via* a 1,2 fluorine atom migration to the planar 1,1,2-trifluoroethyl cation **52**. Said process is calculated to be 30.3 kcal/mol exothermic, and is a prime candidate for further experimental study of fluorine migrations in the gas and solution phases.

SUMMARY

A limited survey of the C$_3$H$_4$F$_3^+$ energy hypersurface has revealed that it is an extremely flat potential with several shallow wells representing the 1,1,1-trifluoro-2-propyl cation (**31**), the 1,1,2-trifluoro-1-propyl cation (**36**), the 1,1,1-trifluoro-3-propyl cation (**40**) and the 1,1,3-trifluoro-1-propyl cation (**43**). It is concluded that the 1,1,1-trifluoro-3-propyl cation should undergo a 1,3-fluorine atom migration to afford the more stable 1,1,3-trifluoro-1-propyl cation. These calculations are in accord with recent experimental results.[30] This ease of migration is in contrast to calculations on the monofluorinated propyl derivative which predicts the cyclic four membered
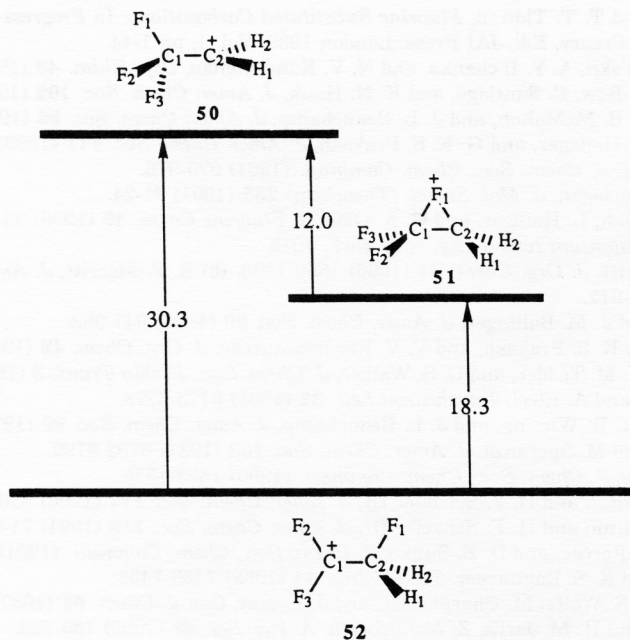
Figure 7. Calculated relative energies (kcal/mol) for $C_2H_2F_3^+$ at MP4/6-31G**//HF/6-31G* + ZPVE.

fluoronium ion to be substantially higher in energy than its open chain isomer.[42] The calculated degeneracy in energy for cations **31** and **40** is an example of fluorine's tendency to destabilize a carbocation when in the β position. Conversely, the stability of **43** is evidence of a fluorine's ability to stabilize a carbocation when bonded directly to the cationic centre.

Analysis of the $C_2H_2F_3^+$ potential surface, and equation (7) in particular, reveals that a single determinant wavefunction is inadequate to even qualitatively describe the nature of this surface. The 1,2 fluorine atom migration from **50** to **52** is calculated to have a barrier of 3.9 kcal/mol at HF/6-31G**//HF/6-31G* + ZPVE. This barrier disappears when a correlated wavefunction was used, leading to the conclusion that formation of $CF_3CH_2^+$ should spontaneously produce $^+CF_2CFH_2$ via a cyclic fluoronium ion structure.

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SAŽETAK

Premošteni fluoronij ioni

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Ab initio molekulsko orbitalni računi plohe potencijalne energije iona $C_3H_4F_3^+$ (I) primjenom postupka MP4/6-31G**//HF/6-31G* pokazali su da globalni minimum odgovara ionu $CH_2FCH_2CF_2^+$. Utvrđeno je također da pregradnja iona $CF_3CH_2CH_2^+$ u prvi ion teče uz 1,3-migraciju fluora posredstvom fluorom premoštenog kationa. Isti postupak primijenjen na ion $C_2H_2F_3^+$ pokazao je da ion $CF_3CH_2^+$ 1,2-migracijom fluoridnog iona spontano izomerizira u kation CH_2FCF_2.