Total acids were determined by adding an aliquot to sodium hydroxide and back-titrating with hydrochloric acid to a phenolphthalein end point.

CIDNP Reactions. Spectrometers were tuned on previously reacted samples (after equilibrating for 20–30 min at elevated temperatures from 90 to 120° to determine qualitative effects of peroxide decomposition rate on spectroscopic abnormalities). ^1H external lock spectra were run on 0.5-ml aliquots of the above peroxide solution in 5-mm thin-walled nmr tubes. Sample tubes were inserted in the preheated probe and repeatedly scanned over selected ranges (generally 350–600 or 200–700 Hz) at 2.5–5 Hz/sec. Initial scans were in progress within 15 sec after inserting the sample in the probe and repeated scans were continued until emission ceased (2 hr at 90°). ^{13}C spectra using a DMSO-d_6 ^2H concentric tube internal lock (see above) were run on 2.5-ml aliquots of the peroxide solution. Normally 15–30 sec was required to establish lock and fine tune so that at best one scan was initiated in the first minute. Strong emission or enhanced absorption peaks were easily detected in single scans at 25 Hz/sec, but other reported signals were observed using the CAT with 25–35 scans at 40 Hz/sec. The distribution of peaks in a spent sample was determined by time averaging (244 scans at 10 Hz/sec) and gave a good correlation with a simulated spectrum based on spectra of the gc identified components and their relative concentrations.

An INDO Theoretical Study of the Geometry of Fluorinated Methyl and Allylic Cations and Radicals[1]

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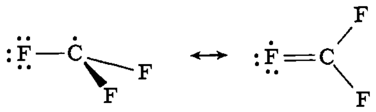
Abstract: LCAMO–SCF calculations in the INDO approximation have been performed on CH_3^+ (**2**), CH_2F^+ (**3**), CHF_2^+ (**4**), and CF_3^+ (**5**), a series of four fluorinated allylic radicals including $CH_2{=}CH{-}CF_2\cdot$ (**6**), $CH_2{=}CF{-}CF_2\cdot$ (**7**), *trans*-$CFH{=}CF{-}CF_2\cdot$ (**8**), and *cis*- $CFH{=}CF{-}CF_2\cdot$ (**9**), and a series of five fluorinated allylic cations including $CH_2{=}CH{-}CF_2^+$ (**10**), $CH_2{=}CF{-}CF_2^+$ (**11**), *trans*-$CHF{=}CF{-}CF_2^+$ (**12**), *cis*-$CHF{=}CF{-}CF_2^+$ (**13**), and $CF_2{=}CF{-}CF_2^+$ (**14**). Fluorinated methyl cations (**3–5**), unlike their radical analogs, were planar as was CH_3^+. The barrier to out-of-plane deformation is shallow at small angles but increases rapidly at large angles. The preference for the planar geometry is due in part to substantial $F \rightarrow C$ back π donation which increases per F–C bond in the series **5** < **4** < **3**. Accompanying $F \rightarrow C$ π donation is a strong $C \rightarrow F$ σ polarization. The two nearly balance so that the net charge density on fluorine does not change appreciably. By attaching a strongly conjugating vinyl group to the $-CF_2\cdot$ function in place of H or F, the preferred geometry at that carbon becomes planar (sp^2) in **6–9**. In addition, the $CF_2\cdot$ plane is also that of the vinyl group. This all planar geometry is rather strongly favored as a result of substantial C–C π-bond character as well as a moderate π contribution in the $\cdot C{-}F$ bonds where $F \rightarrow C$ back π bonding occurs. The unpaired spin density is found mostly on C_1 (and C_3) with a significant portion at C_2 but very little on the terminal fluorines. The magnitude of $F \rightarrow C$ π donation increases markedly going from fluoroallylic radicals **6–9** to fluoroallylic cations **10–14**. In addition, rather large (0.35–0.28) $C_1{-}C_3$ π-bond orders were found in the cations. As the number of terminal fluorines was increased, the 1–3 π-bond order decreased. The $C_1{-}C_2$ rotation barriers in radicals **6–9** and cations **10–14** were obtained and compared. Although complete structure optimization (and symmetrization) was not carried out, moderate changes in the bond lengths and angles do not markedly change the magnitude of the calculated quantities and do not affect the conclusions.

Experimental studies (*i.e.*, infrared, electronic, and esr spectroscopy) have demonstrated that the methyl radical is planar, or almost planar, and that $CF_3\cdot$, $CF_2H\cdot$, and $CFH_2\cdot$ are pyramidal.[2–6] Theoretical studies by Morokuma, Pedersen, and Karplus,[7] using the LCAO–MO–SCF method with Gaussian AO-basis sets, and by Beveridge, Dobosh, and Pople,[8] using the LCAO–SCF method in the INDO approximation, were in agreement with experiment for these radicals. Pauling[9] argued that the electronegativity difference between carbon and fluorine atoms is the major factor which determines the nonplanar configuration of these radicals. Furthermore, Pauling stated that the structure of $CF_3\cdot$ would have FCF angles significantly smaller than the observed value of 112° if there was no double bond contribution to the normal state of the radical (see below) and if nonbonded fluorine repulsions were not operating. Thus, the observed value of 112° for FCF angles is expected. Detailed theoretical calculations comparing the analogous cation series CH_3^+, CFH_2^+, CF_2H^+, and CF_3^+ have not appeared although



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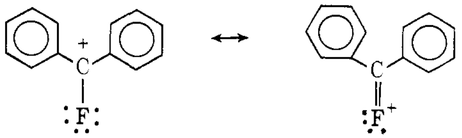
the methyl cation has been exhaustively studied[10–17] and found planar with D_{3h} symmetry. Intuitively, we anticipated that an increased carbon–fluorine double bond character and the decreased electronegativity difference between C^+ and F (*vs.* $C\cdot$ and F) in the cations would favor planar structures for this cation series. Furthermore, the expected contraction of carbon's atomic radius in the cations could increase the importance of nonbonded repulsions in the pyramidal geometry. Thus, geometry-optimized INDO calculations[8] were performed on this cation series to test these assumptions.

Kispert, Pittman, and coworkers[1b] have recently reported INDO calculations on cyclopropyldifluoromethyl cations and radicals. These calculations indicated the cations were planar, but the radicals were nonplanar, despite some measure of conjugative interaction between the carbinyl carbon and the cyclopropyl ring. The very strong conjugative interaction between the cyclopropyl ring and the carbinyl carbon in the cation could have caused the observed planarity in this cation at the carbinyl carbon. In cyclopropylcarbinyl radicals, the conjugation between the ring and the carbinyl carbon is much less intense. Since fluoromethyl radicals and cyclopropyldifluoromethyl radicals are inherently nonplanar, the question arises: could fluorinated radicals be induced to become planar by adding a strongly conjugating group to the $-CF_2\cdot$ center? For example, if a vinyl group were attached to $-CF_2\cdot$, would this provide enough stabilization of the planar conformation to cause the planar geometry to be preferred? In order to investigate this question, INDO calculations were performed on a series of four fluorinated allylic radicals including the parent radical of this series $CH_2{=}CH_2{-}CF_2\cdot$. In addition, calculations were carried out on five fluorinated allylic cations in order to compare their structures with those of the allylic radicals.

Fluorinated allylic radicals are not well known although the unsubstituted allyl radical and its methyl derivatives have been well studied by esr, most successfully by photolysis of a propylene solution of di-*tert*-butyl peroxide.[18] Allylic cations have been well studied,[19] especially in strongly acidic media,[20,21] but structural studies of fluorinated allylic cations have not been reported. However, alkyl and arylfluorocarbonium ions have been directly observed by ^1H and ^{19}F nmr spectroscopy.[22] Large downfield ^{19}F shifts observed in these cations strongly implied significant charge delocalization onto fluorine occurred. For example, in the 2-fluoro-2-propyl cation, the ^{19}F resonance is 267-ppm deshielded from its position of resonance in the 2,2-difluoropropane precursor.[22] In the diphenylfluorocarbonium ion (**1**) where strong resonance interactions exist with the two rings, the value of $\Delta\delta$ ^{19}F is -100.9 ppm, which still suggests that significant backbonding of a fluorine lone pair to the carbinyl carbon occurs. Thus, calculations on fluoroallylic cations were of interest to examine this back donation.



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Method

The INDO and CNDO/2 programs (CNINDO), QCPE No. 141, were obtained from the Quantum Chemistry Program Exchange, Indiana University, and were modified for use on a Univac 1108. The structures were generated using the Gordon–Pople model builder program, QCPE No. 135, which determined the cartesian coordinates of the atoms when bond lengths and angles were supplied. Calculations were performed on an IBM Model 360/50 and on a Univac 1108.

The bond lengths and angles were systematically varied until a minimum energy was obtained for CH_3^+, CFH_2^+, CF_2H^+, and CF_3^+. Bond distances and angles were taken from reported microwave studies[23,24] as a starting point in the calculations performed on the fluorinated allylic cations and radicals. Next the C_1–C_2 and C_1–F distances and the C_1C_2F and FC_2F angles were varied for minimum energy in both the radicals and cations. *Complete structure minimization and symmetry establishment were not undertaken* due to computing expenses. However, for the questions under study in this work, this symmetrization was not a necessary requirement.

Results and Discussion

A. Methyl–Fluoromethyl Cation Series. The preferred geometry of all cations in the series CH_3^+, CH_2F^+, CHF_2^+, and CF_3^+ was planar. The minimized structures are shown in Figure 1 along with the total excess charge densities calculated on each atom. The ions are all in the *xz* plane where the *y* axis is defined perpendicular to the molecular plane. The preference for the planar geometry *vs.* conformations with small out-of-plane deformations is not particularly large. For example, symmetrically distorting all bonds out of the plane by 5° results in an increase in energy of only 2.2, 2.1, 2.2, and 2.4 kcal/mol for the series **2**, **3**, **4**, and **5**, respectively. Thus, the energy well is initially shallow, but it increases more steeply at larger out-of-plane distortions. These results are summarized in Table I along with the C–F π-bond orders, and the p_x, p_y, and p_z charge densities for fluorine and carbon.

Several trends are evident. First, the carbon–fluorine π-bond order increases regularly: $CFH_2^+ > CF_2H^+ > CF_3^+$. As each additional fluorine is added, there is less need for back donation from each fluorine p_y orbital, because other fluorine atoms are already pro-

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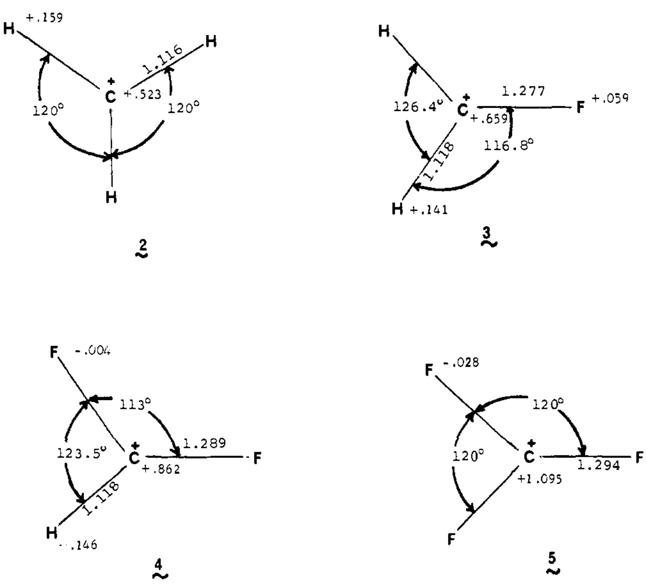

Figure 1. INDO minimized geometries and calculated excess charge densities of the methyl and fluoromethyl cations.

Table I. Out-of-Plane Distortion Energy, π-Bond Orders, and Charge Densities for the Methyl and Fluoromethyl Cations

Calculated quantity	CH_3^+ 2	CH_2F^+ 3	CHF_2^+ 4	CF_3^+ 5
ΔE for 5° out-of-plane distortion, kcal/mol	2.2	2.1	2.1	2.4
π-Bond order for C–F		0.736	0.593	0.507
$q_{C_{p_y}}$	0.00	0.324	0.456	0.520
$q_{C_{p_z}}$	1.106	0.770	0.754	0.712
$2 - q_{F_{p_y}}$		+0.324	+0.228	+0.174
$2 - q_{F_{p_z}}$		−0.466	−0.439	−0.409

viding some of this character. This is also reflected in the total charge density at fluorine which increases in the same order (*i.e.*, $CFH_2^+ > CF_2H^+ > CF_3^+$). In CF_3^+, the carbon p_y orbital contains 0.52 electron. This electron density decreases as fluorines are removed in CF_2H^+ and CFH_2^+ to 0.46 and 0.32 electron, respectively, reflecting the increased demand per fluorine atom for back donation as the number of fluorine atoms drops. Furthermore, the value of $q_{C_{p_y}}$ divided by the number of fluorines present is 0.1735, 0.2279, and 0.3236 for the series CF_3^+, CF_2H^+, and CFH_2^+. This increase shows that the fluorine in CFH_2^+ makes a larger back donation of its p_y electrons than do either of the fluorines in CF_2H^+, each of which back donate more strongly than the individual fluorines in CF_3^+.

Despite the fact that the fluorines' p_y orbitals have a net +0.1735 charge in CF_3^+, each fluorine still bears a net negative charge of 0.0284. This results from a sizeable polarization of the C–F σ bond toward fluorine. In the organic chemist's language, the $C_{sp^2}{}^+–F_{p_z}$ σ bond may be viewed as being strongly polarized toward fluorine in each of the cations. For example in CF_3^+ the value of $q_{F_{p_z}}$ is 1.4091. In other words, the fluorine p_y orbital contains an excess of 0.4091 electron over the value of 1 electron which it would contain in atomic fluorine. It is the fluorine p_z orbital which is participating in the σ bond to carbon. The magnitude of this σ polarization increases going from CF_3^+ to CF_2H^+ to CFH_2^+. That is, as the π back donation from fluorine to carbon increases, the forward σ polarization toward fluorine increases (see Figure 2). While each of these effects is substantial, the net total charge density on fluorine varies by only 0.087 in the series.

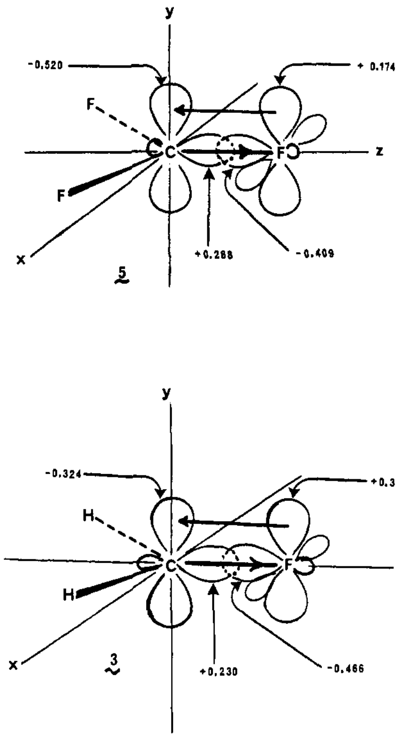

Figure 2. Back π donation and forward σ polarization in fluoromethyl cations.

As the C–F π-bond orders decrease, the C–F distances increase in a regular manner. For the series CFH_2^+, CF_2H^+, and CF_3^+ these distances are 1.277, 1.289, and 1.294 Å, respectively. This trend of increasing length with decreasing π-bond order is even more pronounced when one considers that the carbon has more total charge on it in CF_3^+ (+1.095) than in CFH_2^+ (+0.659). An increased charge density would be expected to cause the C–F distance in CF_3^+ to be less relative to CFH_2^+. Thus, the bond shortening effect of an increase in π-bond order is probably not fully visible in this series.

The C–H distance, optimized by INDO, in the methyl cation of 1.116 Å is longer than that found by OCE–SCF (1.074 Å),[11] extended Hückel (1.023 Å),[13] SCF–MO–LC (LCGO) (1.084 Å),[14] and *ab initio* 4-31G (1.076)[17] but about the same as predicted by *ab initio* STO-3G (1.120)[17] techniques.

B. Fluorinated Allylic Radicals. Calculations were performed on four fluorinated allylic radicals including the 1,1-difluoro-1-propenyl (**6**), 1,1,2-trifluoro-1-propenyl (**7**), *trans*-1,1,2,3-tetrafluoro-1-propenyl (**8**), and *cis*-1,1,2,3-tetrafluoro-1-propenyl (**9**) radicals. In each of these species the $C_1–C_2$, $C_1–F$, and $C_1–F_2$ bond lengths and C_2C_1F, $F_1C_1F_2$, and $C_2C_1F_2$ angles were optimized. Other lengths and angles were not optimized. Figure 3 summarizes the geometries and excess charge densities for radicals **6–9**.

In contrast to the favored pyramidal geometry of fluorinated methyl and cyclopropyldifluoro radicals, all four 1,1-difluoroallylic radicals were planar (sp^2) at C_1. Thus, by incorporating a strongly conjugating group on the

Table II. σ^a and π^b Charge Distributions in Radicals 6–9

Radical	C_1 σ	C_1 π	C_2 σ	C_2 π	F_1 σ	F_1 π	F_2 σ	F_2 π
6	+0.526	−0.067	+0.069	−0.036	−0.441	+0.067	−0.438	+0.068
7	+0.512	−0.099	+0.257	−0.045	−0.431	+0.075	−0.430	+0.078
8 (*trans*)	+0.516	−0.093	+0.243	−0.062	−0.419	+0.067	−0.415	+0.067
9 (*cis*)	+0.526	−0.101	+0.246	−0.058	−0.415	+0.067	−0.420	+0.065

[a] The σ excess charge densities are defined as $3 - (q_{p_x} + q_{p_z})$ for fluorine because the choice of the z axis along the C_1–C_2 bond prevents directly obtaining an electron density in an orbital lying diagonal to either the x, y, or z axis. For carbon the σ excess density is defined as $2 - (q_{p_x} + q_{p_z})$. [b] The excess π-charge density is defined as $1 - q_{p_y}$.

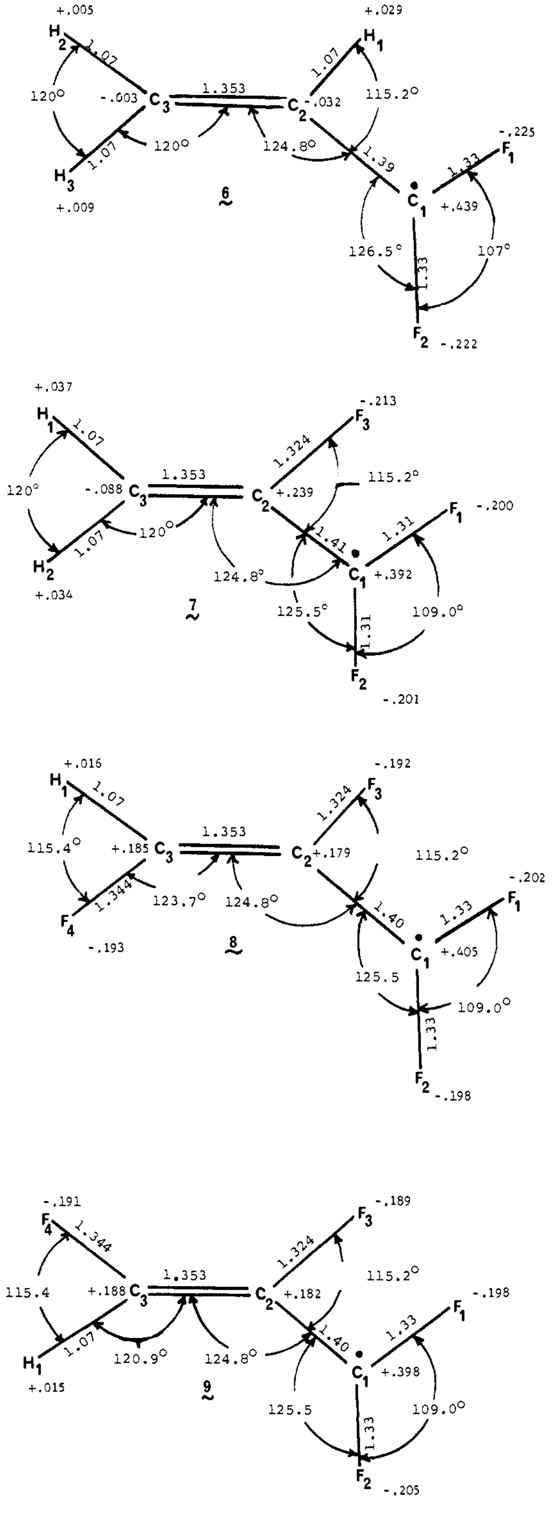

Figure 3. Geometries and calculated excess charge densities of fluoroallylic radicals 6–9.

$-CF_2\cdot$ function, sp^2 hybridization at C_1 is made increasingly more favorable. Furthermore, the plane defined by $F_1C_1F_2$ was also the plane of the vinyl group in the most stable conformation of radicals **6–9**. In fact, the preference for this all planar structure is quite strong as indicated by the large calculated rotational barriers about the C_1–C_2 bond. These varied from a high of 22.9 kcal/mol in **6** to a low 18.8 kcal/mol in **7**. The preference for the planar (sp^2) geometry at C_1 is illustrated by calculations on radical **6** where an out-of-plane deviation of 7° results in an increase in energy of 4.5 kcal/mol.

The total excess charge on F_1 and F_2 decreases when a fluorine is added to C_2 but remains approximately constant when additional fluorines are added to C_3. A more detailed description of the charge densities is given in Table II where a division is made between π and σ charge distribution at C_1, C_2, F_1, and F_2. In each radical a net negative excess charge resides in the C_{1p_y} orbital (this is also true for C_2). Since both the F_1 and F_{2p_y} orbitals exhibit a net excess positive charge, clear evidence for π back donation from fluorine to carbon exists. The magnitude of this donation is fairly small. The π-bond orders of the C_1–F_1 and C_1–F_2 bonds support this concept. As shown in Table III these π-bonds orders are between 0.24 and 0.26 for radicals **6–9**. In addition to F → C π donation, strong C → F σ polarization is evident from the large positive values of the carbon excess σ charge densities and the negative values for fluorine in Table II.

Table III summarizes the π-bond orders, C_1–C_2 rotational barriers, the s- and p_y-orbital spin densities, and the isotropic hyperfine couplings. For radicals **6–9** the unpaired spin density is largely concentrated in the C_{1p_y} orbital (0.59–0.62)[25] with a significant contribution in the C_{2p_y} orbital (−0.22 to −0.24). The terminal fluorines (F_1 and F_2) have only a small unpaired spin density located mainly in the p_y orbitals (0.055–0.066), and this is the third largest contribution (after C_1, C_{3p_y} and C_{2p_y}) found in these radicals. Thus, unpaired spin remains largely on the carbon π system with a small terminal fluorine π contribution.

C. Fluorinated Allylic Cations 10–14. Calculations were performed on five fluorinated allylic cations. There were the 1,1-difluoro-1-propenyl (**10**), 1,1,2-trifluoro-1-propenyl (**11**). *trans*-1,1,2,3-tetrafluoro-1-propenyl (**12**), *cis*-1,1,2,3-tetrafluoro-1-propenyl (**13**), and 1,1,2,3,3-pentafluoro-1-propenyl (**14**) cations. In each cation the C_1–C_2, C_1–F_1, and C_1–F_2 bond lengths and

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[25] The C_{3p_y} orbital in a symmetrical radical would exhibit the same spin density as the C_{1p_y} orbital. However, in **6–9** all the radicals are unsymmetrical. Furthermore, since the C_2–C_3 bond was not minimized, a strict comparison between C_1 and C_3 is not possible. However, qualitatively it is obvious that more spin density is found at the end of the allylic system (C_1 or C_3) containing the most fluorines.

Table III. π-Bond Orders, C_1–C_2 Rotational Barriers, s- and p_y-Orbital Spin Densities, and Isotropic Hyperfine Splittings Calculated for Fluoroallylic Radicals **6–9**

	Radical			
Calculated quantity	CH_2=CH—CF_2· **6**	CH_2=CF—CF_2· **7**	CFH=CF—CF_2· **8** (trans)	CFH=CF—CF_2· **9** (cis)
π-bond orders				
C_1–F_1	0.246	0.255	0.243	0.241
C_1–F_2	0.246	0.251	0.241	0.237
C_1–C_2	0.582	0.530	0.572	0.569
C_2–C_3	0.759	0.771	0.720	0.720
C_2–F_3		0.208	0.194	0.198
C_3–F_4			0.231	0.235
C_1–C_2 rotational barrier, kcal/mol	22.9	18.8	19.68	19.75
Unpaired orbital spin densities				
p_y C_1	0.590	0.621	0.596	0.601
C_2	−0.231	−0.222	−0.240	−0.243
F_1	0.056	0.066	0.057	0.057
F_2	0.056	0.063	0.056	0.055
s C_1	0.033	0.035	0.034	0.034
C_2	−0.018	−0.020	−0.021	−0.020
F_1	0.001	0.001	0.001	0.001
F_2	0.001	0.001	0.001	0.001
Isotropic hyperfine splittings, G				
C_1	26.9	28.3	27.6	27.6
C_2	−15.0	−16.0	−16.6	−16.8
C_3	22.5	20.9	22.3	22.1
F_1	36.6	48.5	43.5	43.9
F_2	37.1	43.8	39.8	41.8
F_3		−13.0	−14.9	−16.1
F_4			36.7	38.3
H_1	5.62	−11.7	−12.5	−11.9
H_2	−12.9	−11.1		
H_3	−12.3			

Table IV. Calculated π-Bond Orders, σ- and π-Charge Densities,[a] and C_1–C_2 Rotational Barriers of Fluorinated Allylic Cations **10–14**

	Cation				
Quantity calculated	**10**	**11**	**12** (*trans*)	**13** (*cis*)	**14**
π-bond orders					
C_1–F_1	0.464	0.474	0.443	0.441	0.423
C_1–F_2	0.460	0.461	0.435	0.429	0.414
C_1–C_2	0.534	0.515	0.582	0.590	0.630
C_2–C_3	0.819	0.816	0.732	0.723	0.662
C_2–F_3		0.183	0.166	0.171	0.154
C_3–F_4			0.417	0.432	0.402
C_3–F_5					0.391
C_1–C_3	0.333	0.352	0.316	0.319	0.284
C_1–C_2 rotational barrier, kcal/mol	11.2	21.2	30.4	32.5	38.4
Excess σ- and π-charge densities[a]					
C_1 σ	+0.437	+0.419	+0.429	+0.430	+0.441
π	+0.420	+0.409	+0.368	+0.359	+0.340
C_2 σ	+0.029	+0.260	+0.246	+0.246	+0.238
π	−0.118	−0.092	−0.154	−0.153	−0.203
F_1 σ	−0.416	−0.399	−0.392	−0.389	−0.383
π	+0.156	+0.163	+0.147	+0.147	+0.136
F_2 σ	−0.422	−0.404	−0.398	−0.403	−0.395
π	+0.153	+0.155	+0.142	+0.138	+0.131
F_3 σ		−0.317	−0.293	−0.296	−0.273
π		+0.035	+0.033	+0.035	+0.030

[a] The σ excess charge densities are defined as $3 - (q_{p_x} + q_{p_z})$ for fluorine and $2 - (q_{p_x} + q_{p_z})$ for carbon. The excess π-charge density is $1 - q_{p_y}$.

$C_2C_1F_1$, $F_1C_1F_2$, and $C_2C_1F_2$ angles were optimized. Other lengths and angles were not optimized. These geometries and the calculated excess charge densities are summarized in Figure 4.

The geometry at C_1 with the lowest energy was planar (sp^2) in each cation, and the plane defined by $F_1C_1F_2$ was also the plane of the attached vinyl function. In view of the planarity of the fluoromethyl cation and fluorinated

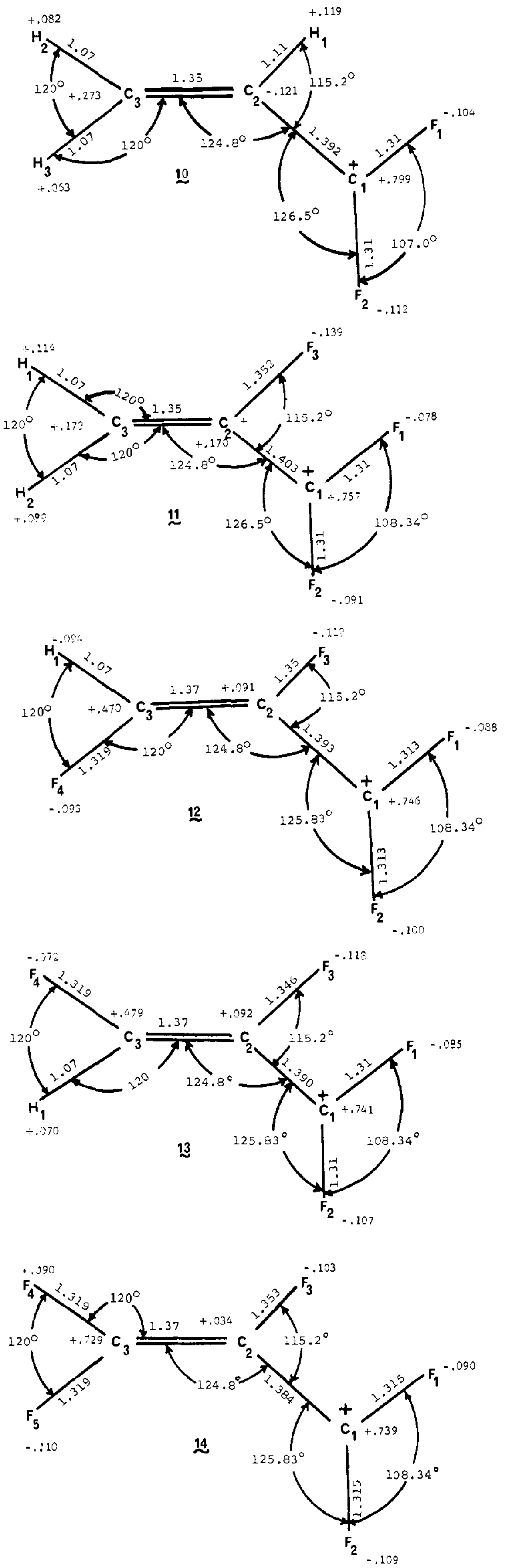

Figure 4. Geometries and excess charge densities of fluoroallylic cations **10–14**. The *y* axis is defined perpendicular to the plane of the cations (the *xz* plane) with the *z* axis along the C_1–C_2 bond.

allylic radical series, the preference for sp^2 hybridization of C_1 and the all planar geometry in allylic cations **10–14** was expected. The preference for planarity at C_1 in **10** is representative. Deforming the geometry out of plane by 1° resulted in a 1.5 kcal/mol increase in energy. The preference for the all planar cation geometry is further demonstrated by the C_1–C_2 rotational barriers of 11.2, 21.2, 30.4, 32.5, and 38.4 kcal/mol for **10–14**, respectively. Comparing these barriers to those of radicals **6–9** shows the cation barriers are larger in each case, except that of cation **10** (*vs.* radical **6**). However, it should be noted that the C_1–C_2 π-bond order in radical **6** (0.582) is greater than that in **10** (0.534). This is a manifestation of the much greater C_1–F π-bond orders in **10**. In fact, all the cations exhibit much larger C_1–F π-bond orders (0.41–0.47) than do the radicals (0.22–0.24). Since the cations exhibit greater F → C_1 back π-bonding, the need for C_1–C_2 π bonding is reduced (although it remains intrinsically larger for cations than radicals). The π-bond orders, charge densities in the σ and π framework, and rotational barriers are listed in Table IV.

In ions **12–14** the C_1–C_2 π-bond orders are greater than their corresponding radicals and in these examples their rotational barriers are markedly greater than those of the radicals. However, the relatively small rotational barrier of ion **10** compared to ion **11** (which has a smaller π-bond order) could also be due, in part, to the magnitude of the C_1–C_3 π-bond order. During rotation this π order goes to zero in all the ions. In ion **11** the C_1–C_3 π-bond order is greater than in **10**. Thus, some greater degree of overlap must be destroyed in **11** than **10** and this may contribute to the larger barrier in **11**.

The question of the importance of 1–3 overlap in allylic cations has been raised on several occasions.[19,21,26] Hückel molecular orbital theory predicts the overlap integral between the C_1 and C_3 to be 1β in cyclopropenyl cations. Simonetta and Heilbronner[27] calculated the charge distribution in the simple allylic cation taking into account contributions of 1,3 π interactions between the terminal carbons and obtained $C_{1\text{ and }3}$ and C_2 charge densities of 0.367 and 0.266, respectively. Olah[21] argued that the large deshielding experience by the C_2 proton in the simple allylic cation (−9.64 ppm) indicated a strong contribution of 1,3 π interaction especially in view of the −10.3 ppm shift of the ring proton in the dipropylcyclopropenyl cation.[28] Deno[19] correlated the uv λ_{max} of the 1,2-dipropylcyclopropenyl cation (below 185 nm), pentamethylcyclobutenyl cation (λ_{max} 245 nm), and the 1,3-dimethylcyclopentenyl cation (λ_{max} 274 nm) with overlap values of 1β, 0.2β, and 0.1β, respectively. Katz,[26] using a transition energy value of 1.93β, calculated the 1,3 π-resonance integral (β_{13}) to be 0.33β in the cyclobutenyl cation. Here the 1,3 interaction is expected to be much larger than that for acyclic allylic cations. Thus, the large C_1–C_3 π-bond orders calculated for ions **10–14** (see Table IV) are somewhat surprising. This is especially true in view of the large C_1–F (hence, C_3–F) π-bond character which would be

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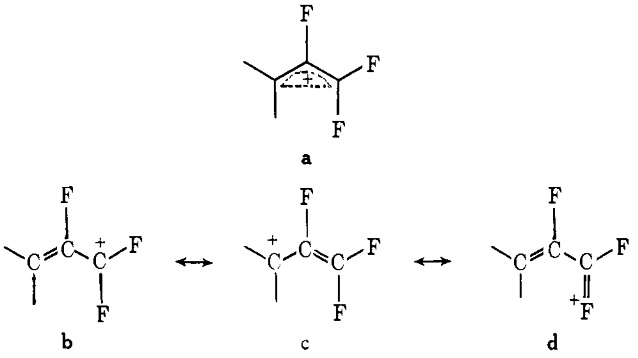
(26) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964).

(27) M. Simonetta and E. Heilbronner, *Theor. Chim. Acta*, **2**, 228 (1964).

(28) R. Breslow, H. Hover, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

expected to reduce the need for 1–3 π bonding. As the number of terminal fluorines is increased from two (**10**) to three (**12**) to four (**14**) the 1–3 π-bond orders steadily decrease from 0.333 to 0.316 to 0.284, respectively, while the introduction of a fluorine at C_2 causes an increase in this order. Extrapolating these results to the unsubstituted allylic cation, we estimate a π-bond order greater than 0.35. These results indicate hybrid **15a** is not unreasonable to invoke as part of an overall description of ions **10–14**.



15

Examination of the σ- and π-charge densities for ions **10–14** reveals that the addition of fluorine at C_2 places a stronger electron demand at C_1 through its strong negative inductive effect (σ polarization). This $-$I effect is not counterbalanced by strong π back donation from fluorine to carbon. This is evident in ion **11** where the C_1–F_1 and C_1–F_2 π-bond orders (0.4735 and 0.4607) are far larger than the C_2–F_3 π-bond order of only 0.1829. This qualitatively agrees with a simple valence bond picture where it is impossible to write a resonance hybrid structure with a double bond between C_2 and F_3 without introducing additional charge separation.

It is interesting to note that the total excess negative charge density on F_1 and F_2 decreases going from **10** to **11** and then increases very slightly going from **11** to **12–14**. The addition of fluorine at C_2 inductively polarizes the σ system causing a net drain on charge at F_1 and F_2. In ion **10** where a somewhat larger π back donation from F_1 and F_2 to C_1 occurs than in **12**, **13**, and **14**, these two fluorines also have the greatest excess negative charge density. In other words, here is an example where the negative charge density increases at fluorine despite the fact these fluorines delocalize more positive charge toward carbon by back π donation. This donation is more than compensated by σ polarization from carbon to fluorine.

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Acidities of Polyfluorinated Hydrocarbons. II. Hexafluoropropanes, Trifluoroethanes, and Haloforms. Intermediate Carbanion Stability and Geometry

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Abstract: Pseudo-first-order kinetic acidities have been determined for a series of 2-substituted 1,1,1,3,3,3-hexafluoropropanes, 1,1,1-trifluoroethanes, and haloforms by hydrogen, deuterium, and tritium isotope exchange reactions. Techniques of ^{19}F nmr, ir, and scintillation counting were used to determine these acidities. The solvent-catalyst system employed was a 50:50 mol % solution of dimethyl sulfoxide and methanol with triethylamine as catalyst. Internal return and α- and β-halogen elimination reactions of the intermediate carbanions were negligible in this solvent system. The acidity data obtained were interpreted in terms of the stabilities and geometries of the intermediate carbanions involved. In these studies, the two main factors that determine fluorocarbanion and halocarbanion stabilities appear to be induction and destabilization by a +R-p-orbital electron feedback mechanism. Probes of carbanion geometries have been made by consideration of (a) stability trends in the series of anions studied and (b) the fact that the +R destabilization mechanism is most effective in planar structures. The data indicate steric factors and the +R effect have substantial influence on carbanion geometries. Also, it is postulated that although the carbanions studied are either close to planar (sp^2 hybridized) or close to pyramidal (sp^3 hybridized), slight forced changes in the geometry of a carbanion which belongs to either group have a significant effect on the stability of that carbanion.

Carbanions (the conjugate bases of "carbon acids") are common in fluoro and halo organic chemistry in general, since the halogens can stabilize carbanions readily by several effective mechanisms. However, the correct interpretation of the stabilization is difficult since so many rationales have been presented.[2,3]

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(1) NSF Trainee 1965–1968, and Phillips Petroleum Fellow 1968–1969. The majority of this work was taken from the Ph.D. thesis of K. J. K., 1969.

(2) For an excellent review see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, London, 1965.

(3) K. J. Klabunde and D. J. Burton, *J. Amer. Chem. Soc.*, **94**, 820 (1972).