Structures of Gas-Phase $C_7F_7^+$ Ions

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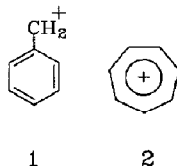
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In an ion cyclotron resonance spectrometer, less than 96% of the $C_7F_7^+$ cation formed on electron ionization of perfluorotoluene reacts with hexamethyldisilazane. In contrast, the $C_7F_7^+$ from perfluoronorbornadiene or perfluorobicyclo[3.2.0]hepta-2,6-diene is nonreactive with hexamethyldisilazane. Collision-induced dissociation results support this dichotomy, although the evidence is not as clear-cut. The reactive ion is assigned the benzyl structure and the nonreactive ion the tropyl structure, on the basis of analogy with the protio cases. By AM1 calculations, the perfluorobenzyl ion is 25 kcal/mol more stable than the perfluorotropyl ion, the opposite of the situation for the protio analogs (-12 kcal/mol). Ab initio calculations at the 3-21G level agree with the semiempirical energy difference to within 0.4 kcal/mol; at the more appropriate 6-31G*/MP2 level, the perfluorobenzyl cation is 9.7 kcal/mol more stable than the perfluorotropyl cation. (*J Am Soc Mass Spectrom* 1993, 4, 813–818)

One of the classic problems in the chemistry of gas-phase ions is the question of the structure of the $C_7H_7^+$ ions obtained from electron ionization (EI) of neutral precursors such as toluene [1]. It appears that two isomers of $C_7H_7^+$, the benzyl cation (1) and the tropyl cation (2), are formed in this process. The tropyl form is more stable than the benzyl form by 12 kcal/mol [2] and is produced in appreciable amounts even from toluene as a precursor [3–17]. The ratio of the two forms is a function of the structure of the neutral precursor, the mass spectral time frame in which the ion population is analyzed, and the energy of the ionizing electrons [18]. In some cases, the possibility of other $C_7H_7^+$ structures, such as tolyl ions, has been invoked [19]. At lower internal energies, the structural isomerization is thought to occur on the $C_7H_8^{+\cdot}$ radical cation surface, followed by loss of a hydrogen to produce $C_7H_7^+$. At higher internal energies, the $C_7H_7^+$ isomers can directly interconvert.


1   2

Although much research has centered on the structure of $C_7H_7^+$ ions emanating from C_7H_8 and C_7H_7X neutral precursors, there appears to be little information in the literature with regard to the structures of the analogous cations that arise from the perfluorinated analogs of the neutral precursors. The $[M - F]^+$ ion is the base peak in the spectra of $C_6F_5CH_2X$ species, but the structure was assumed to be tropyl, with no evidence presented [20]. McLafferty and Amster [21] have examined the $C_7H_6F^+$ ions from monofluorinated toluenes and cycloheptatrienes via collision-induced dissociation (CID) and shown that there is less extensive isomerization than for the $C_7H_7^+$ case, although some still occurs. In solution, α-fluorocarbenium and perfluorocarbenium ions, including benzyl, are stable species at temperatures where the protio analogs react [22]. The perfluorotropyl cation is also stable in solution [23]. The perfluorinated C_7F_8 neutrals would be expected to yield C_7F_7 cations on EI. The question of whether such ions would be of benzyl or tropyl structure is intriguing because our semiempirical molecular orbital calculations indicate that the perfluorobenzyl cation is 25 kcal/mol more stable than the perfluorotropyl cation, the opposite of the relative stabilities of the protio analogs.

We investigated the benzyl/tropyl ratio of $[M - F]^+$ ions arising from EI of three C_7F_8 neutral precursors, using as structural probes both their chemical reactivity in an ion cyclotron resonance (ICR) spectrometer

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and the low-energy (quadrupole mass spectrometer) CID mass spectrum. The perfluorinated precursors investigated are perfluorotoluene (PFT) (3), perfluorobicyclo[2.2.1]heptadiene [perfluoronorbornadiene (PFN)] (4), and perfluorobicyclo[3.2.0]hepta-2,6-diene (PFH) [5]. The intermediacy of perfluorocycloheptatriene (6) is also discussed.
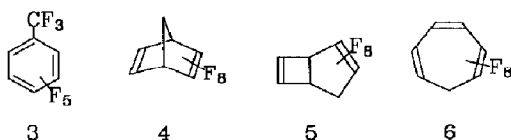
Experimental

The ICR spectrometer is a homebuilt instrument that has been described elsewhere [24]. The $C_7F_7^+$ ions were produced by EI at 30-eV electron energy. Reduction of this energy to 13 eV did not affect the reactivities reported below. The CID spectra were obtained on a VG Instruments (UK) ZAB-EQ mass spectrometer of BEqQ geometry [25] at 70-eV ionizing electron energy for primary ion formation. These experiments were also done by producing the $C_7F_7^+$ ions from all three precursors at 12-eV ionizing electron energy, with essentially no change in the CID spectra. For the CID experiment, the parent $C_7F_7^+$ ions were at 50-eV laboratory frame kinetic energy; the argon collision gas pressure was nominally 6×10^{-6} torr. The actual argon pressure in the collision quadrupole is approximately 200 times greater than this value, which was measured downstream from the cell on the pumping line. Conditions for all three precursors were set identically rather than optimizing the conditions for each precursor. CID of "cold" $C_7F_7^+$ was recorded by setting the magnetic and electrostatic sectors to transmit the product of the first field-free region (FFR) metastable transition, $C_7F_8^{+\cdot} \rightarrow C_7F_7^+$, then collision with CID gas in the first quadrupole, followed by mass analysis of CID products in the second quadrupole.

The AM1 semiempirical molecular orbital calculations [26] were carried out with the MOPAC 5.0 program (Program No. 455, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN) on the UTK Vax 6000 system. All radical cations were calculated at the unrestricted Hartree-Fock level, and all geometric variables were optimized without restraint. Because of time considerations, the transition state energies given are not precise saddle points based on imaginary frequencies; rather, they are energy maxima during reasonable geometric variation between structures that are energetic minima. They are thus upper limits to the transition state energies but are probably within 2 kcal/mol of the correct values. AM1 calculations predict the enthalpy of the benzyl $C_7H_7^+$ ion to be 12 kcal/mol greater than that of the tropyl isomer;

experimentally, benzyl is 12 kcal/mol greater than tropyl [2]. Thus, AM1 calculations appear to be accurate for carbenium ion energetics of this type.

Ab initio molecular orbital calculations were carried out with the Gaussian 90 program (Gaussian, Inc., Pittsburgh, PA) on an IBM 3094 computer. The perfluorobenzyl cation was constrained to C_2v symmetry and the perfluorotropyl cation to D_7h symmetry.
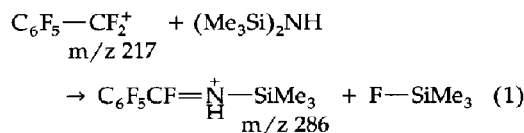
PFT and hexamethyldisilazane were obtained from Aldrich Chemical Co. (Milwaukee, WI) and were pure by ICR and EI mass spectrometry. The two perfluorobicyclic isomers were obtained from Lemal and Dailey [23] and were used as received but were protected from light. The ICR and EI mass spectra of these showed no species other than C_7F_8.

Results

Ion Cyclotron Resonance Results

The relative amounts of benzyl and tropyl cations in the $C_7F_7^+$ population were determined on the basis of their differing reactivity. This methodology has been successfully employed in earlier investigations of $C_7H_7^+$ ions by assuming that the part of that ion population that reacts in ion–molecule reactions with various aromatic and unsaturated neutral nucleophiles is the benzyl form and that the nonreactive population is in the more stable tropyl form [13]. We find, however, that the $C_7F_7^+$ ion from PFT, which might be assumed to have at least some of the benzyl structure present, is unreactive with the neutrals used (benzene, toluene, naphthalene, and xylene) as probes for the structure of $C_7H_7^+$. With benzene there is a $C_7H_5F_2^+$ ion formed, as expected, but double resonance indicates that its precursor ion is the parent $C_7F_8^{+\cdot}$ ion, not $C_7F_7^+$. Charge transfer from $C_7F_8^{+\cdot}$ to benzene is also observed.

Use of $(Me_3Si)_2NH$, as a more nucleophilic species with a structure sensitive to the presence of fluorine atoms, proved successful. Reaction 1 proceeds with $k = 1 \times 10^{-10}$ cm³/molecule/sec at 305 K. The entire (> 96%, based on the signal-to-noise ratio) $C_7F_7^+$ population from PFT reacts in this fashion:

$$C_6F_5-CF_2^+ + (Me_3Si)_2NH$$
$$m/z\ 217$$

$$\rightarrow C_6F_5CF=\overset{+}{\underset{H}{N}}-SiMe_3 + F-SiMe_3 \quad (1)$$
$$m/z\ 286$$

In contrast, when the $C_7F_7^+$ ions from either PFN or PFH are formed in the presence of $HN(SiMe_3)_2$, the m/z 217 ion abundance is not observed to decrease ($k < 1 \times 10^{-12}$ cm³/molecule/s), and no product ion at m/z 286 is observed above the noise level. Thus, the $C_7F_7^+$ ions from PFT are over 96% in one (reactive) form, and those from PFN and PFH are a different (> 96% nonreactive) form or forms. In parallel to the

$C_7H_7^+$ results, it is reasonable to assume that the reactive population consists of the benzyl structure. We assume likewise that the nonreactive population is the tropyl structure, although it could also be a mixture of forms, or some other nonreactive form besides tropyl. As noted below, the tropyl cation is expected to be the most stable cation of the nonbenzyl possibilities and also has the least positive charge on the carbenium carbons, so low reactivity for it might be expected.

ICR spectrometry does not measure ionization and appearance energies very accurately because of the presence of the potential trapping well in the cell and the smaller dynamic range than for electron multiplier detectors. For PFT, we find an ionization energy of 10.2 eV (9.9 eV [2]) and an appearance energy for $C_7F_7^+$ of 13.6 eV. The relative value of these two measurements is probably more accurate than their absolute values, indicating that fluorine loss requires approximately 3.4 ± 0.4 eV (78 ± 10 kcal/mol) of energy above ionization. This is a reasonable value for a bond strength in a radical cation.

Collision-Induced Dissociation

The results from low-energy CID support the above conclusions in that the spectra of $C_7F_7^+$ from PFH and PFN are very similar and are appreciably different from that from PFT. Although the CID spectra from the three neutrals consist of the same masses, as shown in Table 1, in PFT the m/z 69 (CF_3^+) ion is 60% more intense relative to the base fragment peak at m/z 167 ($C_6F_5^+$) than in the spectra from either PFH or PFN. The latter two CID spectra are identical to within 3%. It is indicative that the CF_3^+ ion is more intense in the spectrum of the (presumed) benzyl form, where there is more than one fluorine atom on some carbon in the precursor structure. The m/z $69^+/167^+$ intensity ratio for PFT is the same for an ionizing electron energy of 70 and 12 eV, respectively, indicating that the effect of internal energy on the CID results are minimal. Also, we find that $C_7F_7^+$ metastable ions from 3, formed in the first FFR, show essentially the same CID spectrum

as those produced by direct EI. The $69^+/167^+$ ratio in this metastable/CID experiment was 10% greater than for the source-produced $C_7F_7^+$ ions, but all other ions abundances relative to 167^+ were the same to within 3%. There was insufficient sample of 4 and 5 to carry out the metastable/CID experiments with these isomers.

Discussion

Although the results here indicate that there are at least two discrete isomers of $C_7F_7^+$ formed by EI of various precursor neutrals, some further justification for their lack of interconversion is desirable. We carried out ab initio calculations on the perfluorobenzyl and perfluorotropyl cations. As shown in Table 3, at the 3-21G level, the benzyl form is 25.8 kcal/mol more stable than the tropyl form. However, the presence of fluorine atoms makes it necessary to use polarization functions to obtain reasonable energies in such ab initio calculations. At the 6-31G* level, the benzyl is only 2 kcal/mol more stable than the tropyl. Further refinement at the MP2 level of correlation interaction using the 6-31G* geometry results in the benzyl being 9.7 kcal/mol more stable than the tropyl. The MP2 correlation energy amounts to approximately 2 hartrees. Because of the prohibitive cost of such calculations, we carried out further work at the semiempirical level.

AM1 semiempirical calculations [26] were carried out for the various structures on the $C_7F_8^+\cdot/C_7F_7^+ + F\cdot$ hypersurface to examine possible pathways for interconversion of these isomers (Table 2). These indicate that the perfluorobenzyl cation is 25.5 kcal/mol more stable than the perfluorotropyl cation, reasonably close

Table 1. Collision-induced dissociation fragments from m/z 217 $(C_7F_7^+)^a$

m/z	Formula	Relative abundance		
		PFT	PFN	PFH
167	$C_7F_5^+$	100	100	100
148	$C_6F_4^+$	15	13	13
129	$C_6F_3^+$	4	5	5
117	$C_5F_3^+$	45	37	40
93	$C_3F_3^+$	14	11	13
69	CF_3^+	66	42	42

^{a} VG ZAB EQ, in the qQ sector, 50-eV parent ion laboratory frame kinetic energy, 6 μtorr Ar collision gas pressure, 70-eV ionizing electron energy. PFT, perfluorotoluene; PFN, perfluoronorbornadiene; PFH, perfluorobicyclo[3.2.0]hepta-2,5-diene.

Table 2. AM1 calculated heats of formation pertinent to the $C_7F_8^+\cdot$ surface^a

	Neutral	Cation	
C_7F_8			
PFT, 3	−338.8	−111.8	
PFN, 4	−279.6	−52.2	
PFH, 5	−273.9	−44.8	
Perfluorocycloheptatriene, 6	−296.3	−78.8	
"Ipso" form, 7	—	−77.3	
o-Isotoluene, 8	−310.5	−105.3	
Norcaradiene, 9	−283.6	−64.5	
$C_7F_7^+$			
Benzyl	−277.3	−68.6	(0)
Tropyl	−244.3	−43.1	25.5
m-Tolyl	—	13.5	82.1
2-Allyl of 5	—	4.9	73.5
C-7 carbenium of 4	—	18.3	86.9

^{a} ΔH°, (kcal/mol). Abbreviations as in Table 1.

to the best ab initio calculation. The structures are somewhat looser than in the ab initio calculations, as shown in Table 3. Of the various neutral isomers, only PFT has an experimentally known enthalpy of formation [27] and ionization potential [2]. The AM1 calculations reproduce the $\Delta_f H°$ (PFT) only moderately well (-303 kcal/mol experimental [27] versus -339 kcal/mol calculated); however, the experimental $\Delta_f H°$ (PFT) disagrees with the $\Delta_f H°$ (PFT) of -351 kcal/mol predicted by group additivity [28] by 48 kcal/mol! It thus appears that the neutral thermochemistry for PFT may be in considerable error. In contrast, AM1 calculations yield a very good adiabatic ionization potential (9.84 V calculated versus 9.9 V experimental [2]) for PFT. To verify that AM1 calculations are reliable for perfluorinated aromatic species, we examined the corresponding data for hexafluorobenzene. In this case, AM1 calculations give $\Delta_f H° = -231$ kcal/mol; experimentally, the value is -228 kcal/mol [27]. Thus, we suspect that the experimental PFT value is in error, not the AM1 calculations. For the ionization energy of hexafluorobenzene, AM1 calculations give 9.79 eV; experimentally, it is 9.91 eV [2]. It appears that AM1 calculations are reasonably accurate (± 5 kcal/mol) for these perfluorinated species and that the experimental $\Delta_f H°$ (PFT) may be in error.

Table 3. Geometries and energies for perfluorobenzyl and perfluorotropyl cations (AM1 and ab initio calculations)[a]

|	AM1	3-21G	6-31G*/MP2
Perfluorobenzyl cation[b]			
$C_\alpha - C_i$	1.4169	1.3706	1.3853
$C_i - C_o$	1.4373	1.4153	1.4286
$C_o - C_m$	1.4087	1.3532	1.3601
$C_i - C_p$	2.8555	2.7465	2.7685
$F - C_\alpha$	1.3148	1.2834	1.2484
$F - C_o$	1.3389	1.3239	1.2918
$F - C_m$	1.3455	1.3353	1.3027
$F - C_p$	1.3306	1.3141	1.2789
$C_\alpha - C_i - C_o$	120.64	120.53	120.89
$C_i - C_o - C_m$	120.68	120.12	120.70
$F - C_\alpha - C_i$	125.34	123.65	123.39
$F - C_o - C_i$	119.23	119.55	119.59
$F - C_m - C_o$	120.32	120.89	121.33
Hartree-Fock energy		-955.53621	-962.80574
Perfluorotropyl cation[c]			
$C - C$	1.4216	1.3746	1.3824
$F - C$	1.3486	1.3279	1.2910
Hartree-Fock energy		-955.49516[d]	-962.79034[e]

[a] Bond lengths in angstroms, bond angles in degrees.
[b] AM1: complete geometry optimization; was planar and near C_{2v}; 3-21G and 6-31G*: constrained to C_{2v} geometry; C_i is the ipso carbon.
[c] AM1: complete geometry optimization, within 0.0002 Å of D_7h; 3-21G and 6-31G*: constrained to D_7h geometry.
[d] Perfluorobenzyl more stable than perfluorotropyl by 25.76 kcal/mol.
[e] Perfluorobenzyl more stable than perfluorotropyl by 9.66 kcal/mol.
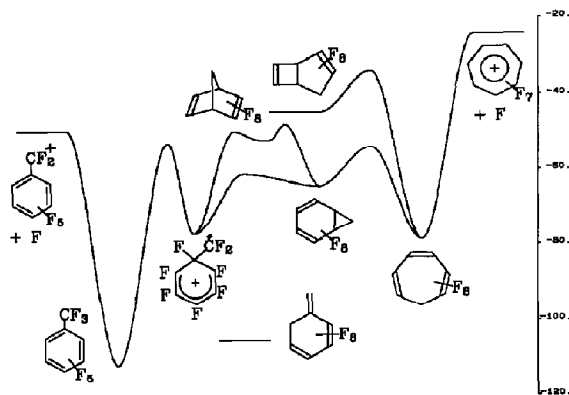
Figure 1. Minimum energy reaction pathway for the $C_7F_8^{+·}/C_7F_7^+ + F·$ system, by AM1 calculations.

The pathways for isomerization/fragmentation selected are the analogs of those for the minimum energy reaction pathways (MERPs) chosen for the protio case [29]. Part of the AM1 calculated surface is shown in Figure 1. It must be remembered that under our experimental conditions, the actual molecular interconversions occur in vibrationally excited states, 2–3 eV above the channels for production of $C_7F_7^+$, and that the rates of the processes are determined not only by the potential energy surface shown, but also by the density of excited states above each isomer. The fragmentation channels are especially favored, beyond that shown on the energy surface, owing to separation into two species and the resultant increase in the number of accessible states. We assume that loss of fluorine via direct bond cleavage is a barrierless process. The calculated fragmentation threshold for PFT of 62 kcal/mol compares favorably with our rough measurement of 78 kcal/mol.

There is no reasonable isomerization pathway leading from **5** to the benzyl cation without going through **6**, so that production of the nonreactive perfluorotropyl ion is reasonable. Isomerization of **4** could go either way energetically, via a 1,3 shift of the bridging carbon to the norcaradiene structure **9** or via a simple bond cleavage to the "ipso" isomer **7**. Fluorine loss could occur directly from **7** as well. There is a preference at lower internal energies for rearrangement products, relative to bond cleavages, in mass spectral fragmentations [30], so production of **9**, continuing on to the tropyl cation, can be rationalized also. There was no energetic minimum found for the radical cation of perfluoroquadricyclane.

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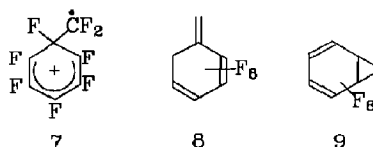
In addition to the isomerization shown in Figure 1 there are two other MERPs possible, one involving direct isomerization of the $C_7F_7^+$ ions after loss of fluorine and one for isomerization of the o-isotoluene radical cation 8 via distonic radical cation species. Although 8, as shown in Figure 1, is relatively low in energy, further intermediates for that isomerization are at -26 and $+4$ kcal/mol $\Delta_f H$, such that it is unlikely to be an accessible pathway near threshold for production of $C_7F_7^+$. This is in contrast to the protio case [29], where the distonic ion MERP and the one comparable to that shown in Figure 1 are competitive in terms of the potential energy surface.

Finally, there are other $C_7F_7^+$ isomers possible: a perfluorotolyl ion from loss of a ring fluorine in 3, an allyl cation from loss of a fluorine from the CF_2 group in 5, and the C-7 carbenium ion in 4 are some of these. All of these are considerably higher in energy than the benzyl or tropyl ions and are, respectively, 48, 57, and 61 kcal/mol higher in energy than the perfluorotropyl cation by AM1 calculations. Therefore, thermochemically by AM1 calculations, the most reasonable structure for the nonreactive form is tropylium.

Comparing the ICR and CID results, it is evident that the low-energy ion–molecule data imply a considerable difference in the populations of $C_7F_7^+$ ions formed from PFT versus PFN and PFH. In contrast, the CID results appear to be rather insensitive to structure in these cases, although the small differences observed support the ICR results.

Is there any justification for the reversal of stability of the $C_7F_7^+$ isomers, relative to the protio cases? Fluorine stabilizes an adjacent cation by a π-donation interaction, so it should have a larger stabilizing effect when the bulk of the charge is localized at a site where this donation effect can operate [22]. In the perfluorobenzyl cation, by AM1 calculations, there are 0.59 charge units on the exo-CF_2 group, whereas in the benzyl cation itself there are 0.47 charge units on the exo-CH_2 group. The fluorines are thus localizing the charge at the α-carbon, relative to the protio case.

Conclusions

In contrast to the well-known benzyl/tropyl $C_7H_7^+$ case, for the perfluoro analogs the benzyl form appears to be favored thermodynamically, presumably because of the ability of the fluorine to stabilize localized charge at the α-carbon in the benzyl cation better than the delocalized charge at the carbons in the tropyl cation. The benzyl form appears to be the major product of EI/fragmentation of PFT. This is based on reaction of $C_7F_7^+$ with hexamethyldisilazane, a reagent that has the potential for being a general probe for the structure of fluorinated carbenium ions. In contrast, two other C_7F_8 isomers, PFN and PFH, yield $C_7F_7^+$ ions that are not reactive with the structure probe. Because the tropyl structure is calculated to be so much more stable than any other reasonable alternative carbenium

ion structure, other than the benzyl one, we assign the tropyl structure to the nonreactive $C_7F_7^+$ ions.

Acknowledgments

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