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Structure and Relative Stability of Halogenated Carbocations: The $C_2H_4X^+$ and $C_4H_8X^+$ (X = F, Cl, Br) Cations

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Abstract: Ab initio calculations are reported for the $C_2H_4X^+$ and $C_4H_8X^+$ cations using MP2/6-31G**//MP2/6-31G** where the halogen is fluorine or chlorine. The bromine substituted cations were computed with use of a pseudopotential (LANL1DZ) basis set. The final MP2 energies show that dimethyl substitution has no effect qualitatively on the preference for α-halo isomers in the case of fluorine and chlorine and halogen bridged isomers in the case of bromine. Comparison of the computed hydride affinities across halogens did turn up significant differences in the relative abilities of different halogens to stabilize a carbocation depending on the level of substitution. For the more highly alkyl substituted cation ($C_4H_8X^+$), fluorine substitution is more favorable than chlorine substitution. This is consistent with conventional wisdom that fluorine is a better electron donor than chlorine in spite of its greater electronegativity because of superior overlap between the fluorine and carbon 2p orbitals. For $C_2H_4X^+$ this preference for fluorine substitution over chlorine substitution disappears with both giving virtually identical stabilities. Reducing alkyl substitution further (CH_2X^+) leads to a significant preference for chlorine over fluorine. In general, these results argue that electron-donating substituents favor α-fluoro cations while electron-withdrawing substituents favor α-chloro cations. Finally the computed gas-phase halocation stabilities are compared directly to a well-known stable cation, *tert*-butyl, and found to be surprisingly competitive.

Introduction

The structure and energetics of halogen substituted cations have generated widespread interest in recent years.[1-8] High-level ab initio calculations have been reported for the $C_2H_4X^+$ cation where X is fluorine,[3] chlorine,[4] or bromine.[5] These calculations all find two classes of minima (Figure 1), one where the halogen is bridged (**1**) and a second where the halogen is directly bound to the cationic center (**3**). For each halogen the classical 2-haloethyl cation is least stable, and it is found to be a transition state, not a minimum, on the potential energy surface when the halogen is chlorine or bromine. For the fluorine[3] and chlorine[4] substituted cations the α-halo isomer (**3**) is most stable. The bridged cation is most stable when the halogen is bromine.[5] These results are consistent with gas-phase[6,7] and solution[1,2] studies which find bromine exhibits the greatest propensity to form bridged halonium ions followed by chlorine. A recent matrix isolation study[8] for $C_2H_4Cl^+$ and $C_2H_4Br^+$ confirms the theoretical result that the most stable isomer for the chloro cation is **3** while for bromine it is **1**. There is no experimental evidence for the fluoronium ion being a minimum, although it has been identified recently as a transition state for 1,2 fluorine shifts.[9]

By computing hydride affinities it is possible to compare the halogens to each other. This has been done[10] for $C_2H_4X^+$ and leads to a prediction that the bromine (bridged) substituted cation is most stable followed by chlorine (α-halo) and fluorine (α-halo). Surprisingly, the same order is found even when comparing only the α-halo isomers in contradiction to superacid[1] studies which appear to show that fluorine is the best halogen at stabilizing an adjacent cation.

Calculations for $C_2H_4X^+$ are valuable in providing insight into the stability of halogen substituted carbocations. There is a real question, however, as to whether the simple ethyl cation is a reasonable model for larger halocations. Most systems of practical importance involve generation of secondary or tertiary carbocations (in a doped polymer for example), not extremely unstable primary cations. One might argue that the ethyl system is strongly biased toward nonclassical bridged or α-halo cations since this is the only way to avoid a primary cation. The next highest analogue for examining the relative stability of bridged and α-substituted halocations is the 2-butyl system[9,11] $C_4H_8X^+$. Halogenated 2-butyl cations should be better models for larger halogenated cations, and the relative stabilities of the classical, bridged, and α-halo isomers computed for this system should be correspondingly more general.

Procedure

All stationary points involving fluorine or chlorine were located using the HF/6-31G** basis set as implemented in the Gaussian88[12] and Gaussian90[13] programs. In the case of bromine substituted cations a pseudopotential basis set (LANL1DZ) was used which is double-ζ in the valence region.[14] Using the pseudopotential basis set for the bromine substituted cations significantly reduces computation time, but it should be comparable in the valence region to the valence double-ζ basis set employed for the other halogens. It has been observed that polarization functions are necessary to obtain the correct relative energies for **1c** and **3c**,[5] therefore, the final MP2 calculations were carried out with d-functions on carbon and bromine. The d-exponent for bromine was set at 0.40 as suggested by Hamilton and Schaefer.[5] The d-exponent on carbon was kept at the 6-31G** value in order to be consistent with the other cations. All critical points were tested by computing the Hessian matrix at the HF level. Where more than one conformer was examined, the force constants were computed only for the most stable conformer.

It is widely accepted[15,16] that correlation effects are particularly important when studying nonclassical ions, therefore, all stationary points were recomputed at the MP2 level. In cases such as **5** and **6**, only the lowest energy conformation as determined by MP2 single-point calcula-

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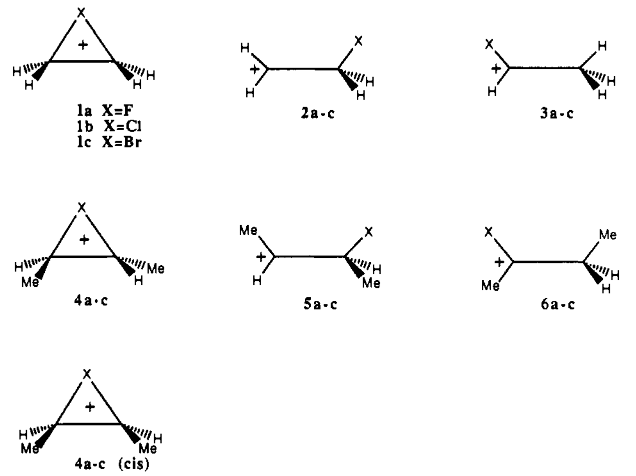

Figure 1. Isomers of $C_2H_4X^+$ and $C_4H_8X^+$ where X is fluorine, chlorine, or bromine.

tions was recomputed with full optimization at the MP2 level. This procedure leads to final energies for the fluorine and chloride substituted cations which were computed using the MP2/6-31G**//MP2/6-31G** model. For bromine the final energies were obtained using MP2/LANL1DZ*//MP2/LANL1DZ*.

In order to determine the relative stabilities of all carbocations in this study it is necessary to compute hydride affinities. The hydride affinities allow us to speak not only to energetic differences between isomers of the same halocation but also to the relative abilities of different halogens to stabilize carbocations. This is important with respect to many practical applications including photoresists[17] and conducting polymers.[18,19] The hydride affinities quoted in this paper have been calculated using a total energy for H^- which has been estimated from the experimental[20] ionization potential and electron affinity of hydrogen. The experimental energy of H^- gives better agreement with measured hydride affinities than HA's calculated using the 6-31G** energy of H^-. The reason is that H^-, like all anions, requires a basis set augmented with diffuse functions in order to get reasonable energies. Otherwise the computed energies are much too positive. Rather than use mixed basis sets to compute hydride affinities or add unnecessary diffuse functions to the cations, the hydride affinities were computed using the experimentally derived total energy of H^-. Of course, the choice of reference energy for H^- has no effect on the *relative* hydride affinities.

$C_2H_4X^+$ Cation

The computed energies and hydride affinities (HA) for $C_2H_4X^+$ are reported in Table I. The α-fluoro cation (**3a**) is found to be most stable at the HF level with the α-chloro cation (**3b**) close behind. Both bromo cations (**1c**,**3c**) are less stable than **3a** and **3b**, but the least stable cation is found to be the fluorine bridged structure, **1a**. Inclusion of electron correlation at the MP2 level has a dramatic effect on the relative stabilities of both isomers of the brominated cation, especially **1c**. In general, inclusion of electron correlation preferentially reduces the energy of the cations containing the heavier halogens. MP2 also favors the bridged cations reducing the preference in the fluorides and chlorides for **2**.

At the MP2 level both isomers of the bromine substituted cations are more stable than any of the other halocations. The bridged isomer (**1c**) is preferred over the α-bromo isomer (**3c**) by 3.3 kcal/mol, but both are more than 5 kcal/mol more stable than the fluoro or chloro substituted cations. The preference for **1c** over **3c** is consistent with Hamilton and Schaefer's[5] double-ζ CI calculations which gave a 2.7-kcal/mol preference for **1c** over **3c**. As a side issue, this close correspondence between the LANL1DZ and all electron double-ζ[5] calculations for **1c** and **3c** provides support for the practice of using pseudopotentials for calculations involving heavy atoms.

After the bromine substituted cations (**1c** and **3c**), the next most stable cations are the α-chloro (**3b**) and α-fluoro (**3a**) cations. These cations have almost identical HA's. Cation **3a** is favored over **3b** by only 0.1 kcal/mol, a margin well within the uncertainty of the calculation. The HA for **1b** is significantly higher and the HA for the last bridged cation, **1a**, is higher still. In fact, **1a** is computed to be over 34 kcal/mol higher in energy than **1c**. This is a testament to the unsuitability of fluorine for forming bridged cations. In all cases the classical primary cations are least stable. For the classical chlorine and bromine substituted cations, examination of the HF force constants shows that they are not even minima on the potential energy surface.

Several trends emerge from these calculations. First, the bridged fluoronium ion (**1a**) is extraordinarily unstable relative to both other $C_2H_4X^+$ cations and its structural isomer the α-fluoroethyl cation (**3a**). Only the classical 2-fluoroethyl and 2-chloroethyl cations are less stable. The large computed HA (poor stability) for **1a** is consistent with previous calculations[3] and the fact that experimental evidence for this cation has been elusive. The α-fluoro isomer (**3a**) is much more stable with a computed HA which is roughly equivalent to the α-chloro cation (**3b**). Thus, α-substituted fluorine and chlorine have very similar electron-donating abilities in spite of their different electronegativities. This contrasts with their strikingly different abilities to form bridged halonium ions. The ethylenechloronium ion (**1b**) is 21 kcal/mol more stable than the ethylenefluoronium ion (**1a**). The greater ability of chlorine to form a bridged cation relative to fluorine can be explained in terms of both its greater polarizability and its ability to form a back-coordinated π-complex.[21] The near equivalence in HA's for **3a** and **3b** is more difficult to explain. Part of the reason fluorine is more competitive with chlorine in **3** is doubtless superior overlap between the empty carbon 2p orbital and the filled fluorine 2p orbital versus the filled 3p orbital in chlorine. This apparently compensates for other factors which disfavor fluorine, such as its greater electronegativity and lower polarizability.

Some of these cations have been studied experimentally in the gas phase by Beauchamp et al.[6,22] Their results are given in Table II for comparison. Whereas calculations give roughly equivalent HA's for the α-fluoro (**3a**) and chloro (**3b**) cations, experimental studies find the α-chloro cation (**3b**) to be 4 kcal/mol more stable than the α-fluoro cation (**3a**) in the gas phase. By contrast, superacid studies[1] find that α-fluoro cations are generally more stable than α-chloro or α-bromo cations. The superacid order has been ascribed to superior overlap between the fluorine 2p and carbon 2p atomic orbitals.[1,2] The argument is that although the other halogens are less electronegative than fluorine they are also less capable of π donation due to orbital mismatch between the empty carbon 2p AO and the filled chlorine and bromine 3p and 4p AO's. The computed and experimental gas-phase HA's run counter to this logic. Thus it appears that in the gas phase fluorine is not always more capable of stabilizing an adjacent positive charge than chlorine or bromine. On the contrary, for $C_2H_4X^+$ the order of gas-phase stabilities for the α-halo cations (**2**) is Br > Cl ≥ F. This is consistent with the predicted order if only the relative electronegativities are considered, although **3a** might be expected to be even less stable based on electronegativity alone.

$C_4H_8X^+$ Cation

The total energies and computed hydride affinities of $C_4H_8X^+$ where X = Fl, Cl, and Br are also given in Table I. Rotation about the internal C–C bond in cations **5** and **6** leads to several competing conformations for each of these cations (Figures 2 and 3). In addition, **4** can exist as two isomers: cis and trans. For all three halogens the *cis*-dimethyl isomer of **4** is less stable than the *trans*-dimethyl isomer. This is due to simple steric considerations and should be well-characterized at the HF level. Therefore, the

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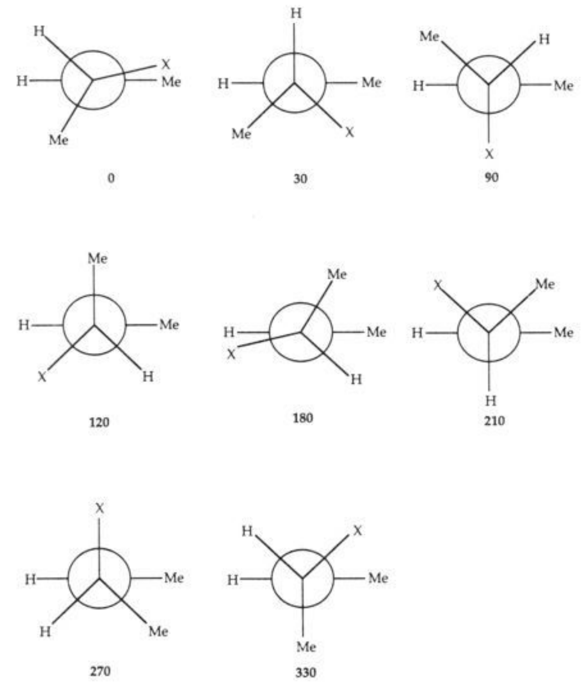

Figure 2. Rotamers (0–330°) of the classical $C_4H_8X^+$ cation **5**.

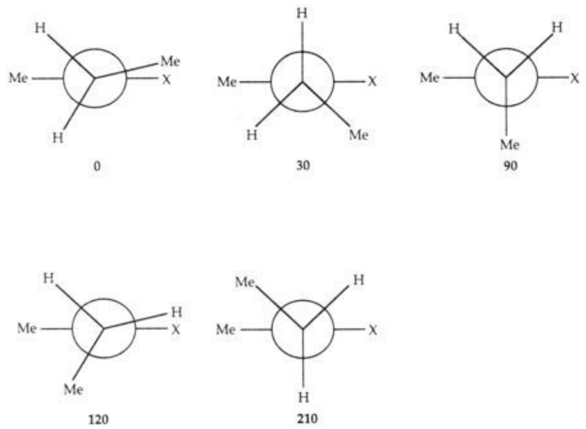

Figure 3. Rotamers (0–210°) of the α-halo $C_4H_8X^+$ cation **6**.

cis-dimethyl isomers were not recomputed with MP2.

The rotamers of **5** and **6** are more complicated. In both cases rotation about the C–C bond leads to not only steric effects (i.e. gauche versus trans) but also electronic effects due to hyperconjugation or electrostatic interactions. In order to determine the most stable conformations of **5** and **6** the relative energies of the most probable rotamers were first computed at the HF level. The energy of each rotamer was then recomputed with MP2 at the HF geometry. Finally, the lowest energy conformer of each isomer as determined using the MP2 single point energies was recomputed to allow complete optimization at the MP2 level.

The most stable conformer of the classical cation depends on the halogen. For fluorine the 0° (Figure 2) conformer **5a**(0) is most stable. When the halogen is chlorine or bromine the 90° conformer **5**(90) is most stable. Thus is due to the much greater ability of chlorine and bromine to stabilize the classical cation by hyperconjugation relative to the more electronegative and less polarizable fluorine. Indeed the structures of **5b**(90) and **5c**(90) show that the halogens are significantly displaced toward the empty p orbitals in geometries which are only slightly distorted from the bridged isomers (**4b**,**4c**) (Figures 4–6). Given the flat potential surface in this region, **5b** and **5c** would most likely proceed on to the bridged structures **4b** and **4c**, and cannot really be considered classical structures. The next most stable isomers of **5b** and **5c** are the 330° conformations (Figure 2) which allow

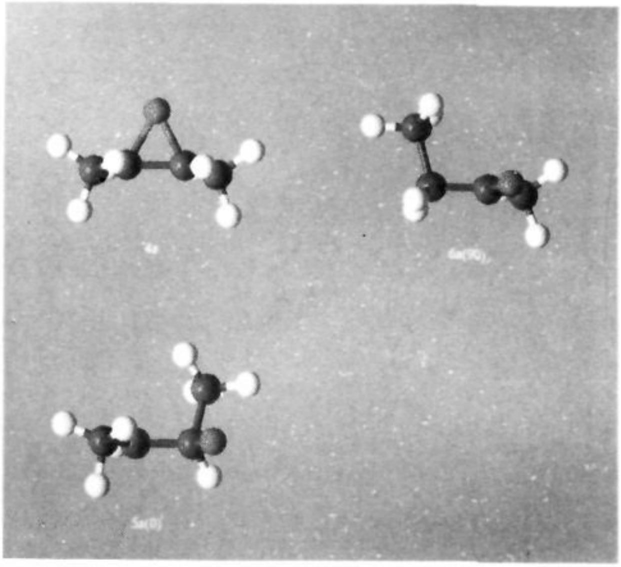

Figure 4. Best computed structures for **4a**–**6a**.

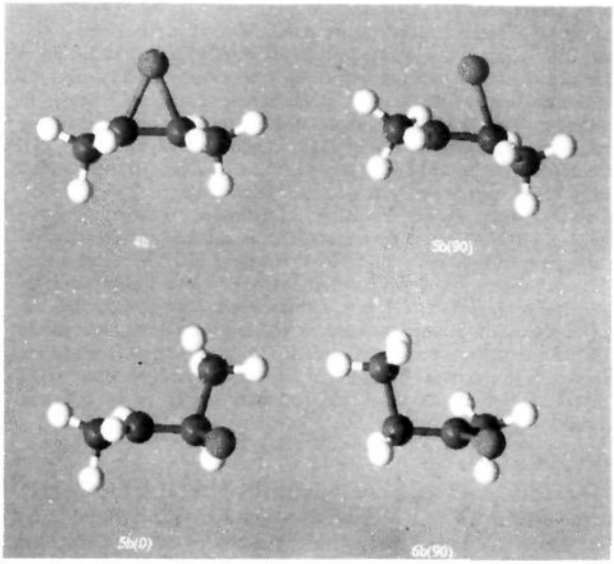

Figure 5. Best computed structures for **4b**–**6b**.

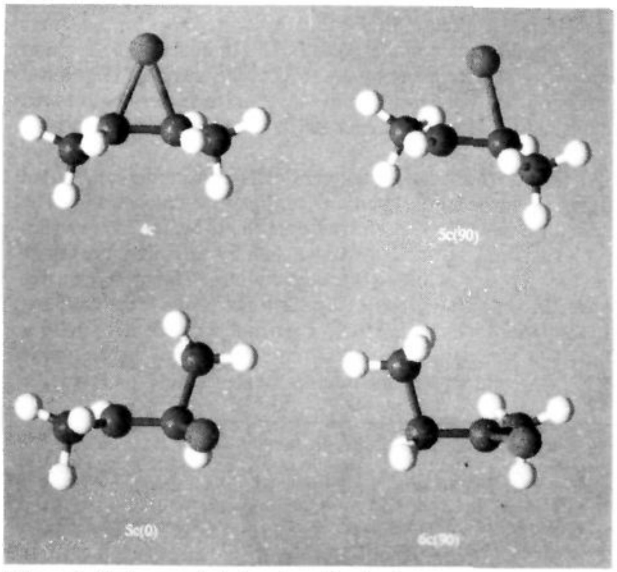

Figure 6. Best computed structures for **4c**–**6c**.

Table I. Computed Total Energies (in hartrees) and Hydride Affinities^a (kcal/mol)

	HF/6-31G**^{b}		MP2 (single point)^{b,c}		MP2 (opt)^{b,d}	
structure	total *E*	HA	total *E*	HA	total *E*	HA
1a	−177.134 856 8	265.4	−177.572 006 2	281.7	−177.584 534 9	282.1
2a	−177.143 326 3	260.1	−177.560 499 6	289.0	−177.574 247 2	288.5
3a	−177.182 175 4	235.7	−177.610 781 9	257.4	−177.624 269 5	257.1
1b	−537.218 853 3	246.6	−537.620 215 8	261.2	−537.641 169 0	260.9
2b	−537.195 591 4	261.2	−537.576 570 7	288.6	−537.597 791 4	288.1
3b	−537.229 046 8	240.2	−537.626 575 1	257.2	−537.647 052 1	257.2
1c	−90.625 861 2	248.4	−91.033 909 3	252.1	−91.046 060 5	248.0
2c	−90.602 405 2	263.1	−90.986 568 6	281.8	−90.993 448 7	281.1
3c	−90.624 287 3	249.4	−91.034 473 0	251.8	−91.040 825 5	251.3
4a	−255.255 608 2	241.8	−255.981 444 8	258.6	−256.004 775 1	258.8
4a(cis)	−255.253 201 3	243.3				
5a(0)	−255.272 444	231.2	−255.982 506 7	257.9	−256.007 207 9	257.3
5a(30)	−255.268 549 4	233.7	−255.977 484 2	261.1		
5a(90)	−255.257 511 2	240.6	−255.965 037 6	268.9		
5a(120)	−255.268 830 7	233.5	−255.978 404 8	260.5		
5a(180)	−255.268 883 4	233.5	−255.977 350 5	261.1		
5a(210)	−255.266 516 4	235.0	−255.975 149 3	262.5		
5a(270)	−255.256 562 2	241.2	−255.965 765 2	268.4		
5a(330)	−255.269 458	233.1	−255.979 830 5	259.6		
6a(0)	−255.300 130 9	213.8	−256.016 341 3	236.7		
6a(30)	−255.299 879	214.0	−256.016 077 2	236.8		
6a(90)	−255.299 604 2	214.2	−256.016 407 2	236.6	−256.040 821 7	236.2
6a(120)	−255.298 390 3	215.0	−256.014 934 0	237.6		
6a(210)	−255.298 509 1	214.9	−256.014 930 6	237.6		
4b	−615.329 299 7	226.3	−616.019 430 3	242.6	−616.051 475 9	242.1
4b(cis)	−615.327 230 5	227.6				
5b(0)	−615.317 446 7	233.8	−615.992 963 7	259.2	−616.025 022 5	258.7
5b(30)	−615.316 099 2	234.6	−615.991 042 6	260.4		
5b(90)	−615.326 246 5	228.2	−616.012 572 6	246.9	−616.045 596 2	245.8
5b(120)	−615.317 938 2	233.5	−615.992 978 6	259.2		
5b(180)	−615.315 229 3	235.2	−615.988 991 5	261.7		
5b(210)	−615.314 692 1	235.5	−615.988 996 9	261.7		
5b(270)	−615.324 280 6	229.5	−616.023 220 1	248.0		
5b(330)	−615.317 225 3	233.9	−615.993 275 5	259.0	−616.029 079 9	256.2
6b(0)	−615.337 763 6	221.0	−616.024 158 2	239.6		
6b(30)	−651.337 444 4	221.2	−616.023 680 7	239.9		
6b(90)	−615.338 151 8	220.8	−616.024 629 5	239.3	−616.056 036 8	239.3
6b(120)	−651.336 862 1	221.6	−616.023 220 1	240.2		
6b(210)	−651.336 690 8	221.7	−616.022 874 1	240.4		
4c	−168.708 200 2	226.4	−169.397 875 4	233.6	−169.414 300 7	230.2
4c(cis)	−168.706 750 2	227.3				
5c(0)	−168.692 582 2	236.2	−169.367 718 1	252.6	−169.379 533 6	252.0
5c(30)	−168.692 525 5	236.2	−169.366 595 1	253.3		
5c(90)	−168.706 468 4	227.5	−169.391 018 9	238.0	−169.408 072 9	234.0
5c(120)	−168.695 194 2	234.6	−169.368 856 4	251.9		
5c(180)	−168.691 170 6	237.1	−169.363 713 4	255.1		
5c(210)	−168.691 531 3	236.9	−169.364 212 6	254.8		
5c(270)	−168.704 805 2	228.5	−169.389 324 9	239.0		
5c(330)	−168.694 085 2	235.3	−169.369 071 1	251.7	−169.383 622 1	249.4
6c(0)	−168.702 989 5	229.7	−169.367 718 1	234.5		
6c(30)	−168.702 705 3	229.9	−169.395 997 1	234.8		
6c(90)	−168.704 622 3	228.7	−169.397 386 4	234.0	−169.408 689 7	233.7
6c(120)	−168.702 910 5	229.7	−169.395 624 9	235.1		
6c(210)	−168.702 251 7	230.1	−169.395 009 6	235.4		
C_2H_5F	−178.085 348 5		−178.548 395 0		−178.561 531 8	
C_2H_5Cl	−538.139 335 3		−538.563 914 4		−538.584 397 7	
C_2H_5Br	−91.549 160 80		−91.963 198 30		−91.968 855 1	
C_4H_9F	−256.168 417 2		−256.920 999 1		−256.944 733 2	
C_4H_9Cl	−616.217 479 1		−616.933 484 1		−616.964 805 4	
C_4H_9Br	−169.596 499 6		−170.297 716 0		−170.308 550 5	

[a] Energy of H^- (331.0 kcal/mol) estimated from the experimental[11] ionization potential and electron affinity of H. [b] Cations containing bromine were computed using the LANL1DZ basis set. [c] Computed at the HF geometry using MP2(frozen core). Polarization functions were added to the LANL1DZ basis set for bromine containing cations. [d] Optimized completely at the MP2(all electron) level.

hyperconjugation with a methyl substituent. Once again, these conformations are best characterized as bridged cations. This is consistent with calculations for the unsubstituted 2-butyl cation which show that the classical cation is unstable with regard to methyl or hydrogen bridged structures.[23] The lowest energy classical conformations for these cations are the 0° conformations (**5b**(0) and **5c**(0)). The classical chloro and bromo cations are very much less stable than the bridged (**4**) or α-halo (**6**) isomers.

For all three α-halo cations (**6**) the lowest energy conformer is the 90° conformation. This conformation is most stable due to a favorable hyperconjugative interaction between the β-methyl and cationic center (Figure 3). In each case the potential for this rotation is very flat with several conformers within 0.5 kcal/mol of each other. Thus rotation about the central C–C bond in **6** is predicted to be essentially unhindered regardless of X.

The calculations reported here are consistent with previous work[3] in predicting that fluorine substitution favors the α-halo

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Table II. Computed and Experimental[6] Hydride Affinities (kcal/mol)[a]

structure	MP2	MP2 + ZPE	exptl
1a	282.1	274.3	
2a	288.5	278.6	
3a	257.1 (9.1)	248.0 (8.1)	262.1 (7.2)
1b	260.9 (12.9)	253.4 (13.5)	263.7 (8.8)
2b	288.1	277.8	
3b	257.2 (9.2)	248.1 (8.2)	258.1 (3.2)
1c	248.0 (0.0)	239.9 (0.0)	254.9 (0.0)
2c	281.1	270.8	
3c	251.3 (3.3)	242.1 (2.2)	256.3 (1.4)
4a	258.8	249.9	
5a(0)	257.3	247.7	
6a(90)	236.2	227.6	
4b	242.1	233.8	
5b(0)	258.7	248.9	
6b(90)	239.3	230.6	
4c	230.2	221.6	
5c(0)	252.0	242.2	
6c(90)	233.7	225.0	

[a] Relative values in parentheses.

isomer **6a** very strongly over either the classical (**5a**) or bridged (**4a**) isomers. The 22.6-kcal/mol preference for **6a** over **4a** is smaller than the difference computed for the parent isomers **3a** and **1a** of 25.0 kcal/mol, but it is still very large. When the halogen is changed to chlorine the α-halo cation is still found to be most stable, but the margin drops precipitously to 2.8 kcal/mol. This difference is smaller, but comparable, to the 3.7-kcal/mol advantage enjoyed by **3b** over **1b** in the parent. In both cases the margin for the dimethyl substituted cation is slightly smaller than the margin for the parent cation. One can draw three conclusions with respect to fluorine and chlorine substituted cations from these results. First, the relative stabilities of the α–halo and halogen bridged isomers of the parent and dimethyl substituted cations give qualitatively the same results with respect to which isomer is most stable for any given halogen. Second, dimethyl substitution leads to a slight reduction in the magnitude of the difference between α-halo and halogen bridged cations. Third, since there is semiquantitative agreement between the parent and dimethyl systems one can extrapolate to other alkyl systems with reasonable confidence.

When the halogen is bromine a threshold is crossed whereupon the bridged isomer is more, not less, stable than the α-halo isomer. This is true for the parent and dimethyl substituted cations. Cation **1c** is computed to be 3.3 kcal/mol more stable than **3c**, and the preference **4c** over **6c** is 3.5 kcal/mol. In this case the relative energy difference is unaffected by dimethyl substitution. The greater stability of the bromo-bridged cations (**1c** and **3c**) is consistent with a large body of experimental evidence for bromonium ions.[2,6,24]

The hydride affinities allow direct comparison of cation stability across the board. As expected the dimethyl substituted cations are uniformly more stable than their corresponding parent cations. The most stable cation studied is **4c**. It is followed closely by the α-bromo cation, **6c**. After the bromine substituted cations, the next most stable cations are the α-fluoro (**6a**), α-chloro (**6b**), and chlorine bridged (**4b**) butyl cations. The most stable haloethyl cation (**1c**) is approximately 6 kcal/mol less stable than **4b**.

The α-halo cations are worth examining in detail. It is often asserted that fluorine is superior to any other halogen at stabilizing an adjacent cation via direct π donation.[1,2,25] The argument for this is that even though fluorine is most electronegative, a factor which tends to destabilize cations through induction, it also has a filled 2p AO (instead of 3p or 4p) which can overlap more effectively with the empty 2p AO at the cationic site. Calculations and experimental gas-phase studies contradict this argument for the $C_2H_4X^+$ cation. For **3** the order of stabilities is computed to be bromine > chlorine = fluorine. Obviously in this case the greater ability of fluorine to conjugate with the cation does not overcome the destabilizing inductive effect of fluorine. Indeed the stabilities correlate well with electronegativity.

Table III. Comparison of α-Halo Cation Stabilities (kcal/mol)

structure	MP2 HA[a]	rel HA	structure	MP2 HA[a]	rel HA
3a	257.1	23.4	**7a**	282.2	48.5
3b	257.2	23.5	**7b**	277.7	44.0
3c	251.3	17.6	**7c**	271.0	37.3
6a(90)	236.2	2.5	**8a**	281.7	48.0
6b(90)	239.3	5.6	**8b**	249.3	15.6
6c(90)	233.7	0.0	**8c**	244.2	10.5
			$C_4H_9^+$	234.2	0.5

[a] Geometries were fully optimized at the MP2 level. Cations involving bromine were computed using the LANL1DZ* basis set. All others were computed using the 6-31G** basis set.

The relative stabilities of the α-halo isomers of $C_4H_8X^+$ are very different, however. When comparing **6a**, **6b**, and **6c** we find that the order of stabilities is bromine > fluorine > chlorine. The α-bromo cation remains most stable, but methyl substitution at the cationic site alters the relative stabilities of the fluorine and chlorine substituted α-halo cations. These and other[10,26] theoretical calculations for halogen substituted cations are begining to show that the question of which halogen is better at stabilizing a cation by direct π donation is complex. There may be no simple ordering which can consistently be applied. Instead it appears that there is a balance between the inductive effect which decreases from fluorine to bromine, polarizability which increases from fluorine to bromine, and π overlap which decreases from fluorine to bromine. All may play a greater or lesser role depending on the other substituents adjacent to the cation. If the other two substituents are good electron donors through induction, then fluorine is favored over chlorine because of its superior ability to conjugate with the cationic center. If, however, the other substituents are electron withdrawing by induction chlorine is favored because of its lower electronegativity and greater polarizability.

This can be illustrated with the hydride affinities in Table III. The computed hydride affinities of **3a**, **3b**, **6a** and **6b** are compared with those of CH_2X^+ (**7**)[25] and CX_3^+ (**8**).[25] As alkyl substitution increases from **7** to **6**, the fluorine substituted cations go from less stable than the chlorine substituted cations to more stable. At **3** the energies are almost equivalent. When all three substituents are halogens (**8**) the preference for chlorine over fluorine rises to more than 30 kcal/mol. Therefore, one cannot say that fluorine is always superior to chlorine at stabilizing an adjacent cation or vice versa. The relative electron-donating abilities of fluorine and chlorine depend very strongly on the electron demand placed on the cationic center by the other two substituents. When those substituents are electron releasing, fluorine substitution is more favorable; when the other substituents are electron demanding, chlorine substitution is more favorable.

Examination of the relative energies of the classical dimethyl and unsubstituted α-halo cations, **5** and **3**, provides semiquantitative insight into the ability of halogen to stabilize a cation relative to methyl. Perhaps it is surprising, but in all three cases halogen substitution adjacent to the carbocation (**3**) is more favorable than methyl substitution (**5**) if one omits the 90° rotamers of **5** which collapse to halogen bridged structures. This comparison is not completely fair because **5** does suffer potentially from the inductive effect of halogen β to the cation and any charge/dipole or hydrogen bonding interaction which might be present between halogen and the methyl group. Nevertheless, comparison of **3** and **5** does indicate that dialkyl substituted cations are *less* stable in the gas phase than cations substituted with a single alkyl group and halogen. Further evidence of the stabilizing influence of direct halogen substitution on carbocations comes from comparison of **6a–c** with the *tert*-butyl cation (Table III). The bromine substituted cation (**6c**) is found to be just as stable as the *tert*-butyl

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Table IV. HF Computed Vibrational Frequencies and Intensities (in parentheses)[a]

1a	**3a**	**1b**	**1a**	**3a**	**1b**
817 (170)	519 (21)	441 (47)	1421 (13)	1537 (30)	1316 (0)
884 (6)	804 (6)	567 (108)	1601 (11)	1539 (26)	1335 (8)
1053 (0)	945 (9)	904 (3)	1663 (5)	1726 (197)	1593 (14)
1142 (8)	1260 (16)	1033 (0)	3341 (17)	3142 (59)	1652 (7)
1263 (1)	1266 (27)	1056 (0)	3349 (0)	3198 (36)	3329 (22)
1311 (0)	1445 (213)	1219 (0)	3467 (0)	3198 (36)	3329 (22)
1354 (1)	1492 (22)	1282 (32)	3467 (0)	3332 (13)	3333 (1)
			3477 (52)	3357 (11)	3445 (0)
					3457 (62)
3b	**1c**	**3c**	**3b**	**1c**	**3c**
422 (5)	857 (0)	679 (48)	1494 (15)	1606 (30)	1575 (41)
833 (9)	937 (9)	850 (10)	1544 (27)	1655 (11)	1616 (22)
855 (12)	994 (0)	1082 (138)	1606 (28)	3368 (34)	3153 (75)
1127 (226)	1219 (0)	1110 (0)	3140 (66)	3373 (1)	3216 (10)
1149 (1)	1227 (95)	1255 (21)	3193 (23)	3500 (0)	3383 (5)
1252 (25)	1309 (53)	1452 (88)	3340 (5)	3510 (54)	3398 (14)
1454 (96)	1331 (0)	1509 (40)	3350 (23)		
4a	**6a**(90)	**4b**	**4a**	**6a**(90)	**4b**
147i	416 (0)	416 (28)	1542 (28)	1542 (25)	1546 (1)
441 (8)	531 (16)	486 (17)	1543 (8)	1547 (43)	1574 (5)
496 (0)	609 (2)	524 (82)	1569 (0)	1592 (7)	1586 (26)
759 (119)	833 (2)	903 (1)	1581 (18)	1607 (26)	1605 (30)
904 (0)	880 (1)	994 (18)	1605 (23)	1615 (34)	1613 (19)
994 (15)	945 (25)	1075 (15)	1614 (19)	1627 (40)	1640 (15)
1076 (10)	1042 (12)	1083 (25)	1667 (10)	1666 (138)	3196 (2)
1076 (32)	1077 (34)	1166 (3)	3197 (6)	3150 (46)	3196 (1)
1210 (10)	1154 (66)	1190 (12)	3198 (0)	3218 (6)	3284 (2)
1226 (9)	1195 (27)	1225 (15)	3282 (1)	3239 (3)	3284 (2)
1282 (4)	1334 (15)	1300 (2)	3320 (1)	3262 (10)	3322 (1)
1311 (1)	1397 (34)	1346 (1)	3321 (0)	3303 (7)	3323 (0)
1368 (0)	1420 (108)	1444 (2)	3379 (0)	3317 (0)	3360 (0)
1451 (4)	1490 (53)	1546 (12)	3386 (6)	3321 (1)	3369 (12)
				3338 (6)	
6b(90)	**4c**	**6c**(90)	**6b**(90)	**4c**	**6c**(90)
408 (0)	500 (0)	539 (14)	1500 (52)	1608 (40)	1577 (14)
417 (4)	911 (0)	612 (22)	1541 (1)	1624 (80)	1625 (23)
575 (0)	1004 (3)	898 (3)	1549 (3)	1637 (30)	1638 (11)
732 (23)	1059 (68)	942 (57)	1604 (19)	1641 (1)	1642 (22)
879 (1)	1079 (13)	952 (68)	1612 (6)	3207 (1)	1653 (14)
950 (30)	1152 (3)	1073 (34)	1615 (16)	3312 (1)	3162 (42)
984 (81)	1180 (26)	1110 (36)	1637 (13)	3312 (7)	3239 (15)
1034 (44)	1210 (23)	1166 (18)	3141 (44)	3358 (6)	3262 (2)
1107 (36)	1301 (0)	1312 (40)	3218 (7)	3359 (0)	3293 (2)
1146 (31)	1360 (24)	1347 (70)	3235 (1)	3399 (0)	3339 (9)
1306 (49)	1457 (0)	1409 (27)	3266 (4)	3409 (18)	3352 (4)
1352 (71)	1571 (25)	1436 (23)	3301 (6)		3355 (5)
1394 (23)	1573 (11)	1536 (63)	3315 (1)		3360 (1)
1428 (50)	1589 (19)	1570 (2)	3318 (2)		
			3335 (3)		

[a] Vibrations less than 400 cm^{-1} have been omitted.

cation and the other α-halo cations are only 2–5 kcal/mol less stable.

Vibrational Frequencies

In order to facilitate experimental identification of the cations in this study HF vibrational frequencies and intensities are reported in Table IV for the α-halo and halogen bridged cations. Beyond the normal errors which apply to computed vibrational energies, the frequencies reported here suffer from additional uncertainty due to lack of any allowance for correlation effects. Nevertheless, they may be useful for characterizing the IR spectra of these unstable carbocations.

Only three structures (**2b**, **2c**, and **4a**) are not minima on the potential surface at the HF level. Two of these structures correspond to the unsubstituted primary classical cations **2b** and **2c**. Surprisingly, the fluorine substituted primary cation **2a** is a minimum at the HF level even though it is very unstable. For the butyl system only the fluorine bridged cation (**4a**) is not a minimum. Substitution leads the fluorine bridged structure to become a transition state for interconversion between much more stable secondary classical cations. Many of these species exhibit several very-low-energy vibrations. This is due to low energy internal rotations. For example, the dimethyl substituted cations all have two low-energy vibrations due to methyl rotations. In addition the low barrier for rotation about the central C–C bond found for **6a–c** during the conformational analysis of these cations is seen in the force calculations as a near zero vibrational frequency. One consequence of these low-energy internal rotations is that they may lead to significant errors in the computed zero-point energies. Because of this zero-point corrections should be applied cautiously.

Conclusion

When comparing bridged, classical, and α-halo isomers of a given carbocation the relative stabilities of the butyl cations are consistent with the parent unsubstituted cations. When comparing across halogens, however, there is much less consistency. This is particularly true of the α-halo isomers. For example, in **3** the fluoro and chloro substituted cations have virtually identical stabilities, but in **6** the fluorine substituted cations is more stable than chlorine by 3 kcal/mol. Conversely, in **8** chlorine is favored over fluorine by more than 30 kcal/mol. Thus in progressing from the more highly alkyl substituted cation (**6**) to the trihalo cation (**8**) the fluorine substituted cations change from being most stable to least stable by a wide margin. For the ethyl cation (**3**) fluorine and chlorine have identical effects on cation stability.

These results show that it is not possible to make a blanket statement with regard to the relative ability of halogens to stabilize an adjacent cationic center through direct π donation. From the limited examples examined here it appears that electron-releasing substituents favor fluorine and electron-withdrawing substituents favor chlorine. Bromine is found to be uniformly superior to fluorine or chlorine at stabilizing an adjacent carbocation. For bromine, however, the bridged isomer, where possible, is even more stable.

Finally, it is interesting to note that halogens are remarkably good at stabilizing gas-phase carbocations given their high electronegativities. There are many examples of bromine in particular stabilizing cations via bridging, but the calculations reported here argue that cations which place a halogen directly adjacent to the cationic center should also be very favorable, in some cases being competitive with cations of well-known stability such as *tert*-butyl.

Registry No. 1a, 53172-39-7; **1b**, 23134-14-7; **1c**, 20174-90-7; **2a**, 29526-62-3; **2b**, 41797-39-1; **2c**, 20500-81-6; **3a**, 29526-61-2; **3b**, 41797-38-0; **3c**, 83490-90-8; *trans*-**4a**, 78195-76-3; *cis*-**4a**, 78195-75-2; *trans*-**4b**, 78195-74-1; *cis*-**4b**, 78195-73-0; *trans*-**4c**, 52754-93-5; *cis*-**4c**, 52754-94-6; **5a**, 53172-45-5; **5b**, 53172-23-9; **5c**, 143171-84-0; **6a**, 51608-55-0; **6b**, 53176-16-2; **6c**, 143171-85-1; H, 12184-88-2.

Ab Initio Calculations of the Barriers to Rotation in 1,1-Difluoroallyl Radical and an Analysis of the Factors That Govern Rotational Barriers in Fluorinated Allylic Radicals

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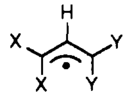
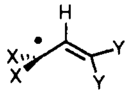
Abstract: The energies required to rotate the CF_2 and the CH_2 group out of conjugation in 1,1-difluoroallyl radical have been calculated at the SD-CI/6-31G*//UHF/6-31G* level of theory. In agreement with experiment, the barrier to CF_2 group rotation in this allylic radical is computed to be much larger than that in 1,1,3,3-tetrafluoroallyl radical. The factors that govern the size of rotational barrieirs in allylic radicals are analyzed, and the origin of the difference in barriers to CF_2 group rotation in these two fluorinated allylic radicals is discussed.

Ab initio calculations[1] have found, in agreement with experiment, that the rotational barrier in 1,1,3,3-tetrafluoroallyl radical (**1**)[2] is considerably lower than that in the parent allyl radical (**2**).[3a,b] The calculations showed that this difference is due to the strong preference of CF_2 radical centers for pyramidal geometries. The pyramidalization energy that is recovered on twisting a CF_2 group out of conjugation in **1** was found to comprise the major part of the difference between the CF_2 rotational barrier in **1** and the CH_2 rotational barrier in **2**.

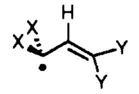
Although, to the best of our knowledge, the CF_2 and CH_2 rotational barriers in 1,1-difluoroallyl radical (**3**) have not been measured precisely, there is experimental evidence[2,3a] that they are both considerably higher than the CF_2 rotational barrier in **1**. This seems rather surprising. One might have expected that in **3**, although the energy required to rotate the CH_2 group out of conjugation would be high and close to that in **2**, the barrier to rotating the CF_2 group would be low and similar to that in **1**.



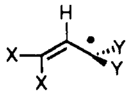
1a, X = Y = F
2a, X = Y = H
3a, X = F, Y = H



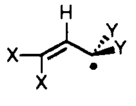
1b, X = Y = F
2b, X = Y = H
3b, X = F, Y = H



1c, X = Y = F
2c, X = Y = H
3c, X = F, Y = H



3d, X = F, Y = H



3e, X = F, Y = H

In this paper we report the results of our calculations on the rotational barriers in **3**. In agreement with experiment, we find that the CF_2 rotational barrier in **3** is substantially higher than that in **1**, whereas the CH_2 rotational barrier in **3** is lower than that in **2**. The results of our calculations permit the factors that govern the rotational barrier heights in **1**–**3** to be analyzed.

Computational Methodology

Reactant and transition state geometries were fully optimized in C_s symmetry at the UHF level,[4] using the 6-31G* basis set.[5] All stationary points were characterized by vibrational analyses. Electron correlation, beyond that in the UHF wave function, was taken into account by performing configuration interaction (CI) calculations at the optimized UHF/6-31G* geometries. All single and double excitations were included (SD-CI). The C and F 1s electrons were frozen in the SD-CI calculations. The calculations were carried out using either the GAUSSIAN 86[6] or GAUSSIAN 90[7] package of ab initio programs.

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