SCIENCE DIRECT®

Tetrahedron 60 (2004) 1191–1196

Tetrahedron

Computational studies of vinyl-stabilized halonium ions

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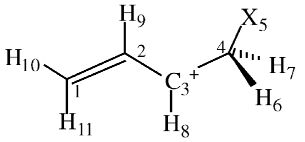
Received 12 September 2003; revised 18 November 2003; accepted 18 November 2003

Abstract—Conformational studies of 1-halo-2-butenylcations have been carried out by means of density functional and ab initio calculations. The presence of an adjacent vinyl group reduced the importance of bridging by halogen atoms as evidenced by geometric and energetic analyses. Eclipsed forms were found to be minima in several cases.

1. Introduction

Halonium ions are well-documented species formed as intermediates in a variety of chemical processes, particularly in the electrophilic addition of halogens and similar reagents to alkenes.[1] The extent of halogen bridging to cationic centers that is the formation of halonium ions, is reasonably expected to depend on structural factors stabilizing the cationic center. For example, for bromonium ions formed from ethene, propene, and 2-methylpropene, less stabilization by contribution of electron density is required as alkyl substitution increases at the cationic center. This is illustrated by a comparison of calculated electrostatic potential maps and geometric features.[2] For example, cationic center: C–Br distance increases with weaker bridging in unsymmetrical bromonium ions.[2,3] It is of interest to ascertain the effect of vinylic stabilization on bridging by halogen substituents adjacent to a carbocationic center. It may be anticipated that allylic stabilization of a cationic center would reduce the degree of bridging by neighboring halogen, and that the effect might be greater for fluorine and chlorine than with the more effective bromine bridging atom. Viewed another way, the results of these calculations speak to the nature of the intermediates derived from addition of halogens and analogous reagents to dienes.

The simplest systems incorporating these features are the 4-chloro-1-buten-3-yl cation **1**, the corresponding bromine analog and the fluorine analogs **2** and **3**, respectively (Fig. 1).



1: X = Cl
2: X = Br
3: X = F

Figure 1. 4-Halo-1-buten-3-yl cations.

Density functional theory studies of these systems were carried out at the B3LYP/6-311+G(d) computational level (additional computation methods were also used and are noted accordingly). In addition, conformational energy searches were conducted by monitoring the energy changes resulting from 360° rotation about the 3–4 bond. Structural parameters and thermally corrected enthalpies were determined for each stationary point located.[†]

2. Computational methods

All structures were fully optimized by analytical gradient using the Gaussian 98[4] suites. Density functional (DFT) calculations used the exchange potentials of Becke[5a] and the correlation functional of Lee, Yang and Parr.[5b] Electron correlation was included via optimizations utilizing second order Møller–Plesset Perturbation Theory methods (MP2).[6] Frequencies were computed by analytical methods. Reported enthalpies were corrected for zero-point energy differences (ZPVE) (unscaled[‡]) and thermal effects at 298.150 K. Full conformational searches were carried out by systematic changes (15–20° increments) in the 2–3–4–5 dihedral angles followed by full optimizations of the maxima and minima. All stationary points gave rise to the correct number of imaginary frequencies.

Keywords: Carbonium ions; Halogen compounds; Theoretical studies; Olefins.

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[†] The calculated structures are not necessarily identical with intermediates formed in particular reactions. The calculations do not include the presence of counterions as ion pairs and apply to free cations in vacuum.

[‡] Scaling factors for these DFT and MP2 methods are small, 1–3%.[7]

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doi:10.1016/j.tet.2003.11.073

Table 1. Relative enthalpies and structural parameters for **1**: B3LYP/6-311+G(d)

Conformation	C_2–C_3–C_4–Cl[a] (°)	ΔH[b]	C_3–C_4–Cl[c] (°)	Cl–C_4[d]	Cl–C_3[e]
4	0.0	0	118	177	277
5	54.8	13.2	108	180	266
6	99.5	1.79	92.7	183	240
7	180.0	7.04	115	177	274

[a] Dihedral angle.
[b] kJ mol^{-1} at 298.15 K.
[c] Bond angle.
[d] Bond length (pm).
[e] Interatomic distance (pm).

3. Results and discussion

3.1. 4-Chloro-1-buten-3-yl cation (1)

Enthalpy and important structural parameters are shown in Table 1. Relative enthalpies as a function of torsional angle $D(2-3-4-5)$ in **1** are shown in Figure 2. In the 0–180° region two minimum energy structures **4** and **6** are observed, at dihedral angles of 0 and 99.5°, respectively. The minimum energy structure **4** at 0° corresponds to an eclipsed conformation with C_s symmetry (C_2,Cl eclipsed), cf. Figure 2 in which a dashed line or p-orbital depicts the terminus of the attached π-system of the molecular framework. Structure **4** lies 1.79 kJ mol^{-1} lower in enthalpy than the local minimum structure **6** at 99.5°. Dihedral angles of 54.8 and 180° represent transition state conformations **5** and **7**, respectively. Structure **5** lies 13.2 kJ mol^{-1} higher in enthalpy than **4** and corresponds to a conformation in which H_6 and H_8 are nearly eclipsed (separated by a dihedral angle of 5.86°). Structure **7** (C_s symmetry) lies 7.0 kJ mol^{-1} above **4** and corresponds to a conformation in which Cl and H_8 are eclipsed. Figure 3 represents the entire conformational energy curve and includes points at 260.5 and 305.2° representing the mirror image forms of **5** and **6**, respectively.

The conformer **6** corresponding to torsion angle 99.5° shows a lengthening of the 4,5 bond and decrease of the 3,4,5 bond angle, as well as a decrease of the 3,5 internuclear distance. These structural features are consistent with bridging of the cationic center C_3 by chlorine. The chlorine in **6** makes a dihedral angle of 9.5° with the p-orbital axis on C_3 and this near eclipsing is also compatible with weak bridging by chlorine. Bridged structures computed in this study are shown as halonium ions (σ-complexes), and no distinction is made here with formulation of the structures as π-complexes.[8,9]

Evidence for the existence of chloronium ions as intermediates in the addition of chlorine to alkenes includes

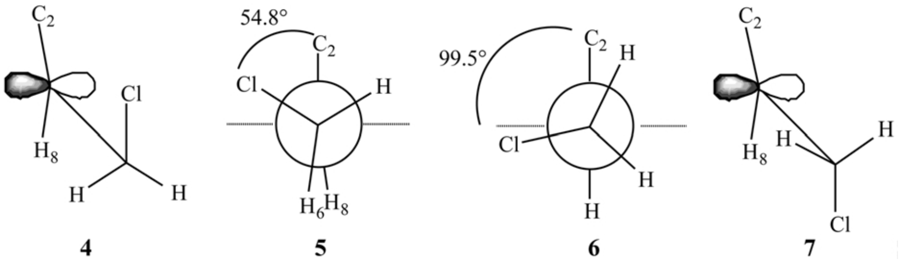

Figure 2. Representations of stationary points for **1**.

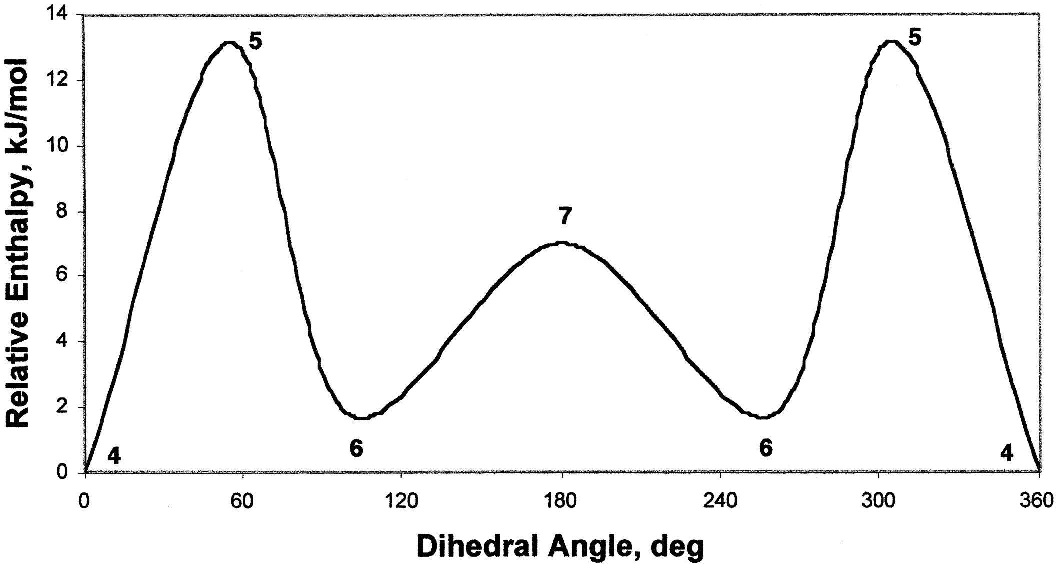

Figure 3. Relative enthalpies vs dihedral angle for **1**: B3LYP/6-311+G(d).

Table 2. Relative enthalpies and structural parameters of **1**

	B3LYP/6-311+G(d)		B3LYP/6-311+G(2d,p)		B3LYP/AUG-cc-pVDZ		MP2/6-311+G(d)	
	4	**6**	**4**	**6**	**4**	**6**	**4**	**6**
ΔH^{a}	0	1.8	0	1.3	0	2.2	0	0.084
$D(2-3-4-5)^{b}$	0	99.5°	0	99.0°	0	99.1°	0	99.1°
$A(3-4-5)^{c}$	117.7°	92.7°	117.6°	92.0°	117.3°	91.9°	116.1°	86.0°
$R(4-5)^{d}$	177	183	177	183	178	—	175	181

[a] Enthalpies are in kJ mol^{-1} at 298.15 K.
[b] *D*, dihedral angle.
[c] *A*, bond angle.
[d] *R*, interatomic distance (pm).

stereoselective *anti* addition. For example, *trans*-2-butene reacts with chlorine in a nonpolar solvent with oxygen present to give 98% *meso*-2,3-dichlorobutane (2% of substitution product was obtained).[10] NMR evidence for a stable chloronium ion has been reported.[11]

In structure **6** the geometry about the cationic center C_3 is planar and this also suggests weak bridging in the chloronium ion **6**. Conformation **4** clearly represents a nonbridged structure since the chlorine is perpendicular to the p-orbital axis. The 3–4–5 bond angle of 117.7° is relatively large, and the C_4–Cl bond length of 177 pm is normal.[12] The nonbonded C_3–Cl distance of 277 pm in **4** is identical to the nonbonded C–Cl distance in chloroethane calculated using B3LYP/6-311+G(d) model chemistry. In both structures 4 and 6 the carbon framework 1–2–3–4 is planar.[§]

The finding that the eclipsed conformation **4** is a stable conformer, slightly more stable than the chloronium ion **6** prompted us to carry out further optimizations with B3LYP using larger basis sets, as well as optimizations with alternative model chemistries. The results are shown in Table 2.

All of the methods in Table 2 show the eclipsed conformer **4** slightly more stable than the weakly bridged chloronium ion **6**. The MP2 calculation shows a significantly smaller Cl–C_4–C_3 bond angle than the B3LYP methods, and also shows very little energy difference between **4** and **6**. A single point calculation at the QCISD(T)/6-31+G(d)//MP2/6-311+G(d) level showed **4** to be 3.9 kJ mol^{-1} more stable than **6**.

In contrast to the vinyl-substituted chloronium ion **6**, the butyl chloronium ion **8** (Fig. 4) shows a strikingly different enthalpy-conformation dependence, the main feature of which is the presence of one dominant stable conformation. Full optimizations of 1-chloro-2-butyl cation show that the most stable conformation is the chloronium ion **8** corresponding to a torsion angle $D(5-1-2-3)$ of 102°. The following structural parameters were found for chloronium ion **8**: bond angle Cl–C_1–C_2=75.9° (considerably smaller than the corresponding angle in **6**), C_2–Cl distance=207 pm (considerably shorter than the corresponding distance *R*3–5 in **6**; note that the numbering differs for **6** and **8**). The Cl–C_1 bond length in **8** is 186 pm, which is essentially unchanged from **6**. The dihedral angle in **8** Cl–C_1–C_2, p-orbital axis is approximately 12°, and the cationic center C_2 in **8** is close to planar.

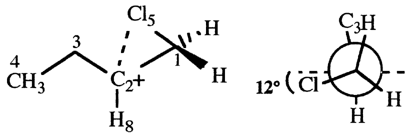

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Figure 4. Representations of the 1-butylchloronium ion.

Based on the comparison of structural parameters, chloronium ion **8** is more strongly bridged than the vinylchloronium ion **6**. The butyl chloronium ion **8** is approximately 23 kJ mol^{-1} more stable than the nearest minimum energy conformation. Consequently, vinyl stabilization of a cationic center lessens the need for bridging by an adjacent chlorine.

A second instructive comparison is that with the isomeric *trans*-2-butylchloronium ion **9** (Fig. 5). In this more highly symmetrical bridged structure the C–C–Cl angle is 67.3° and the C–Cl–C angle is 45.4° based on B3LYP/6-311+G(d) optimization. Halonium ions derived from symmetrical methyl-substituted ethenes are more strongly bridged than those from unsymmetrical alkenes.[3] The conclusion is that bridging is weaker in the unsymmetrical chloronium ion **8** than in symmetrical structure **9** and still weaker in the vinylchloronium ion **6**. This is attributed to delocalization of positive charge by resonance in the vinyl group in **6**.

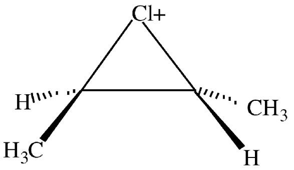

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Figure 5. *trans*-2-Butylchloronium.

3.2. 4-Bromo-1-buten-3-yl cation (2)

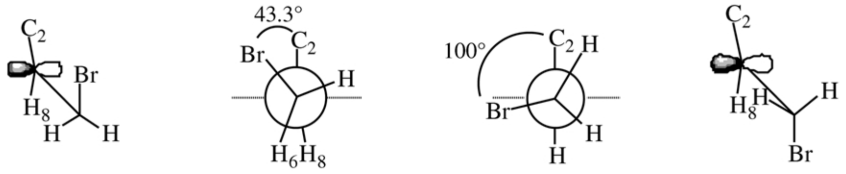
Optimized enthalpies and structural parameters were determined as a function of torsion angle for **2** and the results are shown in Table 3 and in Figures 6 and 7.

[§] The AIM[4b] (Atoms in Molecules) calculated covalent bond orders are 0.36 for the Cl–C3 bond compared with 1.02 for the Cl–C4 bond in **1**. For comparison, the bond order for the C–Cl in *trans*-2-butylchloronium ion vide infra is 0.80.

Table 3. Relative enthalpies[a] and structural parameters for **2**:B3LYP/6-311+G(d)

C_2–C_3–C_4–Br[b]	Δ*H*	C_3–C_4–Br[c] (°)	Br–C_4[d]	Br–C_3[e]
0.0° (**2a**)	18.0	119	193	293
43.3° (**2b**)	22.2	112	196	286
100° (**2c**)	0.0	90.0	200	247
180° (**2d**)	24.3	116	193	289

[a] Enthalpies in kJ mol^{-1} at 298.15 K.
[b] Dihedral angle.
[c] Bond angle.
[d] Bond length.
[e] Interatomic distance (pm).



2a **2b** **2c** **2d**

Figure 6. Representations of stationary points for **2**.

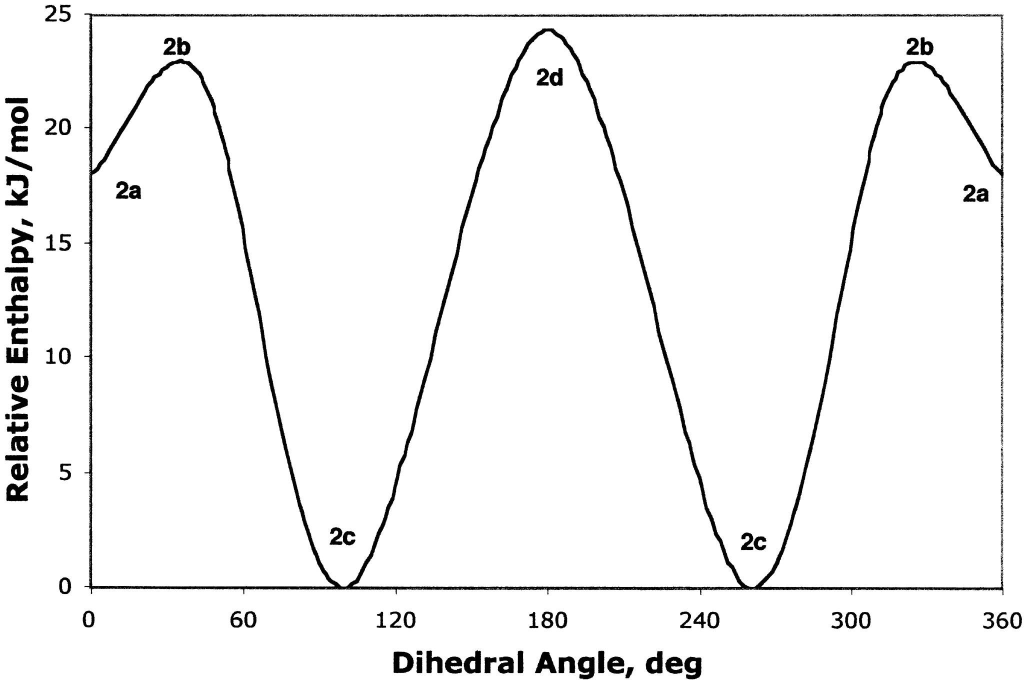
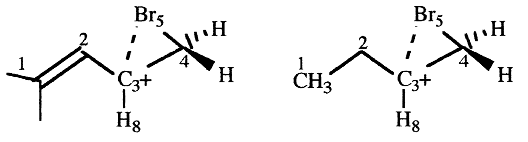


Figure 7. Relative enthalpies vs. dihedral angles for **2**: B3LYP/6-311+G(d).

In contrast to the chlorine analog, the most stable conformer for **2** occurs at a torsion angle of 100°, corresponding to the bromonium ion **10** (Fig. 8). The bromonium ion is characterized by a longer C_4–Br bond length, a shorter C_3–Br internuclear distance, and a smaller C_3–C_4–Br bond angle relative to other conformations.

The bromonium ion is lower in energy by 18 kJ mol^{-1} than the local minimum energy conformer at a torsion angle of 0° as a consequence of bromine bridging. The geometry about the cationic center C_3 in **10** is planar, as with the analogous chloronium ion, with angles C_2–C_3–H_8, C_4–C_3–H_8, and C_2–C_3–C_4 adding to 360.0°.

The butyl bromonium ion **11**[¶] (Fig. 8) is more strongly bridged than the vinylbromonium ion **10**, with a Br–C_4–C_3 bond angle of 75.1°, a C_4–Br bond length of 203 pm, and a Br–C_3 interatomic distance of 217 pm. This again demonstrates the stabilizing effect of the vinyl group on the cationic center in **10**, leading to less effective bridging in **10** relative to **11**.



10 **11**

Figure 8. Bromonium ions **10** and **11**.

We also found that the structure of the bromonium ion **10** is unaffected by the polarity of the medium. A full optimization in a dielectric continuum corresponding to that of water (78.39 D) led to a structure that was only slightly

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[¶] The structure for **11** was optimized using B3LYP/6-31+G(d) model chemistry.

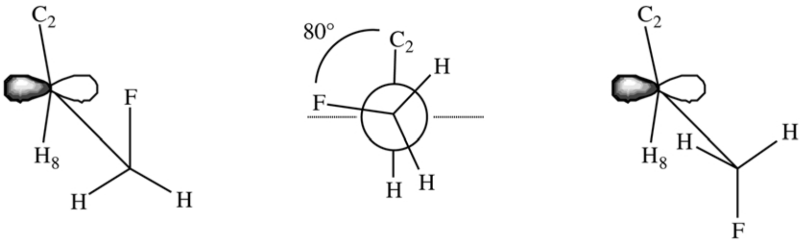

Figure 9. Representations of stationary points of **3**: B3LYP/6-311+G(d).

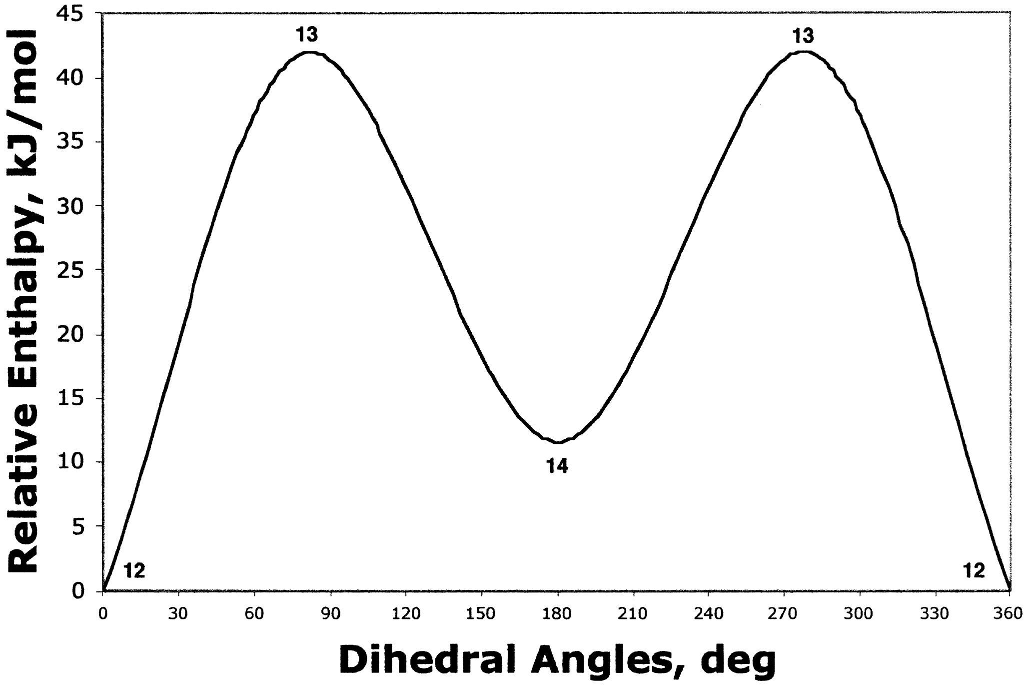

Figure 10. Relative enthalpy vs dihedral angle for **3**: B3LYP/6-311+G(d).

different from the structure obtained under vacuum conditions. The major difference was the C_3–C_4–Br angle, which expanded from 92.0 to 94.7°.

3.3. 4-Fluoro-1-buten-3-yl cation 3

A preliminary conformational search showed minimum energy conformations at 0 and 180° dihedral angles, and energy maxima in the vicinity of 90 and 270°. Full optimizations of **3** were carried out at the B3LYP/6-311+G(d) and MP2/6-311+G(d) levels. Stationary points were obtained at dihedral angles $D(2-3-4-5)$ of 0 and 180° (conformations **12** and **14** respectively, Figure 9), both minima, and formula **13** at about 80°, a transition state conformation. Figure 10 shows the change of relative enthalpy with dihedral angle $D(2-3-4-5)$ for **3**. In this case, the putative fluoronium ion **13** is a first-order saddle point in contrast to the chloronium and bromonium ions and eclipsed forms are energy minima.

Enthalpy data and structural parameters for these structures optimized by both the B3LYP and MP2 methods are given in Table 4.

Table 4. Relative enthalpies and structural parameters for **3**

Conformations	B3LYP/6-311+G(d)			MP2/6-311+G(d)		
	12	**13**	**14**	**12**	**13**	**14**
ΔH^a	0	41.9	11.6	0	37.6	12.6
$D(2-3-4-5)^b$	0°	79.9	180°	0°	81.6°	180°
$A(3-4-5)^c$	113.2°	101.5°	111.8°	111.9°	102.3°	110.7°
$R(4-5)^d$	136	140	136	136	139	136

[a] Enthalpies are in kJ mol^{-1} at 298.15 K.
[b] D, Dihedral angle.
[c] A, Bond angle.
[d] R, Interatomic distance (pm).

4. Summary

A comparison of the three 4-halo-1-buten-3-yl cations **1-3** shows a clear trend. With the bromine analog in which bridging with the cationic center is strongest, the bridged conformer is lower in enthalpy by 18.0 kJ mol^{-1} than the local minimum enthalpy conformer (the eclipsed structure with dihedral angle=0°). In the chlorine analog with weaker bridging, the chloronium ion **6** is approximately equal (and in most calculations slightly higher) in enthalpy than the eclipsed conformer **4**. Experimental studies both in the gas-phase and in solution are consistent with these findings and show the greater tendency of bromine to form bridged halonium ions.[13–16] Computational studies of bromo- and chlorocations derived from several cycloalkenes have also shown that bromonium ions are more stable than the analogous chloronium ions in those systems.[17]

The fluorine analog is particularly interesting. In this case conformation **13** with a dihedral angle of about 80° is not a stabilized bridged form, and in fact proved to be a saddle point with enthalpy about $38-42\ \mathrm{kJ\ mol^{-1}}$ above the eclipsed form **12**. An AIM (Atoms in Molecules) calculation[4b] revealed that the covalent bond order between F and C_3 was only 0.15. Saturated fluoronium ions have been represented as transition structures by others.[18–21] In contrast to the results with bromine, calculations have shown that the 0° conformer in which the fluorine is eclipsed with the adjacent carbon atom 2 is the most stable conformer for the 3-fluorobut-2-yl cation.[18]

Clearly, there is a delicate balance among the competing factors that are involved in stabilizing the cationic centers. What is not clear are the factors that favor eclipsed forms over more conventional staggered conformations.

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