Computational Studies of Halonium Ions of Cyclohexene and Cyclopentene

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A computational study of a variety of $C_2H_4X^+$, $C_5H_8X^+$ (cyclopentyl), and $C_6H_{10}X^+$ (cyclohexyl) species, where X is F (for $C_2H_4X^+$ and $C_6H_{10}X^+$), Cl (for $C_2H_4X^+$ and $C_6H_{10}X^+$), and Br (for $C_2H_4X^+$, $C_5H_8X^+$, and $C_6H_{10}X^+$), has been carried out. The $C_2H_4X^+$ system has been reexamined to assess the computational level necessary to achieve reasonable energy comparisons for the larger cyclopentyl and cyclohexyl cations. Both basis set and correlation studies indicate that a good representation of the energetic differences depends more on the quality of the basis set. Thus, studies of the larger cyclopentyl and cyclohexyl cations at the equivalent of MP2/6-311G(d,p)//MP2/6-31G(d) were sufficient to obtain relative energies for the lowest energy of these species: the 1-bromocyclopentylium, 1-halocyclohexylium, 1,2-bromo-bridged cyclopentyl, 1,3-bromo-bridged cyclopentyl, 1,2-halo-bridged cyclohexyl cations, and 1,4-halo-bridged cyclohexyl cations. Calculations at this level show that the bridged 1,2-bromocyclopentyl cation is the lowest energy $C_5H_8Br^+$ species by about 4 kcal/mol. The lowest energy species found on the $C_6H_{10}F^+$ potential surface is the 1-fluorocyclohexylium cation. On the $C_6H_{10}Cl^+$ potential surface, the lowest energy species found is the bridged 1,4-chlorocyclohexyl cation, but its energy is very similar to that of the 1-chlorocyclohexylium cation. The bridged 1,4-bromocyclohexyl cation is found to be more stable than the 1-bromocyclohexylium and the bridged 1,2-cyclohexyl cations by about 5 and 10 kcal/mol, respectively. A comparison of the relative energies of the cations has been made by computing their hydride affinities. The bridged 1,4-bromocyclohexyl cation is shown to be the most stable cation species studied. The computed hydride affinities of the 1-halocyclohexylium cations indicate that the 1-fluoro is more stable than either the analogous chloro or bromo cations, which are of the same stability. Analysis of the charge distributions suggests that there are electrostatic and size effects that dominate the stability of the cations.

Introduction

Halonium ions have played vital roles as intermediates in organic chemistry.[1] Bridged species such as the bromonium ion first proposed by Roberts and Kimball in 1937 to explain the stereochemistry of dibromine addition to alkenes have been of particular interest.[1,2] Although the presumed intermediacy of bridged bromonium ions codified a large body of stereochemical information on alkene additions, it was the development of experimental conditions for stabilizing cations in super-acid media by Olah and co-workers that first allowed direct observation of these and related halonium ions.[1,3] Since the introduction of these techniques, many halonium ions of diverse structure have been observed, although bridged fluoronium ions have not.[1,3−8]

Gas-phase studies have been important in measuring various thermochemical parameters of halonium ions[9] and in studying their reactivity.[9,10] The thermochemical data have in some cases served as benchmarks for computational studies.[4,5,11]

One very interesting aspect of the stable ion studies by Olah, Prakash, and co-workers has been the elusive nature of the bridged bromonium ion **1** that might be expected to result from dibromine addition to cyclohexene.[12] A report in which nitronium tetrafluoroborate was
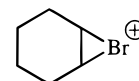
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reacted with bromocyclohexane yielded exclusively *trans*-1-fluoro-2-bromocyclohexane, which was presumed to

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result from **1**.[13] However, although the analogous cyclopentene bromonium ion has been observed under stable ion conditions, attempts to observe **1** under such conditions have been unsuccessful.[12] Instead, the 1,4-bridged bromonium ion **2** was obtained by the routes shown in eq 1. Olah, Prakash, and co-workers suggest that **2** is
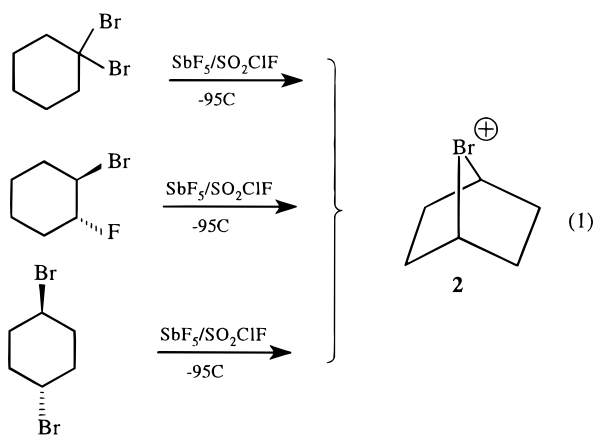
formed in the first two examples in eq 1 by a succession of 1,2-hydride shifts. They indicated that this was the first transannular bromine participation in a six-membered ring and likely results because of the large size of bromine. These workers also carried out semiempirical MNDO computations on **1** and **2**, finding that **2** is more stable by 2.6 kcal/mol. Chair and boat conformations of the 4-bromocyclohexylium cation were reported to be less stable than **2** by 2.9 and 3.6 kcal/mol, but the 1-bromocyclohexylium cation was determined to be the most stable isomeric cation studied on this potential energy surface, more stable than **2** by 1.1 kcal/mol. Cation **1** also is the likely intermediate in nucleophilic trapping studies carried out in methanol by Nagorski and Brown[14] under conditions that are vastly different from the stable ion studies of Olah, Prakash, and co-workers. Attempts to prepare the analogous chloronium ion always yielded 1-methylcyclopentenyl cation.[12]

Various other aspects of halonium ion chemistry have been a rich area for computational study in recent years and testify to the continuing interest in such systems.[4,5,8,11,15-19] Particularly important are studies indicating that the importance of bridging is highly dependent on the computational level.

In 1990, Hamilton and Schaefer, using polarization basis sets and configuration interaction methods, reported that bridged $C_2H_4Br^+$ is 1.5 kcal/mol more stable than the 1-bromoethyl cation.[16] The 2-bromoethyl cation is a transition state, which is about 25 kcal/mol higher in energy than the bridged cation and resembles bromoethene with a hydrogen bridged at the C−Br end. It is clearly not a transition state "connecting" the bridged

bromonium ion and 1-bromoethyl cation. Hamilton and Schaefer noted that the energies were relatively insensitive to both basis set and electron correlation effects.

Reynolds has studied $C_2H_4X^+$ and $C_4H_8X^+$ (where X is F, Cl, and Br) and shown that both systems are qualitatively similar.[4,5] For both $C_2H_4Br^+$ and $C_4H_8Br^+$, the 1-bromoethyl and 2-bromo-2-butyl cations, respectively, are less stable than the corresponding bridged bromonium ions. When X = F and Cl, the 1-haloethyl and 2-halo-2-butyl cations are more stable than the bridged species. In extensive studies of $C_2H_4Cl^+$, Hopkinson and co-workers reported similar results.[8] These are consistent with experimental observations of both cyclic chloronium ions and their corresponding open α-chloro cations, since the computed energy difference between the bridged and open species is fairly small (6.4 kcal/mol for $C_2H_4Cl^+$ and 5.3 kcal/mol for $C_4H_8Cl^+$). However, neither experimental nor computational studies suggest that bridged fluoronium ions should be observable in these or related systems.

Reynolds' studies have also addressed the thermochemical stability of various halogen-containing cations by computing hydride affinities.[4,5,11] The resulting hydride affinities of bridged and acyclic $C_2H_4X^+$ and $C_4H_8X^+$ (where X = F, Cl, and Br) suggest that bridged $C_4H_8Br^+$ is the most stable cation (0.0 kcal/mol) relative to acyclic $C_4H_8Br^+$ (3.5), t-C_4H_9 cation (4.0), and acyclic $C_4H_8F^+$ (6.0). In the acyclic $C_2H_4X^+$ series, bromine-containing cations are more stable than either chlorine- or fluorine-containing cations, which are of equal stability. In contrast, acyclic, bromine-containing cations are more stable than fluorine-containing cations, which are more stable than chlorine-containing cations in the $C_4H_8X^+$ series. Reynolds suggests as a result that the stability of such cations is largely dependent on the electronegativity of the halogen, its ability to "back-bond" by p−p overlap, and the substitution pattern of the cation.[4,5,11] These results are in reasonable agreement with hydride affinities determined in gas-phase studies by Beauchamp and co-workers.[9]

Klobukowski and Brown have recently indicated the critical importance of the inclusion of electron correlation and polarization functions on the geometry of the bromonium ion of 2-methylpropene.[15] The tendency toward more bridging as the computational method improves, particularly in terms of enhancing electron correlation and including polarization functions, is consistent with other computations and indicates the importance of their inclusion for consistency with the experimental observation of bridged bromonium ions. They comment that semiempirical computations using older parametrizations are suspect as a result of this and earlier related work. More recently, these authors have reported experimental and computational studies (using effective core potentials) of the deuterium kinetic isotope effect for the addition of dibromine to ethylene.[20]

Such computational studies of X^+ adducts of small alkenes as well as the experimental studies of Olah, Prakash, and co-workers related to the bridged bromonium ion of cylohexene[12,21] suggest that a detailed computational study of $C_6H_{10}X^+$ could provide important

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Table 1.   Relative Energies (kcal/mol) of $C_2H_4Br^+$ Isomers with the MP2/SB Geometry[a]

cation	MP2/SB[b]	QCISD/SB	MP2/MB1	MP2/MB2	MP2/BB1	QCISD/BB1	QCISD(T)/BB1
bridging **3**	0.0 (0)	0.0	0.0	0.0	0.0	0.0	0.0
cis **4**	0.9 (1)	−0.9	5.7	5.7	6.1	3.7	4.0
trans **5**	−0.9 (0)	−2.4	4.1	4.1	4.3	2.2	2.4

[a] The basis sets are as follows: SB = C,H 6-31G(d) with Br 8s6p2d (using 5d pure polarization functions); MB1 = C,H 6-31G(d) with Br 8s6p3d (using 5d pure polarization functions); MB2 = C,H 6-31G(d) with Br 8s6p3d (using 6d cartesian polarization functions); BB1 = C,H 6-311G(d,p) with 8s6p3d (using 5d cartesian polarization functions); BB2 = C,H 6-311G(d,p) with Br 8s6p3d (using 6d cartesian polarization functions). [b] Number of imaginary vibrational frequencies is listed in parentheses (NIMAG = 1 indicates a transition state).

Table 2.   Relative Energies (kcal/mol) of C2H4Br+ Isomers with MP2 and QCISD Geometries[a]

cation	MP2/BB2// MP2/BB2[b]	QCISD/SB// QCISD/SB	QCISD(T)/SB// QCISD/SB	MP2/BB2// QCISD/BB2	QCISD/BB2// QCISD/BB2	QCISD(T)/BB2// QCISD/BB2
bridging **3**	0.0 (0)	0.0	0.0	0.0	0.0	0.0
cis **4**	6.2 (1)	−1.1	−0.7	6.3	3.5	3.7
trans **5**	4.5 (0)	−2.6	−2.3	4.6	2.0	2.2

[a] The basis sets are as follows: SB = C,H 6-31G(d) with Br 8s6p2d (using 5d pure polarization functions); MB1 = CH 6-31G(d) with Br 8s6p3d (using 5d pure polarization functions); MB2 = C,H 6-31G(d) with Br 8s6p3d (using 6d cartesian polarization functions); BB1 = C,H 6-311G(d,p) with Br 8s6p3d (using 5d cartesian polarization functions); BB2 = C,H 6-311G(d,p) with Br 8s6p3d (using cartesian polarization functions). [b] Number of imaginary vibrational frequencies is listed in parentheses (NIMAG = 1 indicates a transition state).

Table 3.   Absolute and Relative Energies of $C_2H_4X^+$ Cations 3, 4, and 5 (X = F, Cl, and Br)[a−d]

cation	MP2/BB2 absolute energies	MP2/BB2 relative energies	QCISD(T) absolute energies	QCISD(T) relative energies
3 (X = F) bridged	−177.660 19(0)	28.2	−177.703 88(0)	27.7
4 (X = F) cis	−177.703 49(1)	1.0	−177.746 50(1)	1.0
5 (X = F) trans	−177.705 17(0)	0.0	−177.748 06(0)	0.0
3 (X = F) bridged	−537.684 72(0)	1.7	−537.737 33(0)	3.3
4 (X = F) cis	−537.684 75(1)	1.7	−537.740 21(1)	1.5
5 (X = F) trans	−537.687 39(0)	0.0	−537.742 59(0)	0.0
3 (X = F) bridged	−2650.690 61(0)	0.0	−2650.729 95	0.0
4 (X = F) cis	−2650.680 86(1)	6.1	−2650.723 61	4.0
5 (X = F) trans	−2650.683 64(0)	4.4	−2650.726 05	2.4

[a] The basis sets are as follows: (for X = F and Cl) C, H, X, 6-311G(d,p) (using 6d cartesian polarization functions); (for X = Br) C, H, 6-311G(d,p) with Br 8s6p3d (using 6d cartesian polarization functions). [b] The number of imaginary vibrational frequencies is listed in parentheses (NIMAG = 1 indicates a transition state). [c] At MP2/6-31G(d) geometries for F and Cl; at MP2/SB geometries for Br. [d] Absolute energies are in hartrees, and relative energies are in kcal/mol.

information on the relative stability of bridged halonium ions vs various halocarbocations. Since most of the computational studies on halonium ion have been carried out on fairly small cations or at low computational levels for large cations, we undertook and report here a comprehensive study of a large number of $C_6H_{10}X^+$ isomers, where X = F, Cl, and Br. More limited computations of $C_5H_8X^+$, for X = Br, are also reported. We have also reexamined the $C_2H_4X^+$ surface (X = F, Cl, and Br) for quantitative evaluation of the basis set and correlation effects.

Computational Methods

Final ab initio calculations on the ethyl, cyclopentyl, and cyclohexyl species were carried out with the Gaussian 92 and 94 suites of programs.[22,23] Standard basis sets were used except for bromine, where those of Dunning (8s3p2d and 8s6p3d), first reported by Bauschlicher, Schaefer, and Bagus, were used.[16,24] A series of high-level computations were carried out on the $C_2H_4X^+$ (X = F, Cl, and Br) cations to examine basis set and correlation effects in order to determine what minimal level of theory would be applied to the larger cyclopentyl and cyclohexyl species. Five different basis sets were used predominantly: (1) SB (small basis) = C,H 6-31G(d) with Br 8s6p2d (using 5d pure polarization functions), (2) MB1 = C,H 6-31G(d) with Br 8s6p3d (using 5d pure polarization functions), (3) MB2 = C,H 6-31G(d) with Br 8s6p3d (using 6d Cartesian polarization functions), (4) BB1 = C,H 6-311G(d,p) with Br 8s6p3d (using 5d pure polariation functions), and (5) BB2 = C,H 6-311G(d,p) with Br 8s6p3d (using 6d Cartesian polariza-

tion functions). All calculations on F and Cl systems used standard basis sets with the 6d option for the six Cartesian d functions. Calculations on Br used either 5d pure functions (SB, MB1, and BB1) or 6d functions (MB2 and BB2) in the basis sets. The smaller basis sets were chosen to minimize the computer time necessary for the optimization of the large number of Br-containing species studied. Various combinations of these basis sets and correlation methods such as MP2,[25−27] QCISD,[28] and QCISD(T)[28] (all using the frozen core approximation) were used with different optimized geometries (see the Discussion). The uncorrected computational results are presented in Tables 1 and 2 for the $C_2H_4X^+$ species. (Zero

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Table 4. Absolute and Relative Energies of Cyclohexyl Cations (C$_6$H$_{10}$X$^+$, X = F, Cl, and Br)[a,b]

structure	MP2/6-31G(d)// MP2/ 6-31G(d)[c]	relative energy	MP2/6-311G(d,p)// MP2/6-31G(d)[d]	relative energy
1,4-fluoro-bridged cation (**6**)	−333.1161 (0.1553)	8.5	−333.3322	14.1
1-fluorocyclohexylium cation (**7**)	−333.1297 (0.1540)	0.0	−333.3547	0.0
1,2-fluoro-bridged cation (**8**)	−333.0895 (0.1539)	25.2	−333.3086	28.9
1,4-chloro-bridged cation (**6**)	−693.1383 (0.1539)	0.2	−693.3348	−0.9
1-chlorocyclohexylium cation (**7**)	−693.1386 (0.1525)	0.0	−693.3335	0.0
1,2-chloro-bridged cation (**8**)	−693.1249 (0.1533)	8.6	−693.3220	7.2
1,4-bromo-bridged cation (**6**)	−2806.0394 (0.1530)	−0.2	−2806.3351	−4.9
1-bromocyclo-hexylium cation (**7**)	−2806.0391 (0.1520)	0.0	−2806.3273	0.0
1,2-bromo-bridged cation (**8**)	−2806.0280 (0.1524)	7.0	−2806.3226	2.9

[a] Zero-point vibrational energy is listed in parentheses. **6**, **7**, and **8** (X = F, Cl, and Br) are all mimina. [b] Absolute energies are in hartrees, and relative energies are in kcal/mol. [c] MP2/SB//MP2/SB for bromine-containing cations. [d] MP2/BB2//MP2/SB for bromine-containing cations.

Table 5. Absolute and Relative Energies of Cyclopentyl Cations (C$_5$H$_8$Br$^+$)[a,b]

structure	MP2/SB//MP2/SB energy	relative energy	MP2/BB2//MP2/ SB energy	relative energy
1-bromocyclopentylium cation (**9**)	−2766.8624 (0.1207)	0.0	−2767.1180	4.2
1,2-bromo-bridged cation (**10**)	−2766.8615 (0.1223)	0.6	−2767.1247	0.0
1,3-bromo-bridged cation (**11**)	−2766.8398 (0.1227)	14.2	−2767.1038	13.1

[a] Zero-point vibrational energy is listed in parentheses. **9**, **10**, and **11** are all minima. [b] Absolute energies are in hartrees, and relative energies in kcal/mol.
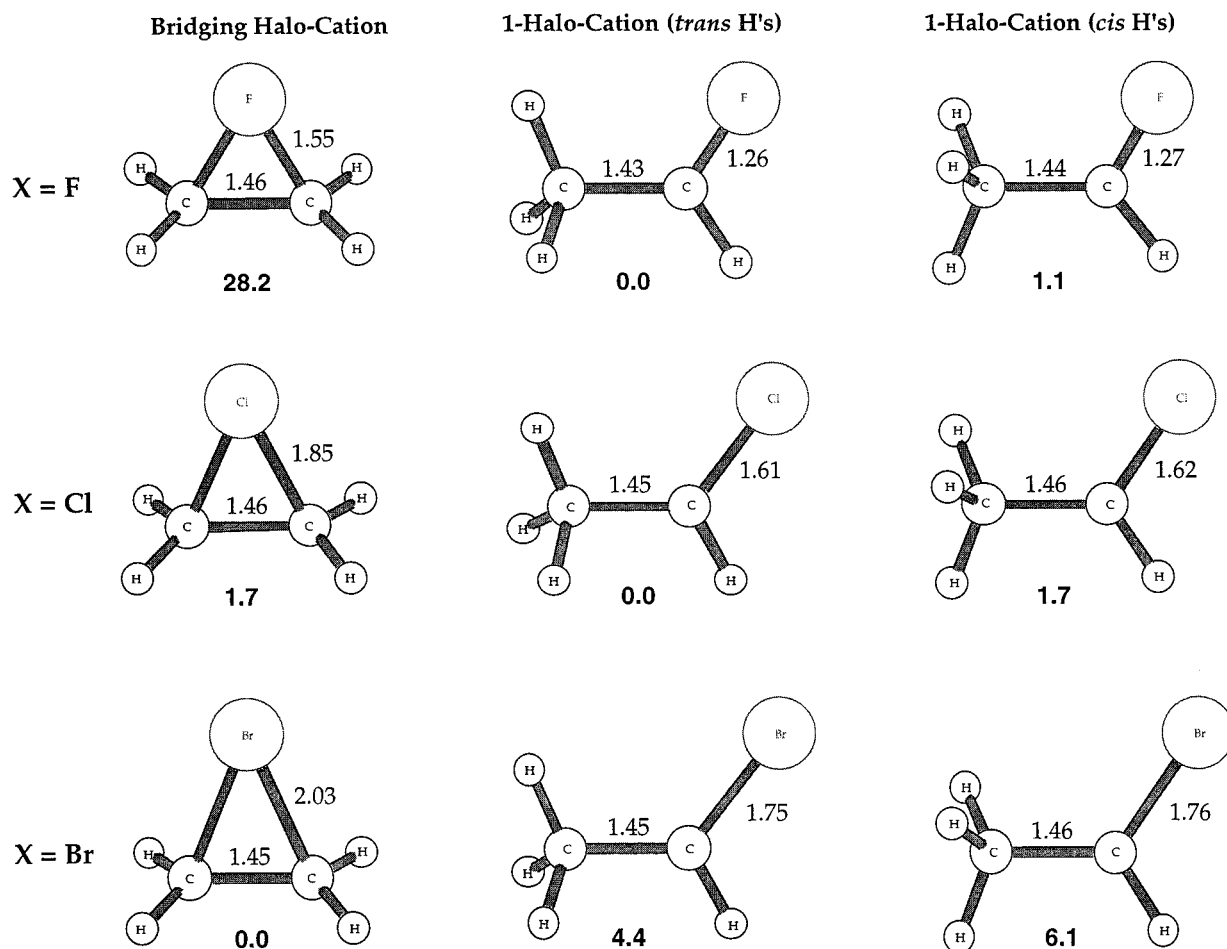

Figure 1. Geometric representations of the C$_2$H$_4$X$^+$ structures. Bond distances are shown in Å. Relative energies (in kcal/mol) were obtained at the MP2/6-311G(d,p)//MP2/6-31G(d) (X = F and Cl) and at the MP2/BB2//MP2/SB (X = Br) level.

point energetic corrections have not been made, but as shown in Tables 4 and 5, the relative energies will change by less than 1 kcal/mol.)

Almost all molecular geometries of the cyclopentyl and cyclohexyl species were optimized using closed-shell restricted Hartree−Fock (RHF) self-consistent field (SCF) calculations at the 6-31G(d) level for F and Cl and the SB basis set for Br, although several critical structures were optimized at the MP2 level with the same basis sets. The frozen core approximation was used for all correlated optimized geometries and frequencies. All structures were further probed by analytically calculating and then diagonalizing the matrix of energy second
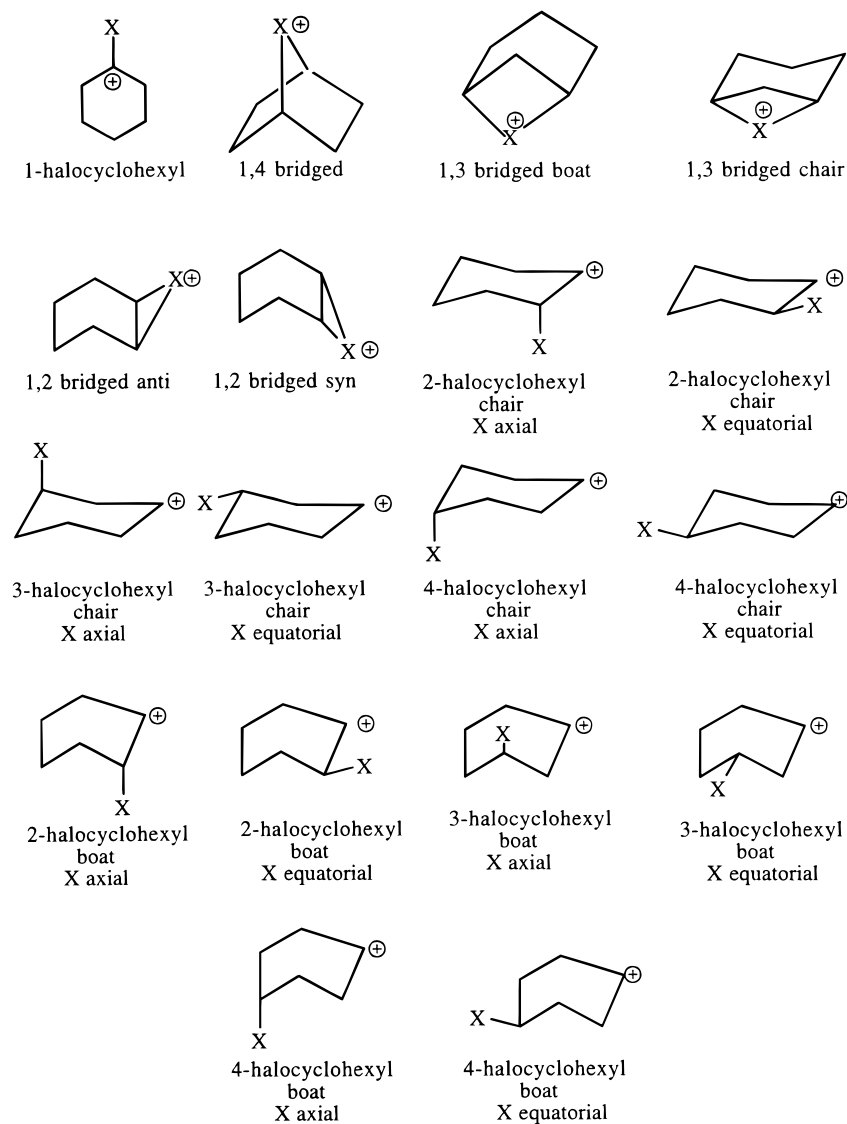
**Figure 2.** Geometric representations of the $C_6H_{10}X^+$ structures that were considered.

derivatives (Hessian). The Hessian is positive definite in all cases except where noted by the number of imaginary vibrational frequencies in parentheses.

The energies of the cyclopentyl and cyclohexyl cations were determined using the RHF-optimized geometries with single-point second-order perturbation theory using the 6-31G(d) (for F and Cl) or the SB (for Br) basis sets. From these preliminary data, it was determined that higher level computations were required for certain of the more stable cations whose energies are very similar. These were computed as single-point energy computations at the MP2/6-31G(d), MP4(SDTQ)/6-31G(d), and MP2/6-311G(d,p) levels for the F- and Cl-containing ions and at the MP2/SB, MP4(SDTQ)/SB, and MP2/BB2 levels for the Br-containing ions. The uncorrected computational results for these more stable cations are presented in Tables 4 and 5. The computational results for the higher energy cations studied are provided in the Supporting Information (see the text for further details).

Charge density analyses using Bader's atoms in molecules methodology have also been carried out.[29-33]

Results and Discussion

An assessment of the computational level necessary to achieve reasonable energy comparisons for the cyclohexyl and cyclopentyl cations was made by reexamining the work of Hamilton and Schaefer on the $C_2H_4X^+$ system.[16,34] Our studies of cations **3−5** (for X = Br)
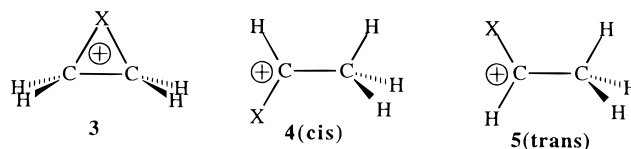
suggest that a proper representation of their energetic differences depends more on the quality of the basis set used than on correlation effects (Tables 1 and 2). Thus, when a small basis set (SB) [C and H at 6-31G(d) and Br at 8s6p2d using pure 5d polarization functions] with either MP2 or QCISD correlation methods is used, the bridged isomer **3** (X = Br) is not the lowest energy cation (Table 1). When, however, larger basis sets are used [C

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3	4	5	6	7
55.2	28.0	27.0	16.2	2.0
28.7	28.7	27.1	4.1	4.9
21.7	27.8	26.1	0.0	4.9

Figure 3. Relative hydride affinities (kcal/mol) of cations **3**−**7** as determined at the MP2/6-311G(d,p)//MP2/6-31G(d) level (X = F and Cl) and at the MP2/BB2//MP2/SB level (X = Br).

and H at 6-31G(d) and Br at 8s6p3d using 5d pure polarization functions or C and H at 6-311G(d,p) and Br at 8s6p3d using 6d pure polarization functions], **3** (X = Br) is the lowest energy cation with either of these correlation methods. All of the results with higher quality basis sets suggest that **3** is more stable than **5** (X = Br) by 2−4 kcal/mol and that **4** (X = Br), which is a transition state, is less stable than **3** by 4−6 kcal/mol.

The optimization level for the geometry has a small effect (Table 2), but the basis set effects are also shown to be dominant for the energies of cations **3**−**5** (for X = Br). Table 2 shows that only with medium and large basis sets is the 1,2-bridged bromonium ion the lowest energy cation of **3**−**5** (for X = Br) at the three optimized geometries studied.

$C_2H_4X^+$ cations **3**−**5** (for X = F and Cl) also have been studied at the MP2/6-311G(d,p)//MP2/6-31G(d) and QCISD(T)/6-311G(d,p)//MP2/6-31G(d) levels of theory. Their absolute and relative energies as well as those for X = Br at comparable levels are given in Table 3. For both X = F and Cl, the trans cation **5** is the more stable isomer by a small amount over the cis transition state **4**. As expected, the bridged fluoronium cation **3** (X = F) is considerably less stable; however, the corresponding chloronium cation **3** (X = Cl) has nearly the same energy as the isomers **4** and **5** (X = Cl) at the MP2 level and is somewhat less stable at the QCISD(T) level.

At both correlation levels, the bromonium cation **3** is more stable than the trans isomer **5**, which is about 1.5 kcal/mol more stable than the cis isomer **4**. In this series of computations (Table 3), the MP2 energies predict the correct qualitative trends but tend to overestimate (by a few kcal/mol) the importance of bridging compared to the higher level QCISD(T) energies.

Selected values for the optimized geometries as well as the QCISD(T) relative energies of the $C_2H_4X^+$ cations

are presented in Figure 1. Most importantly, the C−C bond length is affected very little for bridging vs non-bridging for X = F, Cl, and Br. The C−X bond length is larger for **3** than for **4** or **5** for X = F, Cl, and Br. The increase in the C−X bond length from nonbridging to bridging is relatively constant for F (0.29 Å), Cl (0.24 Å), and Br (0.28 Å). Brown, Klobukowski, and co-workers have commented on the near planarity of the bromonium cation **3**, where the sum of the C−C−H, H−C−H, and C−C−H, computed at the density functional theory level with effective core potentials, is 357.3°.[20] In the work reported here, the sum of these angles for **3** (X = F, Cl, Br) is 359.1, 356.6, and 356.6° computed at the MP2/6-31G(d) level for X = F, Cl and at MP2/SB for X = Br.

Computations on a large number of cyclohexyl (Figure 2 and structures **6**−**8**) and cyclopentyl (structures **9**−**11**) cations have been carried out with geometry optimizations at RHF/6-31G(d) (for F and Cl) and RHF/SB (for Br) levels, followed by single-point energies at the MP2 level. Idealized structures for all of the cyclohexyl cations studied are shown in Figure 2. This theoretical level was
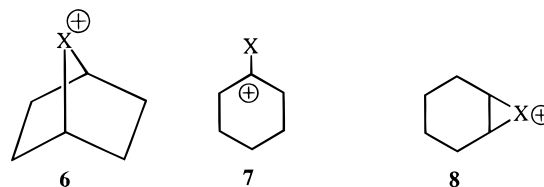
chosen as the most economical one to examine a large number of systems of this size and was adequate to identify structures **6**−**8** as the most stable $C_6H_{10}X^+$ cations for additional study. The large number of other cation isomers that have been studied (Figure 2) are at least 12 kcal/mol higher in energy at this level. Conse-
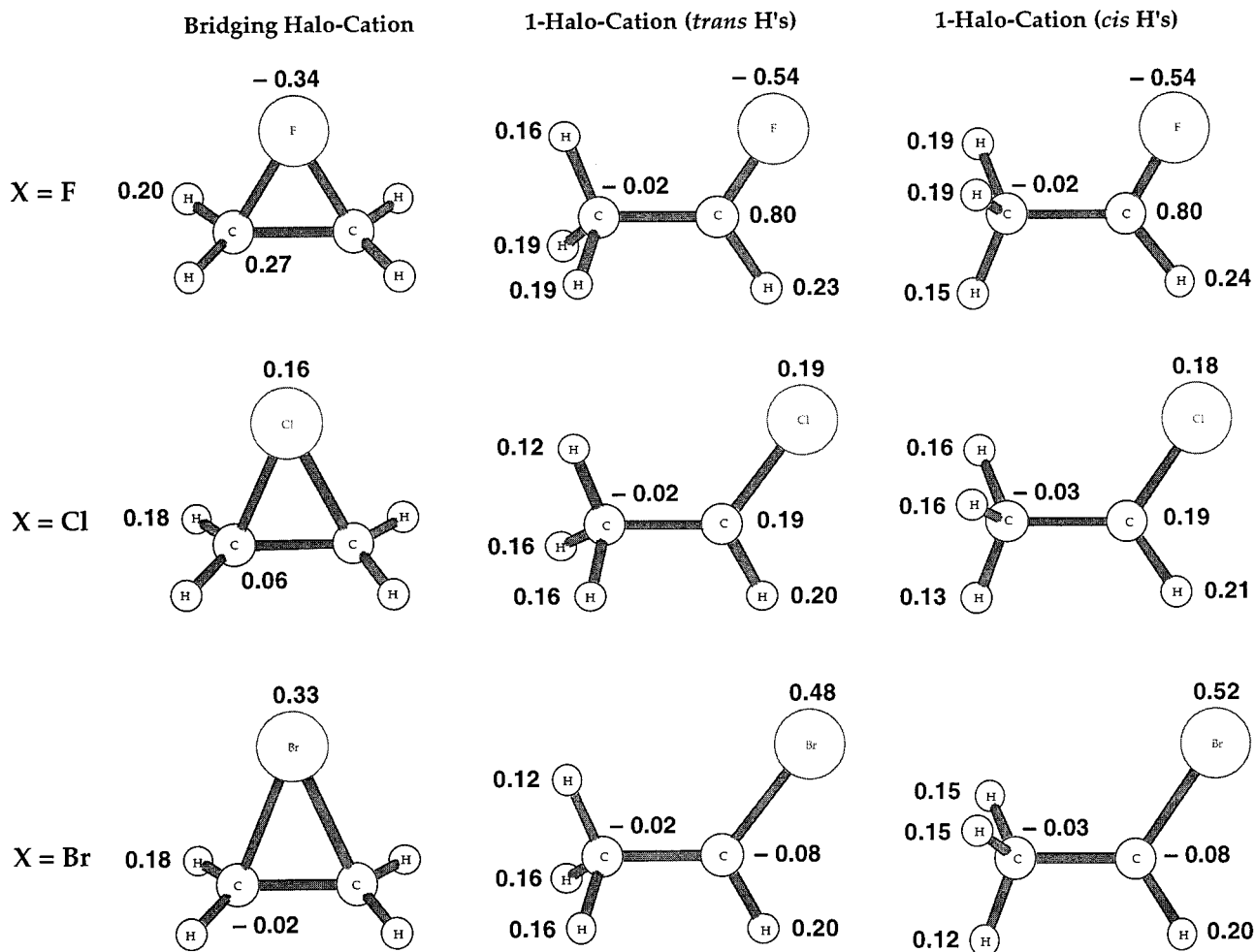
Figure 4. Atomic charges (Bader) for the $C_2H_4X^+$ (X = F, Cl, and Br) structures obtained at the MP2/6-311G(d,p)//MP2/6-31G(d) level (X = F and Cl) and at the MP2/BB2//MP2/SB level (X = Br).

quently, these data are not included in this paper but are available as Supporting Information.

Taking account of the effects just discussed for the $C_2H_4X^+$ (X = F, Cl, and Br) system, it was deemed necessary to carry out higher level computations for the more stable cations, which have similar energies (structures **6**–**8**). These data are presented in Table 4. Detailed structural representations of some of the more important of these cations will be shown later.

Isomers **6**–**8** are the most frequently considered $C_6H_{10}X^+$ structures in discussions of halogen addition reactions to cyclohexene. As indicated previously, stable cation experiments designed to prepare **8** for X = Br have instead led to **6**. No reports of either **6** or **8** for X = Cl or F have been made. 1-Halocyclohexylium cations **7**, on the other hand, have been observed for X = F at 195 K and for X = Cl below 144 K under stable ion conditions.[35] Both of these cations rearranged to the 1-methylcyclopentenyl cation at higher temperatures. These authors suggest that the stability ordering of α-halo carbocations (F > Cl > Br) results from the decreasing back-donating ability of these halogen substituents as the halogen size increases. Thus, the governing effect is suggested to be

the poorer p–p overlap of the halogen orbitals with the cationic center as the halogen size increases. More recent studies by Olah, Prakash, and co-workers on trihalomethyl cations demonstrate a Cl > Br > I stability ordering for these cations. These results are discussed in terms of p–p overlap as well as electronegativity effects.[34-37] Computational studies of hydride affinities of CX_3^+ by Reynolds indicate that CF_3^+ is much less stable than CCl_3^+ or CBr_3^+.[11] Indeed, Reynolds noted that CH_2F^+ was more stable in terms of hydride affinity than CF_3^+. More recently, Frenking and co-workers have shown that the π-donating ability is I > Br > Cl > F for a variety of Group 13 and 14 cations including CX_3^+.[19] These studies suggest again the delicate nature of the factors controlling the stability of halo cations, both in the gas phase and under stable ion conditions in the condensed phase.

Although the MP2/SB level underestimates the effect of bridging, the discussion above for $C_2H_4X^+$ cations suggests that energies obtained at the MP2/BB2 level with the MP2/SB geometry are trustworthy. The bridged 1,4-halonium ions **6** and 1-halocyclohexylium cations **7** are by far the most stable cations on the $C_6H_{10}X^+$

(34) The energies for *cis*- and *trans*-$C_2H_4X^+$ have been inadvertently reversed in ref 16. The geometrical distinction of cis and trans relates the location of the two H's.

(35) Olah, G. A.; Liang, G.; Mo, Y. K. *J. Org. Chem.* **1974**, *39*, 2394–2398.

(36) Olah, G. A.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020–8021.

(37) Olah, G. A.; Rasul, G.; Yudin, A. K.; Burrichter, A.; Prakash, G. K. S.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 1446–1451.
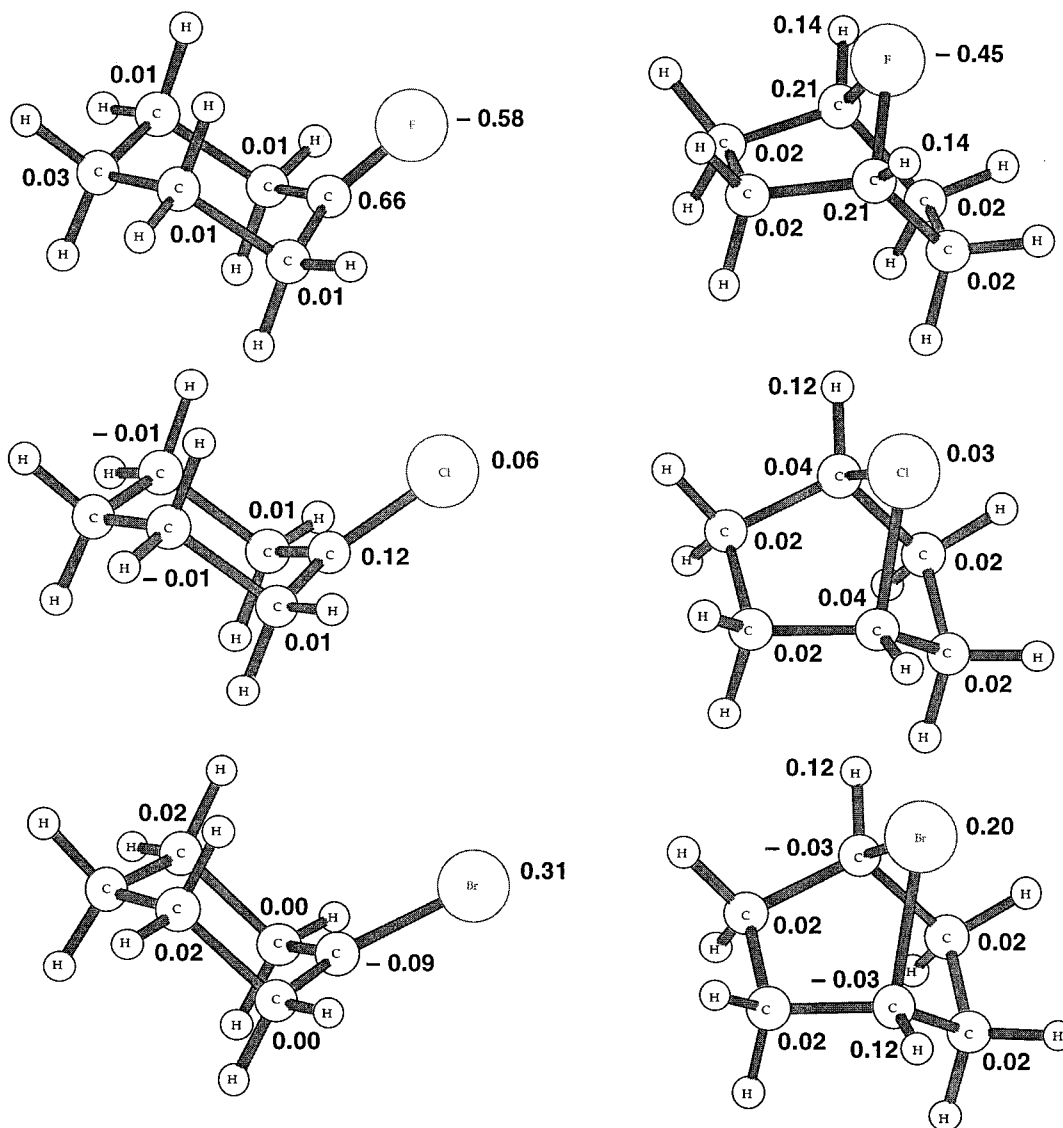
Figure 5. Atomic charges (Bader) for the $C_6H_{10}X^+$ (X = F, Cl, and Br) structures obtained at the MP2/6-311G(d,p)//MP2/6-31G(d) level (X = F and Cl) and at the MP2/BB2//MP2/SB level (X = Br).

potential energy surface for the X substituents studied at this level (Table 4). The bridged 1,4-chloronium ion **6** (X = Cl) and 1-chlorocyclohexylium cation **7** (X = Cl) are of virtually equal energy. In contrast, the 1,4-bromonium ion **6** is some 5 kcal/mol more stable than ion **7** at the MP2/BB2//MP2/SB level, while **7** is considerably more stable than **6** for $C_6H_{10}F^+$ at a similar level Thus, the 1,4-bridged cation is "relatively more stable" for X = Cl and more important still for X = Br.

That Olah, Prakash, and co-workers have been unable to detect the presence of any bridged 1,2-halonium ions such as **8** is not surprising on the basis of the energetics revealed by these computations. The X = Br 1,2-bridged cation **8** is about 8 kcal/mol higher than the corresponding 1,4-bridged cation at our best computational level (MP2/BB2//MP2/SB) (Table 4). This energetic preference may explain why Olah and co-workers did not observe the 1-bromocyclohexylium ion **7** (X = Br) or the 1,2 bridged cation **8** (X = Br).[12]

The relative hydride affinities of **3**–**7** for X = F, Cl, and Br are displayed in Figure 3. These results contrast somewhat with those of Reynolds[4] on $C_2H_4Br^+$ in that the 1,4-bridged cation **6** (X = Br), which is the most stable

of the cations studied, is closer in stability to the 1-fluorocyclohexylium cation **7** (X = F) than to its 1-bromocyclohexylium isomer **7** (X = Br). More significant are the hydride affinities of the 1-halocyclohexylium cations **7** (X = F, Cl, and Br) in which the fluoro cation is more stable than the chloro, which is about equal to the bromo. These values more closely follow the experimental observations of α-halo cations by Olah, Prakash, and co-workers[36–38] than Reynolds' computations on smaller systems.[4,5] The 1,4-bridged cations **6** (X = F, Cl, and Br) show an opposite trend with the bromo cation being the most stable. What seems clear is that the tradeoff between halogen electronegativity and so-called back-bonding effects is very finely tuned in these systems.

In an attempt to gather more information about the nature of this tradeoff, we have used Bader's theory of atoms-in-molecules[29–33] to analyze the charge distribution in these cations. The atomic charges for both the $C_2H_4X^+$ and $C_6H_{10}X^+$ series (**3**–**7** for X = F, Cl, and Br) computed at the MP2/BB2//MP2/SB level are shown in Figures 4 and 5.

(38) Olah, G. A.; Rasul, G.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1996**, *118*, 3580–3583.
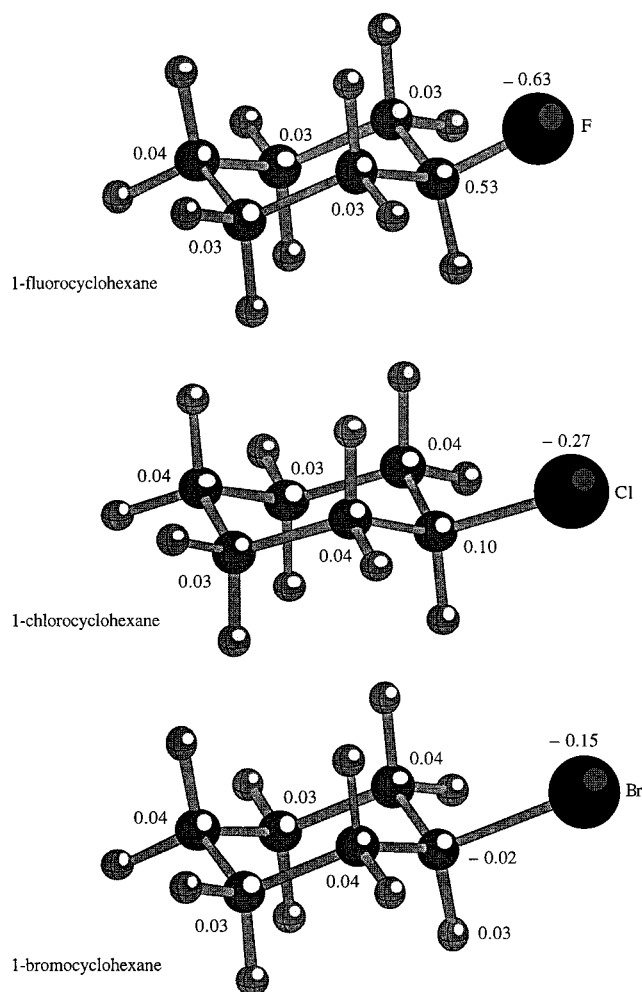
Figure 6. Atomic charges (Bader) of halocyclohexanes ($C_6H_{11}X$ with X = F, Cl, and Br) obtained at the MP2/6-311G(d,p)// MP2/6-31G(d) level (X = F and Cl) and at the MP2/BB2//MP2/ SB level (X = Br).

It is striking in both cation series, whether for open or bridged cations or for 1,2- or 1,4-bridges, that the fluorine atoms have quite high negative charges (−0.3 to −0.6 e), the chlorine atoms are nearly neutral (0.03 to 0.2 e), and the bromine atoms are more positive still (0.2 to 0.5 e). The atomic charges for the carbon atoms attached to the halogens are very positive for X = F, near zero for X = Cl, and slightly negative for X = Br.

A further comparison of the charge densities of the cyclohexyl cations (Figure 5) and their corresponding neutral, parent halocyclohexanes (Figure 6) reveals that the large negative charge on fluorine in the 1-fluorocyclohexylium cation (−0.58 e) as well as the polarity of the C−F bond is very similar to that in fluorocyclohexane (−0.63 e). As seen in Reynolds' calculations for CH_2F^+ vs CF_3^+, the dominant role for F is to polarize the electron density toward itself, almost independently of the rest of the molecule.[11] It appears that very little back-bonding occurs for F.

The corresponding chloro and bromo comparisons reveal an increasingly greater difference between the 1-halocyclohexylium ions (Cl, +0.06 e; Br, +0.31 e) and the halocyclohexanes (Cl, −0.27 e; Br, −0.15 e). As the atomic charges in both the cations and the neutrals become more positive for chlorine and bromine, respectively, the polarity of the C−X bond changes far more

for these than for fluorine substitution. Indeed, the α-carbon atomic charge in the neutral halocyclohexanes are +0.53 e (F), +0.10 e (Cl), and +0.02 e (Br). This positively charged α-carbon feature persists in the 1-fluorocyclohexylium cation, where the α-carbon (+0.66 e) has a positive charge, but there are significant changes in the α-carbon atomic charges for the Cl and Br cases (+0.12 e and −0.09 e, respectively). This suggests that the electronegativity effect is quite dramatic and that even in the 1-halo cation the C−F bond is still polarized C^+-F^-. In addition, an increase of the positive charge at the α-carbon will increase the "strength" of the C−F bond from an electrostatic viewpoint.

It appears that p−p overlap is not the major stabilizing mechanism for α-halo carbocations since much less negative charge is distributed among the atoms of the fluorine-containing cations. In fact, on the basis of the C−X bond polarities, bromine is the best electron-donating halogen of F, Cl, and Br. The large size of the Br atom allows efficient bridging between the carbon atoms. Thus, both electrostatic and size effects are consistent with F cations preferring 1-halo cations and Br cations preferring bridging. As expected, chlorine-containing cations lie somewhere between. It is also striking how evenly distributed the positive charge is in the cations, especially the 1,4-bridged $C_6H_{10}X^+$ series.[39]

The structures of the bridged 1,4-bromonium and 1-bromocyclohexylium cations (**6** and **7** for X = Br) are displayed in Figure 7. A few comparisons with the $C_2H_4Br^+$ species **3** and **5** shown in Figure 1 are of interest. The carbon−bromine bond length in **3** is 2.03 Å compared with 2.05 Å in the 1,4-bridged cation **6**, even though bromine bridges 1,2 and 1,4 carbon atoms in the two systems. Hamilton/Schaefer and Klobukowski/Brown have also reported similar carbon−bromine bond lengths for the bromonium ion of 2-methylpropene.[15,16] Identical "bridgehead" carbon−hydrogen bond lengths are observed in the 1,2-bromonium ion **3** and 1,4-bridged **6** (1.09 Å) (X = Br). The Br−C−H bond angle in these two species is also fairly similar (109.0° for **3** and 107.3° for **6**) (X = Br). The H−C−H bond angle is 117.7° in **3**; a corresponding C−C−H bond angle of 116.3° is computed for **6** (X = Br). Not surprisingly, similarities between the *trans*-1-bromoethyl cation **5** and 1-bromocyclohexylium cation **7** also exist. The bond length between the sp² and sp³ carbons in both **5** and **7** (X = Br) is 1.46 Å. The corresponding carbon−bromine bond lengths are 1.76 and 1.80 Å. This similarity between acyclic and cyclic bromonium ions suggests that neither steric nor torsional effects are dominant in the cyclohexyl cations.

We have also briefly studied three bromocyclopentyl cations: namely, the 1-bromocyclopentylium (**9**), the 1,2-bridged (**10**), and the 1,3-bridged (**11**) cations with
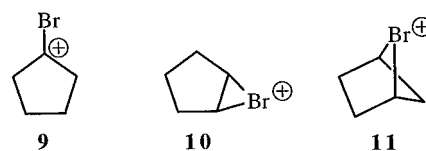
(39) A reviewer has suggested that separation of the σ and π components of the relevant orbitals might provide useful information concerning the effects of different X groups on cation stability. It, however, has not been possible to preserve the separation between σ and π molecular orbitals in the transformation of the **Z** vector density for the MP2 method.
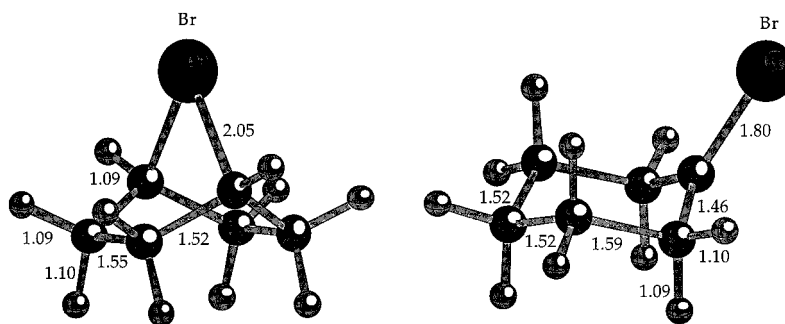
Figure 7. Structures of **6** and **7** obtained at the MP2/SB level. Bond distances are shown in Å.

geometry optimizations at the MP2/SB level (Table 5). These cations are minima on the $C_5H_8Br^+$ potential energy surface. At the MP2/BB2//MP2/SB level, the 1,2-bridged cation (**10**) is more stable than 1-bromocyclopentylium cation (**9**) by about 4 kcal/mol and more stable than the 1,3-bridged cation (**11**) by about 13 kcal/mol. The observation by Olah and co-workers of the 1,2-bridged bromonium ion **10** is consistent with these computations.[12,40] Bridging is also important for the $C_5H_8Br^+$ cations, but 1,3-bridging introduces too much strain. The 1-bromocyclopentylium cation cannot stabilize the positive charge as well as the 1,2-bridged isomer **10**, making the 1,2-bridged isomer the most favorable cation on the $C_5H_8Br^+$ surface.

Summary

Bridged 1,4-halonium ions **6** and 1-halocyclohexylium cations **7** (for X = F, Cl, and Br) are the lowest energy species found in computational studies of a number of halogen-containing cyclohexyl cations at several ab initio levels. For X = F, the 1-halocyclohexylium cation is favored, but for X = Cl, there is essentially no difference between the bridged 1,4-halonium ion **6** and the corresponding 1-halocyclohexylium cation **7** at the MP2/BB2//MP2/SB level. However, for X = Br, the bridged 1,4-bromonium ion is favored at this computational level. Computations on 1-bromo cations (**9**) and the bridged 1,2-bromo (**10**) and 1,3-bromo cations (**11**) of cyclopentene suggest that the bridged 1,2 cation is slightly more stable

than its isomers. Thus, electronegativity effects are the dominant factors in the stability of α-fluorocations in contrast to bromine-containing cations (1,4-bridged cyclohexyl and 1,2-bridged cyclopentyl), where the bromine atom allows efficient bridging. Chlorine-containing cations are intermediate between those containing fluorine and bromine with the result that the 1,4-bridged cyclohexyl and 1-cyclohexylium cations are similar in energy. Electronegativity effects seem to dominate the stability of these cations, but strain effects play a role as well. These computational results have been briefly discussed in terms of the experimental studies of Olah, Prakash, and co-workers.

(40) Olah, G. A.; Liang, G.; Staral, J. *J. Am. Chem. Soc.* **1974**, *96*, 8112−3.