# Density Functional Studies of Halonium Ions of Ethylene and Cyclopentene

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A computational study of a variety of  $C_2H_4X^+$ ,  $C_5H_8X^+$ ,  $C_5H_{8-n}(OH)_nX^+$  (n=1, 2), where X= Cl and Br, has been carried out. The potential energy surfaces of all molecules under investigation have been scanned and the equilibrium geometries and their harmonic vibrational frequencies have been calculated at the Becke3LYP/6-311++G(d,p) level of theory. The bonding in bridged halonium ions is discussed in terms of donor – acceptor interaction between ethylene and halogen orbitals in the parent ethylenehalonium ion. The relative energies, the equilibrium geometries and the proton and carbon NMR chemical shifts calculated are in good agreement with existing experimental and theoretical data.

### **1** Introduction

Organic halogen cations have gained increasing significance both as reaction intermediates and preparative reagents. They are related to oxonium ions in reactivity but they offer greater selectivity. They can be divided into two main categories namely acyclic (open-chain) halonium ions and cyclic halonium ions.[1] In 1937, Roberts and Kimball [2] proposed a cyclic bromonium ion intermediate to explain the stereoselective bromination reactions with alkenes, whereas in 1965, the chloronium ion analogue was found by Fahey et al. [3, 4]

A series of *ab initio* calculations have been reported for the  $C_2H_4X^+$  [X=F, Cl, Br] cation. [5-10] In all these calculations the *trans*-1-bromoethyl cation, **1**, is less stable than the corresponding bridged bromonium ion, **2**, whereas the *cis*-1-bromoethyl cation, **3**, is a transition state. For X=F or Cl structure **1** is more stable than **2**, with **3** being also a transition state.



*Ab initio* and semiempirical calculations have been carried out in more complicated systems like  $C_4H_8X^+$ , [8] and  $C_6H_{10}X^+$ . [10] Except from a brief *ab initio* study of Damrauer et al., [10] of  $C_5H_8Br^+$  and a semiempirical study of  $C_5H_7(OH)Br^+$ [11] there is no systematic study of the potential energy surface for halonium ions of substituted or non substituted cyclopentene.

In this work we present a detailed study of the conformational space of halonium ions of ethylene  $C_2H_4X^+$  and cyclopentenes like  $C_5H_8X^+$  and  $C_5H_{8-n}(OH)_nX^+$  (n=1, 2), where X= Cl and Br at the Becke3LYP/6-311++G(d,p) level of theory. The relative energies, the equilibrium geometries and the proton and carbon NMR chemical shifts calculated are discussed in relation to existing experimental and theoretical data.

# 2 Computational details

The electronic structure and geometry of the halonium ions studied were computed within the density functional theory, using gradient corrected functionals, at the Becke3LYP [12] computational level. The basis set used was 6-311G++(d,p) [13,14]. Full geometry optimizations were carried out without symmetry constraints. Frequency calculations after each geometry optimization ensured that the calculated structure is either a real minimum or a transition state in the potential energy surface of the molecule. The <sup>13</sup>C and <sup>1</sup>H NMR shielding constants of the B3LYP/6-311++G(d,p) optimized structures were calculated with the gauge-independant atomic orbital (GIAO) method [15] at the B3LYP/6-311+G(2d,p) level and were converted to the chemical shifts by calculating at the same level of theory the <sup>13</sup>C and <sup>1</sup>H shieldings in TMS. All calculations were performed using the Gaussian98 package. [16]

# **3 Results and discussion**

# $3.1 C_2 H_4 X^+ (X=Cl, Br)$

An assessment of the computational level and basis set necessary to achieve reasonable energy comparisons for the cyclopentyl cations was made by reexamining previous *ab initio* works on the  $C_2H_4X^+$  (X=Cl, Br) system. The agreement of the relative energies and geometries of the species calculated at Becke3LYP/6-311++G(d,p) level with those found at the CISD, [7] QCISD and MP2 [10] levels of theory suggest that the energy differences depend more on the quality of the basis set used than on correlation effects.



Fig. 1. Internal rotation of trans-1-bromoethyl cation, 1

For X=Br, the bridged bromonium ion, **2**, is more stable than *trans*-1-bromoethyl cation, **1**, by 0.4 kcal/mol. The *cis*-1-bromoethyl cation, **3**, with energy 2.1 kcal/mol above **2**, is a transition state in the maximum of the potential energy path related to the internal rotation of **1**, as shown in Figure 1. Each point in this path has been partially optimized keeping the torsion angle fixed. For X=Cl structure **1** is the global

minimum. The bridged cation, **2**, and the transition state , **3**, are located 6.4 and 1.7 kcal/mol higher respectively.

The bromonium, **2**, C-C bond length was calculated equal to 1.450 Å between the usual values of 1.34 Å for C=C and 1.54 Å for C-C. This distance is 1.449 Å and 1.442 Å for 2-bromoethyl cations **1** and **3** respectively. The C-X bond length is larger for **2** than for **1** or **3** for both X=Cl and Br. For example, in the bromonium ion the C-Br distance of 2.053 Å is a bit longer than a typical single bond length of 1.94 Å. [17] The C-Br distance from the X-ray determination of a substituted ethylenebromonium ion with a Br3- counterion (formed from bromination of adamantylidene-adamantane) [18] is 2.155 Å, which is 0.1 Å longer than our calculated value of for the parent cation. The C-Br bond length was calculated equal to 1.794 Å and 1.791 Å for 2-bromoethyl cations **1** and **3** respectively. The ethylene part of the bromonium ion, **2**, is near planar as the sum of the C-C-H, H-C-H, and C-C-H angles were computed equal to 357.3° for X=Br at the density functional level with effective core potentials [19] and 356.6° and 356.6° for X=Cl and Br respectively at the MP2 level. [10]

Considerable discussion has been done in whether the three membered ring in bridged halonium ions is a  $\sigma$ -complex or a  $\pi$ -complex. The relationship between  $\pi$ -complexes and true 3-membered rings has been discussed by Dewar [20] and Cremer, [21] whereas Schaefer [7] has stated that there is no sharp boundary between the two. Indeed an examination of the orbitals calculated for bromonium ion revealed that both interactions are present. In figure 2 the shapes of the bonding and antibonding orbitals derived from the interaction of the filled ethylene  $\pi$ -orbital and vacant p-orbital of Br (**a**), as well as these derived from the interaction of filled p-orbital of Br and vacant  $\pi^*$ -orbital of ethylene (**b**), are schematically shown.



Fig. 2. Orbital interactions in bridged ethylene bromonium ion

#### $3.2 C_5 H_8 X^+ (X=Cl, Br)$

We have studied the three possible chloro and bromocyclopentyl cations: namely, the 1-halocyclopentylium (**4a,b**), the 1,2-bridged (**5a,b**), and the 1,3-bridged (**6a,b**) cations with geometry optimizations at the Becke3LYP/6-311++G(d,p) level.



The optimized structures are shown in Fig.3, whereas the relative energies and selected optimized geometrical parameters in Table 1. Frequencies calculations have shown that all structures are minima on the potential energy surfaces.



Fig. 3. Optimized structures of  $C_5H_8X^+$  cations

The most stable  $C_5H_8Cl^+$  cation is the 1-chlorocyclopentylium cation (4a) being 6.4 kcal/mol lower in energy than the 1,2-bridged chlorocyclopentylium (5a). In the bromonium cations the energy order is reversed with 5b being 0.1 kcal/mol more stable than 4b. Apparently the larger and less electronegative bromine atom stabilizes more effectively the bicyclic bridged structure than chlorine. These computations are consistent with the observations of Olah and co-workers. [22,23] Thus, although they have achieved to prepare 5b from *trans*-1,2-dibromocyclopentane, in a similar experiment with *trans*-1,2-dichlorocyclopentane they obtained, instead of 5a, only the 4a. The 1,3-bridged structures 6a,b are more higher in energy due to high strain energy.

	<b>4</b> a	5a	6a	4b	5b	6b
Х	Cl	Cl	Cl	Br	Br	Br
C-C' <sup>1</sup>		1.462			1.458	
C-X	1.658	1.969	2.027	1.818	2.123	2.177
X-C-C'	123.9	68.0	57.8	124.0	69.9	59.8
Folding angle <sup>2</sup>		107.2	109.5		108.3	109.7
Rel. Energy	0.0	6.4	18.6	0.1	0.0	14.0

Table 1. Calculated energies (kcal/mol) and geometrical parameters (Å, °) of  $C_5H_8X^+$  cations

<sup>1</sup>C' is C2 in **4a**,**b** and the second bridged carbon in **5a**,**b** and **6a**,**b**. <sup>1</sup>The folding angle is this between XCC' and the four membered carbon chain.

Although in the 1,2 bridged structure the cyclopentene ring is quite planar, it adopts the boat like conformation. No chair conformation has been found as stable point in the potential energy surface. The C-X bond lengths are larger for **6a,b** than in **5a,b** by near 0.5 Å and the folding angle of the XCC' bridge with the rest of the molecule is between  $107-110^{\circ}$ .

comparison of the bridged 1,2-halonium cyclopentylium The and 1halocyclopentylium cations with the corresponding  $C_2H_4X^+$  species 1 and 3 is very interesting. Thus, for X=Cl the C-Cl bond length in 2 and 5a is 1.895 Å and 1.969 Å respectively and the C-H bond lengths are equal (1.085 Å). Furhermore, the Cl-C-H bond angles in these two species are also fairly similar (105.3° for 2 and 108.8° for 5a). There are also similarities between the *cis*-1-chloroethyl cation 3 and 1chlorocyclopentylium cation 4a. For example C-Cl bond lengths are 1.636 Å and 1.658 Å respectively. The same conclusions stand in the case of the corresponding bromonium cations. From these similarities between both acyclic and cyclic structures we can assume that neither steric nor torsional effects are dominant in the cyclopentyl cations.



Finally, the <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts for the studied species calculated using the GIAO method are in very good agreement with the existing experimental data. The <sup>13</sup>C chemical shifts of the carbon atoms and the proton shifts for the two equivalent olefin-type protons for the bridged 1,2-bromonium cyclopentylium are given in 7, along with the experimental values [23] in parentheses.

#### 3.3 C<sub>5</sub>H<sub>7</sub>(OH)X<sup>+</sup> (X=Cl, Br)

The potential energy surface for the chloro and bromo hydroxycyclopentyl cations has been scanned in an energy window of about 20.0 kcal/mol at the Becke3LYP/6-311++G(d,p) level. The optimized structures found and their relative energies are shown in Fig. 4. All structures are real minima since no imaginary frequencies were calculated.



Fig. 4. Optimized structures and relative energies (kcal/mol) of C<sub>5</sub>H<sub>7</sub>(OH)X<sup>+</sup> cations

In contrast to what has been found in the parent halonium cations of ethylene and unsubstituted cyclopentene, the 3-hydroxy-1-halocyclopentyliums, **8a,b**, are the most stable isomer for both chlorine and bromine. However, the tendency of bromine to stabilize the 1,2-bridged structure is present and in this system. Thus, the two bridged 1,2-bridged 3-hydroxybromocyclopentylium, **10b** and **11b**, are only 3.4 and 4.1 kcal/mol higher from 3-hydroxy-1-bromocyclopentylium and much bellow the 2-hydroxy-1-bromocyclopentylium isomer. In the case of chlorine both two hydroxy-1-chlorocyclopentylium isomers are more stable than the two 1,2-bridged structures. In both cases the 1,2-bridged structure with halogen and hydroxyl in *anti* position are more stable by about 1 kcal/mol. All 1,3-bridged isomers are an order of magnitude higher in energy with bromine derivatives being less destabilized.

The presence of hydroxyl does not affect the calculated overall geometry of the isomers. For example the C-X bond length in hydroxy-1-halocyclopentyliums, **8a,b** and **9a,b**, are equal with those of 1-halocyclopentylium, **4a,b**, (C-Br = 1.818 Å and C-Cl = 1.650 Å). The cyclopentene ring is nearly flat in **8a,b-11a,b**, whereas it is

folded in 1,3-bridged cations, **12a,b-15a,b**. The folding angle is about 110° with the bromo 1,3-bridged cations being always less folded.

# 3.4 C<sub>5</sub>H<sub>6</sub>(OH)<sub>2</sub>X<sup>+</sup> (X=Cl, Br)

The 1,3-bridged isomers of the chloro and bromo dihydroxycyclopentyl cations have been calculated in very high energies and thus the study was restricted to dihydroxy-1-halocyclopentylium and 1,2-bridged isomers. The optimized structures, which are real minima on the potential surfaces, as well as their relative energies are shown in Fig. 5.



Fig. 5. Optimized structures and relative energies (kcal/mol) of C<sub>5</sub>H<sub>6</sub>(OH)<sub>2</sub>X<sup>+</sup> cations

As in the case of the hydroxycyclopentene derivatives a dihydroxy-1halocyclopentylium is the most stable isomers for both chlorine (**16a**) and bromine, (**18b**), but the presence of a the second hydroxyl seems to decrease the energy gap between the 1-halocyclopentylium the 1,2-bridged isomers. Once again, the bromine atom stabilizes the 1,2-bridged structures more than chlorine. The optimized geometrical parameters are very similar to those for the corresponding cyclopentene and hydroxysyclopentene derivatives. Finally, the cyclopentene ring is nearly flat in all structures.

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