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Density functional study of potential energy surfaces and relative stabilities of halonium cations of ethylene and cyclopentenes

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Abstract—Potential energy surfaces, hydride affinities and nuclear independent chemical shifts (NICS) of a variety of halonium cations of ethylene $C_2H_4X^+$, cyclopentene $C_5H_8X^+$ and hydroxy substituted cyclopentenes $C_5H_{8-n}(OH)_nX^+$ (n=1, 2), where X=Cl and Br were computed at the Becke3LYP/6-311++G(d,p) level of theory. The potential energy surfaces of all molecules under investigation have been scanned and the equilibrium geometries and their harmonic vibrational frequencies have been calculated. The computed hydride affinities of all conformers, as well as the NICS values for the 1,2-bridged cations indicate that the bromo cations are more stable than the analogous chloro cations. © 2002 Elsevier Science Ltd. All rights reserved.

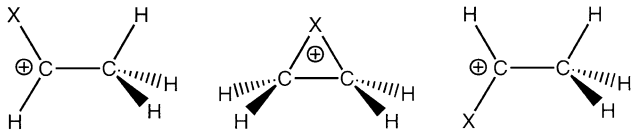
1. Introduction

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] Diphenyliodonium ion was first prepared in 1894 by Hartman and Meyer[2] whereas, the less stable diarylbromonium and -chloronium ions were prepared by Nesmeyanov and co-workers.[3] The key role of dialkylhalonium ions of the type R_2X^+ (X=I, Br, Cl) and of alkylarylahonium ions ($ArRX^+$) as intermediates in alkylation reactions of haloalkanes and -arenes has led to extensive work for their preparation and study.[1,4] In 1937, Roberts and Kimball[5] proposed a cyclic bromonium ion intermediate to explain stereoselective bromination reactions with alkenes, whereas in 1965, the chloronium ion analogue was found by Fahey et al.[6,7]

A series of ab initio calculations have been reported for the $C_2H_4X^+$ (X=F, Cl, Br) cation.[8–13] In all these calculations the 1-bromoethyl cation, **1**, is less stable than the corresponding bridged bromonium ion, **2**, whereas the structure of 1-bromoethyl cation with the methyl group rotated through 60°, **3**, is a transition state. For X=F or Cl, structure **1** is more stable than **2**, with **3** also being a transition state (Scheme 1).

Ab initio and semiempirical calculations have been carried out on more complicated systems like $C_4H_8X^+$,[11] and $C_6H_{10}X^+$.[13] Except for a brief ab initio study of Damrauer et al.[13] of $C_5H_8Br^+$ and a semiempirical study of $C_5H_7(OH)Br^+$[14] 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 calculated proton and carbon NMR chemical shifts are discussed in relation to existing experimental and theoretical data. The relative stabilities of the chloro and bromo analogous species are also discussed in terms of their hydride affinities. Furthermore, in the case of the 1,2-bridged cations, the nuclear independent chemical shifts (NICS) calculated in the center of the three membered ring have been tested as a measure of their relative stability.



1a,b **2a,b** **3a,b**

Scheme 1. Structures of 1-haloethyl and bridged halonium cations (**a**: X=Cl, **b**: X=Br).

Keywords: halonium cations; DFT; nuclear independent chemical shifts; hydride affinity.

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Table 1. Calculated geometrical parameters (Å, °), relative energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of $C_2H_4X^+$ cations

	C–C′	C–X	C′–X	X–C–C′	Rel. energy	Hydride affinity	NICS
1a	1.441	1.636		124.8	0.0	260.0	
2a	1.456	1.895	1.895	67.4	6.4	266.9	−46.5
3a	1.448	1.638		123.9	1.7	262.2	
1b	1.442	1.791		125.3	0.4	259.5	
2b	1.450	2.053	2.053	69.3	0.0	259.1	−48.3
3b	1.449	1.794		124.6	2.1	261.2	

2. Results and discussion

2.1. $C_2H_4X^+$ (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 work 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,[10] QCISD and MP2[13] levels of theory suggests that the energy differences depend more on the quality of the basis set used than on the method of describing correlation effects.

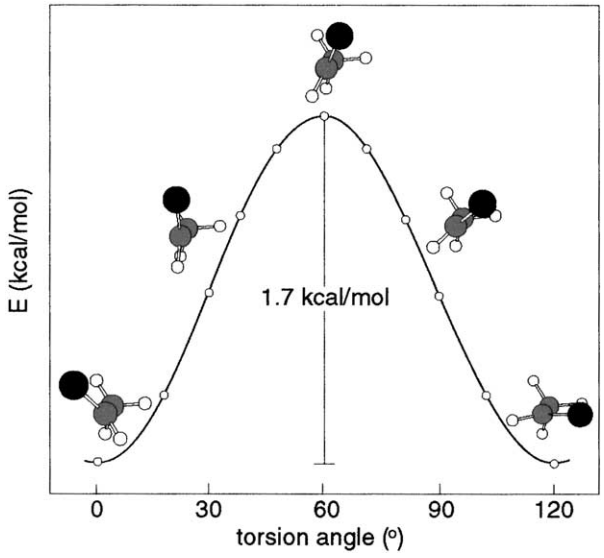


Figure 1. Internal rotation of *trans*-1-bromoethyl cation, **1b**.

The calculated relative energies and selected optimized geometrical parameters are given in Table 1. For X=Br, the bridged bromonium ion, **2b**, is more stable than 1-bromoethyl cation, **1b**, by 0.4 kcal/mol. The structure of 1-bromoethyl cation with the methyl group rotated through 60°, **3b**, has energy 2.1 kcal/mol above **2b** and is a transition state in the maximum of the potential energy path related to the internal rotation of **1b**. The energy of the 1-bromoethyl cation as a function of the torsion angle is shown in Fig. 1. Each point in this path has been partially optimized keeping the torsion angle fixed. For X=Cl the 1-chloroethyl cation, **1a**, is the global minimum. The bridged cation, **2a**, and the transition state, **3a**, are located 6.4 and 1.7 kcal/mol higher, respectively.

The C–C bond length in the bridged bromonium ion, **2b**, was calculated as 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 and 1.442 Å for 2-bromoethyl cations **1b** and **3b**, respectively. The C–X bond length is larger for **2a**,**b** than for **1a**,**b** or **3a**,**b** 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.[15] The C–Br distance from the X-ray determination of a substituted ethylenebromonium ion with a Br^{3-} counterion (formed from bromination of adamantylidene-adamantane)[16] is 2.155 Å, which is 0.1 Å longer than our calculated value

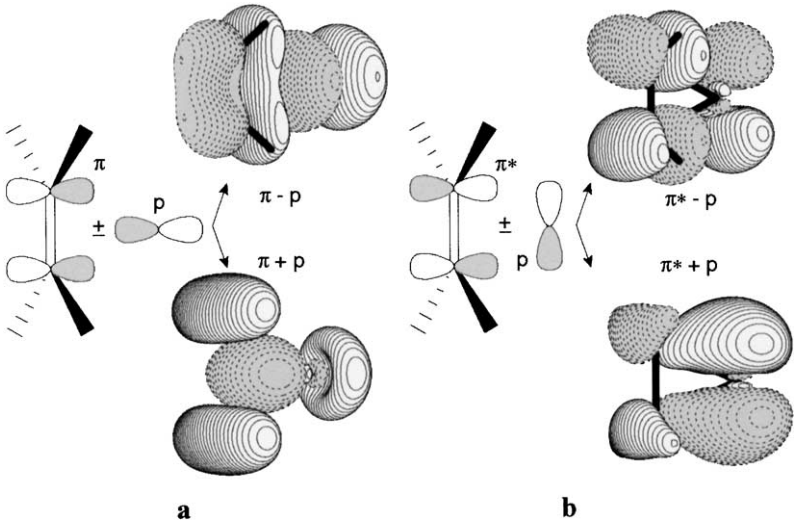
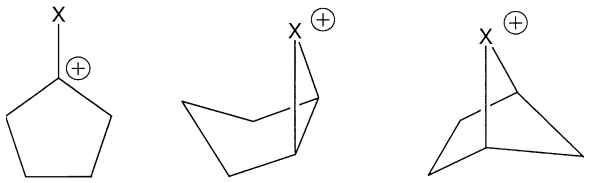


Figure 2. Orbital interactions in bridged ethylene bromonium ion.



Scheme 2. Halonium cyclopentyl cations studied (**a**: X=Cl, **b**: X=Br).

of 2.053 Å for the parent cation. The C–Br bond length was calculated as 1.794 and 1.791 Å for 2-bromoethyl cations **1b** and **3b**, respectively. The ethylene part of the halonium ions, **2a**,**b**, is near planar as the sum of the C–C–H, H–C–H, and C–C–H angles were computed as 357.3° and 357.2° for X=Cl or Br, respectively. This sum was calculated as 357.3° for X=Br at the density functional level with effective core potentials[17] and 356.6° for both X=Cl and Br respectively at the MP2 level.[13]

There has been considerable discussion about whether the three membered ring in bridged halonium ions is a σ-complex or a π-complex. The relationship between π-complexes and true 3-membered rings has been discussed by Dewar[18] and Cremer,[19] whereas Schaefer[10] has stated that there is no sharp boundary between the two. Indeed an examination of the orbitals calculated for bridged bromonium ion revealed that both interactions are present. In Fig. 2 the shapes of the bonding and antibonding orbitals derived from the interaction of the filled ethylene π-orbital and vacant p-orbital of Br (**a**), as well as these derived from the interaction of filled p-orbital of Br and vacant π^* orbital of ethylene (**b**), are schematically shown.

2.2. $C_5H_8X^+$ (X=Cl, Br)

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

The optimized structures are shown in Fig. 3, whereas the relative energies and selected optimized geometrical parameters in Table 2. Frequencies calculations have shown that all structures are minima on the potential energy surfaces.

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 the bicyclic bridged structure more effectively than chlorine. These computations are consistent with the observations of Olah and co-workers.[20] Thus, although they have achieved the preparation of **5b** from *trans*-1,2-dibromocyclopentane, in a similar experiment with *trans*-1,2-dichlorocyclopentane they obtained, instead of **5a**, only **4a**. The 1,3-bridged structures **6a**,**b** are higher in energy due to high strain energy.

The 1,2 bridged structure adopts the boat like conformation. No chair conformation has been found as a stable point in

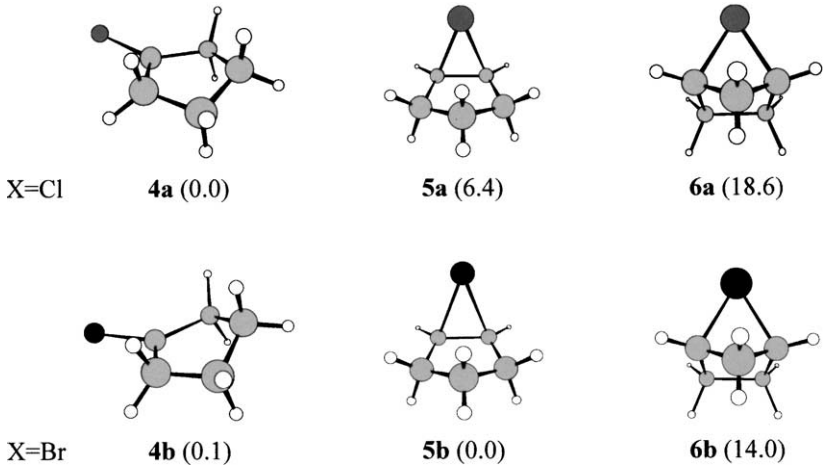


Figure 3. Optimized structures and relative energies (kcal/mol) of $C_5H_8X^+$ cations.

Table 2. Calculated geometrical parameters (Å, °), relative energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of $C_5H_8X^+$ cations

	C–C′[a]	C–X	C′–X	X–C–C′	Folding angle[b]	Rel. energy	Hydride affinity	NICS
4a		1.658		123.9		0.0	236.8	
5a	1.462	1.969	1.969	68.0	107.2	6.4	243.2	−44.5
6a		2.027	2.027	57.8	109.5	18.6	255.4	
4b		1.818		124.0		0.1	236.7	
5b	1.458	2.123	2.123	69.9	108.3	0.0	236.6	−46.2
6b		2.177	2.177	59.8	109.7	14.0	250.6	

[a] C′ is C2 in **4a**,**b** and the second bridged carbon in **5**–**6a**,**b**.
[b] The folding angle is this between XCC′ and the four membered carbon chain.

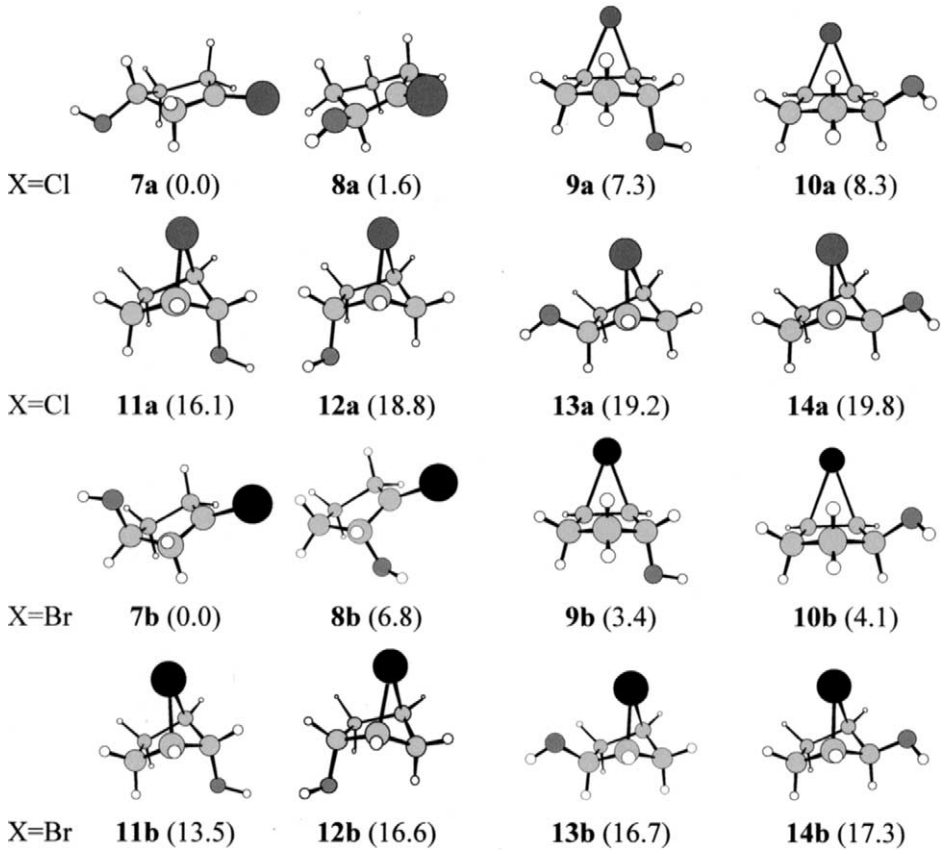


Figure 4. Optimized structures and relative energies (kcal/mol) of $C_5H_7(OH)X^+$ cations.

the potential energy surface. The C–X bond lengths are larger for **6a**,**b** than in **5a**,**b** by nearly 0.5 Å and the folding angle of the XCC′ bridge with the rest of the molecule is between 107–110°.

The comparison of the bridged 1,2-halonium cyclopentylium and 1-halocyclopentylium 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 and 1.969 Å, respectively, and the C–H bond lengths are equal (1.085 Å). Furthermore, 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 1-chlorocyclopentylium cation **4a**. Thus, the C–Cl bond lengths are equal to 1.636 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.

Table 3. Calculated geometrical parameters (Å, °), relative energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of $C_5H_7(OH)X^+$ cations

	C–C′[a]	C–X	C′–X	X–C–C′	X–C′–C	Folding angle[b]	Rel. energy	Hydride affinity	NICS
7a	1.471	1.658		123.7			0.0	239.3	
8a	1.466	1.650		125.4			1.6	241.0	
9a	1.461	2.006	1.923	65.2	71.2	108.0	7.3	246.7	−43.0
10a	1.459	1.971	1.927	66.4	69.6	106.5	8.3	247.7	−44.0
11a		2.001	2.001	56.9	56.9	111.2	16.1	255.5	
12a		1.957	2.114	61.5	54.5	108.8	18.8	258.2	
13a		1.965	2.048	59.3	55.6	109.3	19.2	258.6	
14a		1.995	2.017	57.9	56.9	110.3	19.8	259.2	
7b	1.472	1.816		124.1			0.0	236.4	
8b	1.467	1.820		124.9			6.8	243.7	
9b	1.457	2.157	2.082	67.2	72.7	109.0	3.4	240.3	−44.8
10b	1.454	2.128	2.085	68.2	71.4	107.4	4.1	241.0	−45.8
11b		2.150	2.150	59.0	59.0	111.2	13.5	250.4	
12b		2.124	2.221	62.0	57.6	109.0	16.6	253.5	
13b		2.120	2.182	60.9	58.1	109.3	16.7	253.6	
14b		2.146	2.161	59.8	59.1	110.4	17.3	254.2	

[a] C′ is C2 in **7**–**8a**,**b** and the second bridged carbon in **11**–**14a**,**b**.
[b] The folding angle is this between XCC′ and the four membered carbon chain.

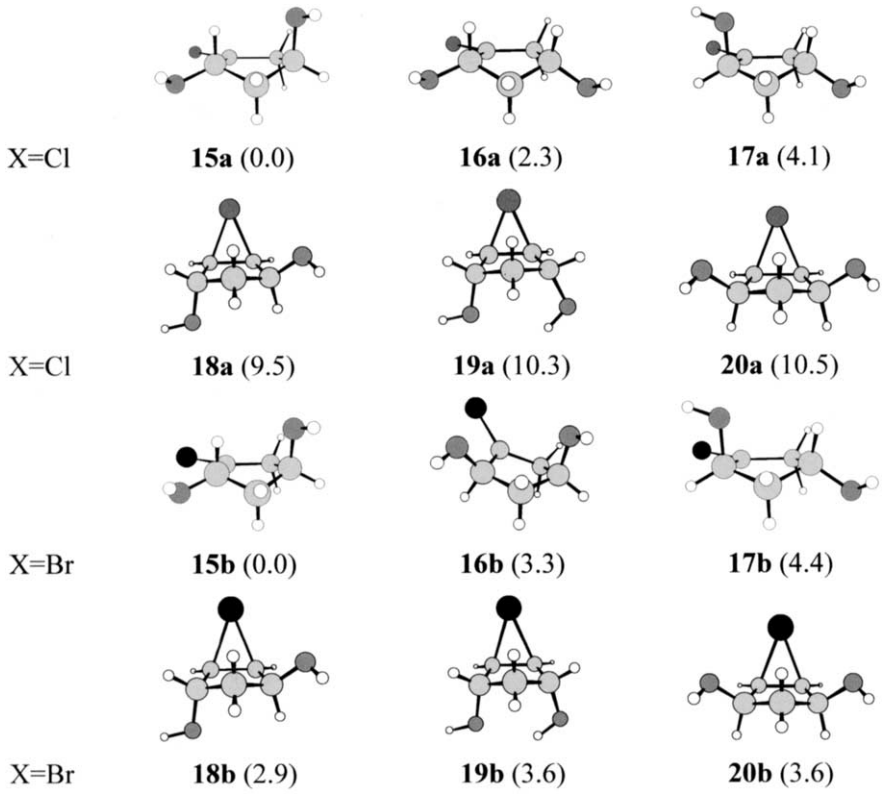


Figure 5. Optimized structures and relative energies (kcal/mol) of $C_5H_6(OH)_2X^+$ cations.

2.3. $C_5H_7(OH)X^+$ (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, whereas selected optimized geometrical parameters in Table 3. All structures are real minima since no imaginary frequencies were calculated. In the course of the potential energy scanning oxygen-bridged bicyclic species has been also located as local minima and will be the subject of a future study.

In contrast to what has been found in the parent halonium cations of ethylene and unsubstituted cyclopentene, for 3-hydroxy-1-halocyclopentyliums, **7a**,**b**, are the most stable isomers for both chlorine and bromine. However, the tendency of bromine to stabilize the 1,2-bridged structure is present in this system. Thus 1,2-bridged 3-hydroxy-bromocyclopentyliums, **9b** and **10b**, are only 3.4 and 4.1 kcal/mol higher in energy than 3-hydroxy-1-bromo-cyclopentylium and much below the 2-hydroxy-1-bromo-cyclopentylium isomer. In the case of chlorine, both 2-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 groups in *anti* positions are more stable by about 1 kcal/mol. All 1,3-bridged isomers are more than 10 kcal/mol higher in energy with bromine derivatives being less destabilized.

The presence of a hydroxyl group does not affect the calculated overall geometry of the isomers. For example the C–X bond lengths in hydroxy-1-halocyclopentyliums, **7a**,**b** and **8a**,**b**, are equal to those of 1-halocyclopentylium, **4a**,**b**, (C–Br=1.818 Å and C–Cl=1.650 Å). The cyclopentene ring is nearly flat in **7a**,**b**–**10a**,**b**, whereas it is folded in 1,3-bridged cations, **11a**,**b**–**14a**,**b**. The folding angle is about 110° with the bromo 1,3-bridged cations being less folded.

2.4. $C_5H_6(OH)_2X^+$ (X=Cl, Br)

The 1,3-bridged isomers of the chloro and bromo dihydroxycyclopentyl cations have been calculated at 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, whereas selected optimized geometrical parameters in Table 4.

As in the case of the hydroxycyclopentene derivatives, dihydroxy-1-halocyclopentylium is the most stable isomer for both chlorine (**15a**) and bromine, (**17b**), but the presence of the second hydroxyl group seems to decrease the energy gap between the 1-halocyclopentylium and 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 hydroxy-cyclopentene derivatives. Finally, the cyclopentene ring is nearly flat in all structures.

Table 4. Calculated geometrical parameters (Å, °), relative energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of $C_5H_6(OH)_2X^+$ cations

	C–C′[a]	C–X	C′–X	X–C–C′	X–C′–C	Folding angle[b]	Rel. energy	Hydride affinity	NICS
15a	1.458	1.660		124.9			0.0	242.2	
16a	1.463	1.649		125.3			2.3	244.2	
17a	1.469	1.649		125.1			4.1	245.9	
18a	1.457	1.937	1.949	68.4	67.5	107.2	9.5	251.7	−42.7
19a	1.461	1.917	1.958	69.9	68.1	108.9	10.4	252.4	−43.6
20a	1.458	1.929	1.929	67.8	67.8	105.7	10.5	252.7	−43.8
15b	1.473	1.806		125.3			0.0	241.8	
16b	1.470	1.799		125.6			3.3	245.1	
17b	1.459	1.818		125.0			4.4	246.2	
18b	1.453	2.094	2.105	70.1	69.4	108.1	2.9	244.7	−44.3
19b	1.458	2.073	2.150	72.7	67.0	109.9	3.6	245.4	−45.3
20b	1.454	2.086	2.087	69.7	69.6	106.6	3.6	245.4	−45.4

[a] C′ is C2 in **15**–**17a**,**b** and the second bridged carbon in **18**–**20a**,**b**.
[b] The folding angle is this between XCC′ and the four membered carbon chain.

2.5. Hydride affinities, chemical shifts and relative stabilities

Hydride affinities allow comparison of not only the energetic differences between isomers of the same halocation but also of the relative abilities of chlorine and bromine to stabilize the halonium cations. The calculated values for all the isomers studied are shown in Tables 1–4. According to the calculated hydride affinities, the bridged bromo cation **2b** is found to be the most stable species of the parent $C_2H_4X^+$ cations, whereas the bromo-isomers are more stable than the chloro-ones. Experimental studies in the gas phase[21,22] and theoretical studies[11,13] showed the same trend. The experimental hydride affinities for **1a** and **1b** are 258.1 and 256.3 kcal/mol and those of **2a** and **2b** are 263.7 and 254.9 kcal/mol, respectively, and agree well with the calculated values.

The cyclopentene cations are systematically more stable than the parent cations. The bromo-cations are more stable than the corresponding chloro-cyclopentene cations for all the isomer studied. The hydroxyl substituents on the cyclopentene ring destabilize the halo cations. Thus, the 1,2-bridged isomers of the unsubstituted cyclopentene halonium cations **5a**,**b** are more stable than those for hydroxy- and dihydroxy-substituted ones **9a**,**b** and **10a**,**b** and **18a**,**b**–**20a**,**b**, respectively. The same is also true for the 1,3-bridged isomers **6a**,**b** and **11a**,**b**–**14a**,**b** and the hydroxy-halocyclopentylium isomers **4a**,**b**, **7a**,**b**–**9a**,**b** and **15a**,**b**–**27a**,**b**.

In order to further compare the relative stability of the 1,2-bridged chlorine- and bromine-cations, we have also used the nuclear independent chemical shifts (NICSs) defined as the negative of the absolute magnetic shieldings, computed at ring centers (non weighted mean of the heavy atom coordinates).[23] Negative NICS values imply delocalization and diatropic ring current, while positive NICS values imply paratropic ring current. NICSs have been extensively used for the study of two or three-dimensional aromaticity and relative stability of ring heterocycles[23,24] or cage molecular systems.[25]

The calculated NICS values for all the 1,2-bridged isomers

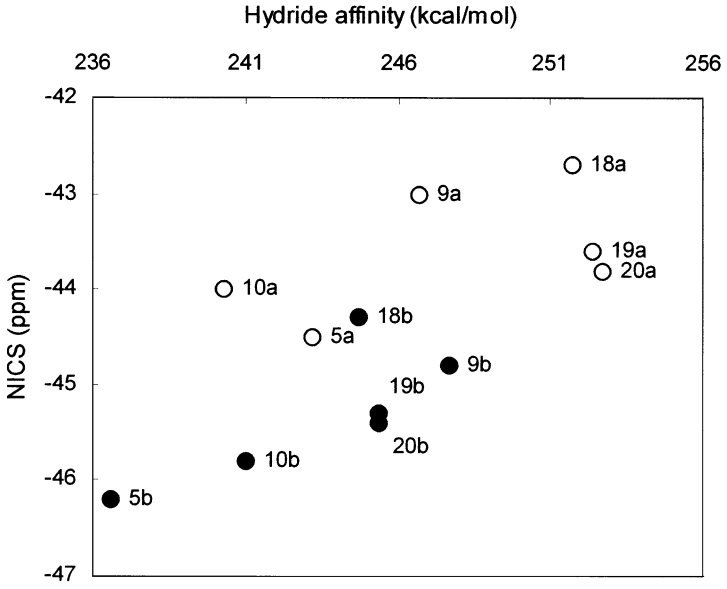
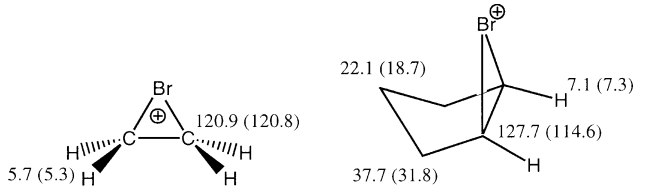


Figure 6. Correlation of calculated hydride affinities and NICS values for the chloro- (○) and bromo- (●) cations of the cyclopentenes and hydroxy substituted cyclopentenes.



21 **22**

Scheme 3. Calculated and experimental ^{13}C and ^{1}H NMR chemical shifts for the bridged 1,2-bromonium cations of ethylene, **21**, and cyclopentene, **22**.

studied, shown in Tables 1–4, further confirm the stability of the bromo-cations relative to the corresponding chloro-cations. The differences between the NICS values of bromo isomers and those of the corresponding chloro isomers (1.6–1.8 ppm) show a remarkable stability of the former. However, the parent bridged $C_2H_4X^+$ cations show more negative NICS values than those of the cyclopentene cations, in contrast to their lower stability based on hydride affinities. This could be explained by the structural differences of these species and by the fact that thermodynamic stability is influenced by strain and many other effects besides delocalization or aromaticity. In the case of cyclopentene halonium cations, where there is a structural resemblance, there is quite a good overall agreement between the stability predictions based on hydride affinities and NICS values. Generally, as shown from the correlation diagram of Fig. 6, an isomer of enhanced stability shows small hydride affinities and more negative NICS values.

Finally, the ^{13}C and ^{1}H NMR chemical shifts for two of the studied species calculated using the GIAO method are in very good agreement with the existing experimental data. The ^{13}C chemical shifts of the carbon atoms and the proton shifts for the olefin-type protons for the bridged 1,2-bromonium cations of ethylene and cyclopentene are given in **21** and **22**, respectively, along with the experimental values[26,27] in parentheses (Scheme 3).

3. Computational details

The electronic structure and geometry of the halonium ions studied were computed within density functional theory, using gradient corrected functionals, at the Becke3LYP computational level.[28] The basis set used was 6-311G++(d,p).[29,30] Full geometry optimizations were carried out without symmetry constraints, with starting geometries corresponding to all possible conformers of the species under investigation. 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 hydride affinities have been calculated using a total energy of H^- equal to 331 kcal/mol, which has been estimated from the experimental ionization potential and electron affinity of hydrogen.[31] All isomers and conformations of the hydride addition product have been considered in each case and the values reported have been calculated on the basis of the energy of the most stable isomer or conformer. The NICS and the ^{13}C and ^{1}H NMR shielding constants of the B3LYP/6-311++G(d,p) optimized structures were calculated with the gauge-independant atomic orbital (GIAO) method[32] at the B3LYP/6-311++G(2d,p) level. The atom shielding constants were converted to chemical shifts by calculating at the same level of theory the ^{13}C and ^{1}H shieldings of CS_2 and TMS, respectively. All calculations were performed using the Gaussian98 package.[33]

4. Conclusions

The potential energy surfaces of halonium cations of ethene $C_2H_4X^+$, cyclopentene $C_5H_8X^+$ and hydroxy substituted cyclopentenes $C_5H_{8-n}(OH)_nX^+$ (n=1, 2), where X=Cl and Br were computed at the Becke3LYP/6-311++G(d,p) level of theory. For the haloethene cations when X=Cl the *cis*-1-chloroethyl cation is the most stable isomer, whereas for X=Br the 1,2-bridged bromonium cations are more stabilized. The same is also true for the cyclopentene cations. In the case of hydroxy substituted cyclopentene halonium ions for both halogens the most stable species are the 1-halocyclopentylium cations, followed by 1,2-bridged chlorocyclopentylium and 1,3-bridged chlorocyclopentylium cations. The calculated hydride affinities serve as a measure of the relative stability of all the cations studied. Bromine is found to stabilize an adjacent carbocation more than chlorine. For bromine, the bridged isomers are even more stable. NICS values could also be used as stability indexes, as they correlate quite well with hydride affinity values, but only in species with structural similarity.

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