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Structure and stability of halonium cations of cycloalkenes. A theoretical study

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Received 20 February 2003; revised 7 April 2003; accepted 1 May 2003

Abstract—A theoretical study of the chloronium and bromonium cations of cyclopropene, cyclobutene, cyclopentene and cyclohexene, $C_3H_4X^+$, $C_4H_6X^+$, $C_5H_8X^+$ and $C_6H_{10}X^+$, have been studied at the ab initio MP2 and density functional B3LYP levels of theory implementing 6-311++G(d,p) basis set. 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 found and the NICS for the bridged cations show that the bromo cations are more stable than the analogous chloro cations, with the bridged 1,4-bromocyclohexyl cation being the most stable cation species studied. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Organic halogen cations since their first identification in the case of some remarkably stable diaryliodonium compounds, have played vital roles as intermediates in organic chemistry.¹ They can be divided into two main categories namely acyclic (open-chain) halonium ions and cyclic halonium ions. In 1894, Hartmann and Meyer were the first to prepare a diphenyliodonium ion salt.² The interest in halonium ions has grown remarkably since their involvement in the halogenation reactions of alkenes and in 1937, Roberts and Kimball³ 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.^{4,5}

Although an extensive series of theoretical calculations have been reported for the parent $C_2H_4X^+$ ($X=F, Cl, Br$) cations,^{6–15} or more complicated open chain alkyl halonium ions like $C_4H_8X^+$,¹¹ little work has been done concerning halonium ions derived from cycloalkenes. Thus, Damrauer et al.,¹⁴ have reported an MP2/6-311G(d,p) study of the whole series of the halonium cations of cyclohexene $C_6H_{10}X^+$ ($X=F, Cl, Br$), as well as a brief study of cyclopentyl bromonium ion, $C_5H_8Br^+$.¹⁴ Density functional and RHF calculations involving effective core potentials were used for the study of the equilibrium isotope effect for the equilibrium involving the formation of the bridged cyclohexyl bromonium ion from cyclohexene and Br_2 .¹⁶

In our previous study, the potential energy surfaces, hydride affinities and Nuclear Independent Chemical Shifts (NICS) of a variety of halonium cations of cyclopentene $C_5H_8X^+$ and hydroxy substituted cyclopentenones $C_5H_8n(OH)_nX^+$ ($n=1, 2$), where $X=Cl$ and Br were computed at the B3LYP/6-311++G(d,p) level of theory.¹⁵ In this work we extend the study to the conformational space of halonium ions of cyclopropene, $C_3H_4X^+$, cyclobutene, $C_4H_6X^+$, cyclopentene, $C_5H_8X^+$ and cyclohexene, $C_6H_{10}X^+$, where $X=Cl$ and Br , at both B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory. In order to determine the relative stabilities of these cations their hydride affinities (HA) were also computed. Furthermore, in the case of 1,2-bridged cations, the nuclear independent chemical shifts (NICS) calculated in the center of the three-membered ring have also been tested as a measure of their relative stability.

2. Results and discussion

The assessment of the computational level and basis set necessary to achieve reasonable energy comparisons for the alkyl halonium ions was made in our previous work¹⁵ by comparing the results of density functional calculations with previous ab initio works on the $C_2H_4X^+$ system and experimental data for cyclopentyl halonium ions $C_5H_8X^+$ ($X=Cl, Br$). It has been found that the energy differences depend more on the quality of the basis set used than on the method describing the correlation effects. In the present study we have used both density functional and MP2 calculations with the same basis set (6-311++G(d,p)).

Keywords: ab initio; halonium cations; DFT; NICS; hydride affinity.

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2.1. $C_3H_4X^+$ ($X=Cl, Br$)

The optimized structures of the isomers found at B3LYP/6-311++G(d,p) level, are shown in Figure 1, whereas the relative energies, zero point energies at the B3LYP level and selected optimized geometrical parameters, at the B3LYP and MP2 level, are given in Table 1. We have initially studied two chloro and bromocyclopropyl cations: namely, the 1-halocyclopropyl cation (**1a,b**), and the 1,2-bridged halonium ion (**2a,b**). The optimized structures **1a** and **1b** are transition states, as they have one imaginary frequency (-139 cm^{-1} for **1a** and -57 cm^{-1} for **1b** at the B3LYP level). Distorting the structures in the direction of the eigenvector corresponding to the imaginary frequency and reoptimization gave the planar open chain 2-haloallyl cations **3a** and **3b** as real minima. Structure **3a** has been also found experimentally in FT-IR matrix isolation studies and located as a minimum in the potential energy surface of 2-chloroallyl cation according to MP2/6-31G(d) calculations.¹⁷ At the MP2 level no 1-chlorocyclopropyl structure, **1b**, has been located.

At the B3LYP level, the 2-bromoallyl cation, **3b**, is more stable than 1-bromocyclopropenium, **1b**, by 11.7 kcal/mol. The bridged bromonium ion, **2b**, is 24.2 kcal/mol above the minimum, **3b**. For $X=Cl$ the 2-chloroallyl cation is also the global minimum. The transition structure, **1a**, and the bridged cation, **2a**, are 13.8 and 31.8 kcal/mol higher, respectively. At the MP2 level the relative stabilities, for both $X=Cl$ and Br , are similar to those at the B3LYP level. These results suggest an enhanced instability of bridged and non-bridged halonium ions of cyclopropene and explain the fact that no similar species have been identified or isolated experimentally.

The B3LYP calculated C–C bond length in the bridged ions, **2a** and **2b**, is equal to 1.420 Å. At MP2 level this bond is longer by 0.01 Å. These values are between the usual values of 1.34 Å for C=C and 1.54 Å for C–C. In the bridged bromonium ion the C–Br distance of 2.055 Å, is equal to that found in the ethylenebromonium ion¹⁵ and a bit longer than the typical single bond length of 1.94 Å.¹⁸ The MP2 calculated distance is 1.999 Å. The B3LYP calculated C–Br bond length was calculated as 1.722 and 1.887 Å for **1b** and **3b**, respectively. The same conclusion also stands in

the case of the C–Cl bond length, which is longer for **2a** than for **3a** and **1a**. At the MP2 level the C–X bond length is shorter than this at B3LYP level. The difference between the C–Cl and the C–Br bond lengths, at both levels of theory, is relatively constant for **2a** (0.151 Å), **1a** (0.156 Å) and **3a** (0.165 Å). Finally, the scaled frequencies of the symmetric and asymmetric stretching modes of the $[CCC]^+$ group for the structure **3a** have been calculated to be equal to 1371 and 1500 cm^{-1} at the B3LYP level, very close to the experimental values of 1424 and 1574 cm^{-1} , respectively.¹⁷

2.2. $C_4H_6X^+$ ($X=Cl, Br$)

We have studied the three possible chloro and bromocyclobutyl cations: namely, 1-halocyclobutyl (**4a,b**), 1,2-bridged (**5a,b**) and 1,3-bridged (**6a,b**) cations with geometry optimizations at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) level. The optimized structures are shown in Figure 2, whereas the relative energies, zero point energies at the B3LYP level and selected optimized geometrical parameters are in Table 2. Frequency calculations, at B3LYP level, have shown that all structures are minima on the potential energy surfaces. The results showed that the bridged structures are the less stable. Thus, at the B3LYP level the most stable $C_4H_6Cl^+$ cation is the 1-chlorocyclobutyl cation (**4a**) being 13.6 kcal/mol lower in energy than the 1,2-bridged chlorocyclobutyl (**5a**). In the bromonium cations the energy order is the same with **4b** being 7.1 kcal/mol more stable than **5b**. It is obvious that the bromine atom stabilizes the bridged structure more effectively than chlorine because it is larger and less electronegative. The 1,3-bridged structures **6a,b** are located at higher energy due to high strain energy. The same order of the relative stability of the isomers has been calculated at the MP2 level.

The C–X bond lengths are larger for **6a,b** than in **5a,b** by nearly 0.07 Å at the B3LYP level and 0.045 Å at the MP2 level, respectively. At MP2 level, the cyclobutene ring in **4a,b** is folded, whereas at B3LYP level it is nearly flat. Furthermore, the calculated C–X bond lengths are longer at the MP2 level. The folding angle between the XCC' bridge and the rest of molecule, for all structures, is between 108 and 116°. There are no steric or torsional effects in the cyclobutyl cations. This conclusion results from the comparison between acyclic and cyclic structures of

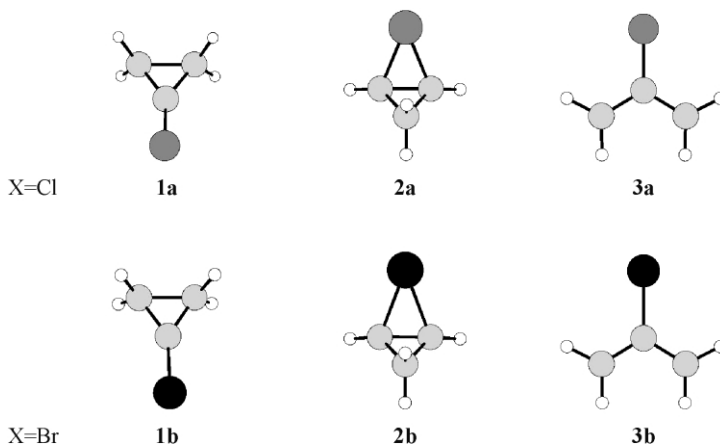


Figure 1. Structures of cyclopropene halonium ions, $C_3H_4X^+$, optimized at the B3LYP level.

Table 1. Calculated geometrical parameters (\AA , $^\circ$), relative energies (kcal/mol), zero point energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of cyclopropene halonium ions, $\text{C}_3\text{H}_4\text{X}^+$

	Method	C–C ^a	C–X	C'–X	X–C–C'	Folding angle ^b	Rel. energy	ZPE	Hydride affinity	NICS
1a	B3LYP		1.618		146.9		13.9	35.9	269.9	
	MP2									
2a	B3LYP	1.421	1.904	1.906	68.0	112.0	31.8	36.7	286.2	–42.3
	MP2	1.431	1.848	1.848	67.2	112.6	24.2		295.5	
3a	B3LYP		1.722		121.2		0.0	36.6	265.0	
	MP2		1.702		122.0		0.0		275.4	
1b	B3LYP		1.774		147.2		11.7	35.6	267.4	
	MP2		1.746		147.3		10.1		281.2	
2b	B3LYP	1.419	2.055	2.055	69.8	112.2	24.2	36.4	279.8	–43.1
	MP2	1.432	1.999	1.999	69.0	112.6	17.3		288.4	
3b	B3LYP		1.887		121.4		0.0	36.1	265.6	
	MP2		1.869		122.2		0.0		276.0	

^a C' is C2 in **1a,b** and the second bridged carbon in **2a,b**.^b The folding angle is this between XCC' and the three-membered carbon ring.**Table 2.** Calculated geometrical parameters (\AA , $^\circ$), relative energies (kcal/mol), zero point energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of cyclobutene halonium ions, $\text{C}_4\text{H}_6\text{X}^+$

	Method	C–C ^a	C–X	C'–X	X–C–C'	Folding angle ^b	Rel. energy	ZPE	Hydride affinity	NICS
4a	B3LYP		1.645		132.0		0.0	54.7	248.7	
	MP2		1.664		122.4		0.0		257.2	
5a	B3LYP	1.467	1.938	1.940	67.7	108.1	13.6	55.7	262.3	–42.1
	MP2	1.473	1.877	1.877	66.9	108.0	13.2		270.4	
6a	B3LYP		2.015	2.025	61.1	114.0	30.2	55.8	278.9	
	MP2		1.926	1.929	60.0	115.6	28.6		285.8	
4b	B3LYP		1.804		132.0		0.0	54.3	248.2	
	MP2		1.826		122.8		0.0		258.2	
5b	B3LYP	1.462	2.097	2.097	69.6	109.0	7.1	55.3	255.3	–45.5
	MP2	1.470	2.038	2.038	68.9	108.5	6.6		264.7	
6b	B3LYP		2.163	2.165	63.1	113.5	25.6	55.4	273.8	
	MP2		2.077	2.077	62.0	115.0	23.5		281.6	

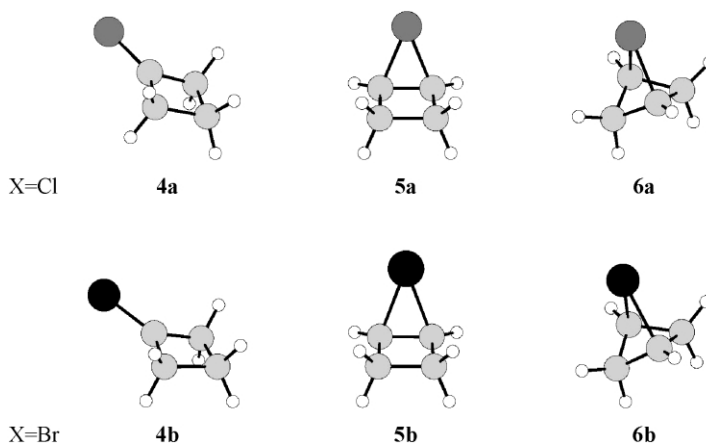
^a C' is C2 in **4a,b** and the second bridged carbon in **5–6a,b**.^b The folding angle is this between XCC' and the three or four-membered carbon chain.

$\text{C}_4\text{H}_6\text{X}^+$ with the corresponding $\text{C}_2\text{H}_4\text{X}^+$ species ($\text{X}=\text{Cl}$, Br).¹⁵ For example, for $\text{X}=\text{Cl}$ the calculated at the B3LYP level C–Cl bond length in **5a** and bridged ethylenechloronium ion is 1.938 and 1.895 \AA , respectively, and the C–H bond lengths are equal (1.085 \AA) in both cases.¹⁵

2.3. $\text{C}_5\text{H}_8\text{X}^+$ ($\text{X}=\text{Cl}$, Br)

We have studied the three possible chloro and bromocyclopentyl cations: namely, the 1-halocyclopentyl (**7a,b**), the 1,2-bridged (**8a,b**), and the 1,3-bridged (**9a,b**) cations with

geometry optimizations at the MP2/6-311++G(d,p) level. The optimized structures are shown in Figure 3, whereas the relative energies, zero point energies at the B3LYP level and selected optimized geometrical parameters are in Table 3, where previous B3LYP results¹⁵ are also given for comparison purposes. All structures are real minima on the potential energy surfaces according to the B3LYP frequencies calculations. At the MP2 level the most stable $\text{C}_5\text{H}_8\text{Cl}^+$ cation is the 1-chlorocyclopentyl cation (**7a**) being only 1.9 kcal/mol lower in energy than the 1,2-bridged chlorocyclopentyl (**8a**). In the bromonium cations the

**Figure 2.** Structures of cyclobutene halonium ions, $\text{C}_4\text{H}_6\text{X}^+$, optimized at the B3LYP level.

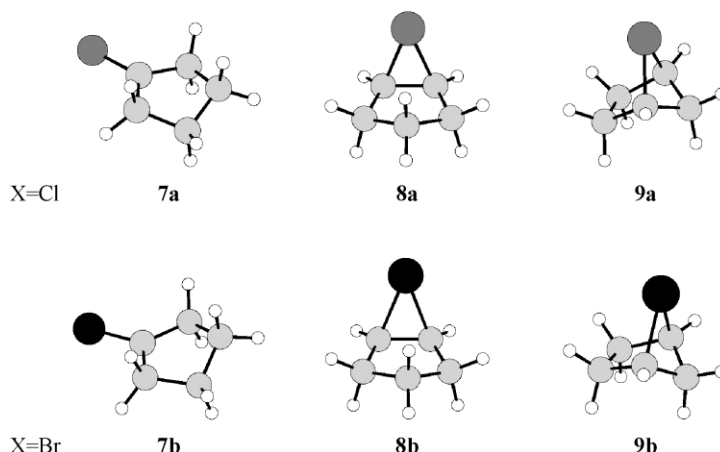


Figure 3. Structures of cyclopentene halonium ions, $C_5H_8X^+$, optimized at the B3LYP level.

energy order is reversed with **8b** being 4.2 kcal/mol more stable than **7b**. Although in the 1,2 bridged structure the cyclopentene ring is quite planar, it adopts a boat like conformation. No chair conformation has been found as stable point in the potential energy surface. The 1,3-bridged structures **9a,b** are higher in energy due to high strain energy. This relative stability and the optimized geometrical features of the three structures are consistent with the previous B3LYP results.¹⁵

2.4. $C_6H_{10}X^+$ ($X=Cl, Br$)

The potential energy surface for the chloro and bromocyclohexyl cations has been searched in an energy window of about 15 kcal/mol at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) level. The optimized structures are shown in Figure 4, whereas relative energies, zero point energies at the B3LYP level and selected optimized geometrical parameters are in Table 4. The optimized structures **13a** and **13b** have one imaginary frequency at the B3LYP level (-64 and -47 cm^{-1} , respectively). All other structures are real minima since no imaginary frequencies were calculated. The 1-halocyclohexyl cations adopt both chair (**10a**, **11b**) and slightly twisted boat conformations (**11a**, **10b**), with the chair conformation being more stable.

The 1,2-bridged isomers adopt a boat up (**12a,b**), a boat down (**13a,b**) and a twisted conformation (**14a,b**). No chair conformation has been found. The 1,3-bridged isomers adopt both chair (**16a,b**) and boat conformations (**17a,b**), whereas the single 1,4-bridged isomer adopts a boat conformation (**15a,b**).

Isomers **10a,b–15a,b** are the most frequently considered $C_6H_{10}X^+$ structures in the studies of halogen addition to cyclohexene.¹⁴ Stable cation experiments designed to prepare 1,2 bridged bromonium ions **12b–14b** have instead led to **15b**. No reports of bridged chloronium ions **12a–14a** or **15a** exist. The 1-halocyclohexyl cation **10a** or **11a** has been observed for $X=Cl$ below 144 K under stable ion conditions.¹⁹

The bridged 1,4-bromonium ion **15b** is the most stable cation on the $C_6H_{10}Br^+$ potential energy surface at both levels of theory. The 1-chlorocyclohexyl cation **10a** is the most stable at B3LYP level. At MP2 level, the 1-chlorocyclohexyl ion **10a** and 1,4-chloronium ion **15a** have almost equal energy. In contrast, the 1,4-bromonium ion **15b** is more stable by 0.4 and 4.4 kcal/mol than ion **10b** at the B3LYP and MP2 level, respectively. The 1,2-bridged chloronium ions **12a–14a** are about 5–13 kcal/mol higher

Table 3. Calculated geometrical parameters (\AA , $^\circ$), relative energies (kcal/mol), zero point energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of cyclopentene halonium ions, $C_5H_8X^+$

	Method	C–C' ^a	C–X	C'–X	X–C–C'	Folding angle ^b	Rel. energy	ZPE	Hydride affinity	NICS
7a	B3LYP ^c		1.658		123.9		0.0	73.7	232.8	
	MP2		1.635		124.1		0.0		254.5	
8a	B3LYP	1.462	1.969	1.969	68.0	107.2	6.4	74.5	239.2	–44.5
	MP2	1.465	1.895	1.895	67.3	107	1.9		256.5	
9a	B3LYP		2.027	2.027	57.8	109.5	18.6	74.7	251.4	
	MP2		1.925	1.925	56.4	110.9	13.3		267.9	
7b	B3LYP		1.818		124.0		0.1	73.3	232.7	
	MP2		1.791		124.3		4.2		255.2	
8b	B3LYP	1.458	2.123	2.123	69.9	108.3	0.0	74.2	232.6	–46.2
	MP2	1.462	2.057	2.057	69.2	107.8	0.0		251.0	
9b	B3LYP		2.177	2.177	59.8	109.7	14.0	74.2	246.6	
	MP2		2.078	2.078	58.6	110.8	12.9		264.0	

^a C' is C2 in **7a,b** and the second bridged carbon in **8–9a,b**.

^b The folding angle is this between XCC' and the four-membered carbon chain.

^c The B3LYP results are from Ref. 15.

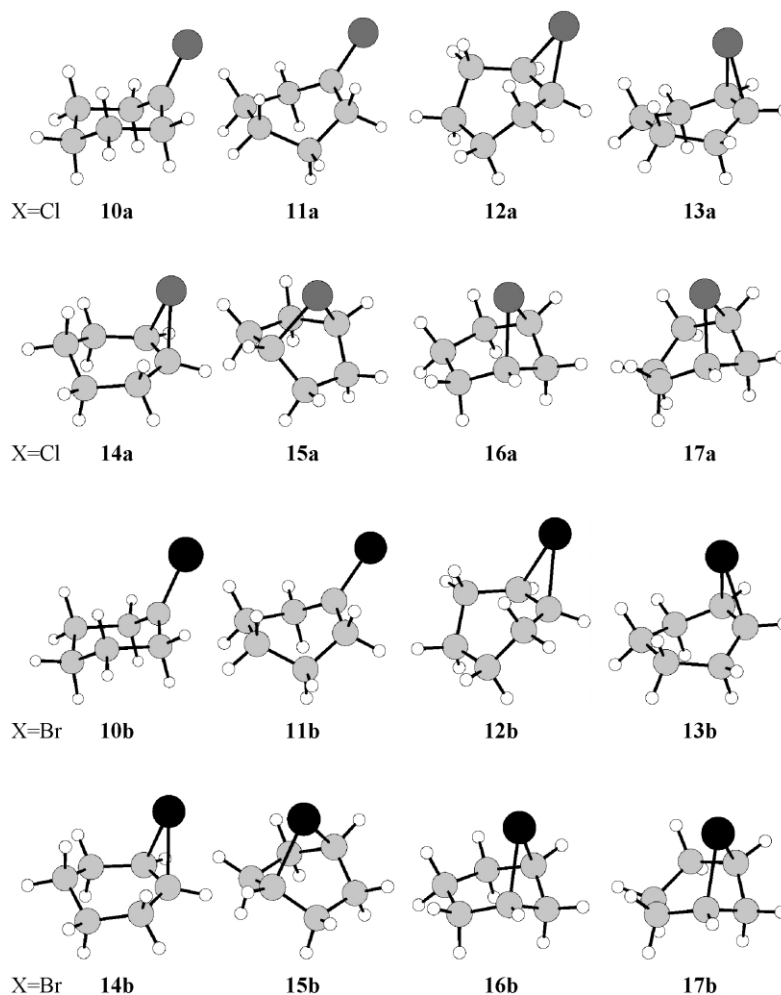


Figure 4. Structures of cyclohexene halonium ions, $C_6H_{10}X^+$, optimized at the B3LYP level.

in energy than the corresponding 1,4-bridged cation **15a**. For $X=Br$ the 1,2-bridged cation **12b–14b** is about 3–10 kcal/mol higher than 1,4-bromonium ion **15b**. This energetic preference may explain why Olah and co-workers did not observe the 1-bromocyclohexyl cations **10–11b** or the 1,2-bridged cations **12a,b–14a,b** for $X=Cl$ and Br .²⁰ The calculated relative stabilities of the various isomers agree well with the MP2/6-311G(d,p) results of Damrauer et al.¹⁴ for $X=Cl$ and Br and the previous density functional study of the 1,2-bridged cyclohexyl bromonium ion.¹⁶

The calculated C–X bond lengths in the 1-chloro and 1-bromocyclohexyl cations, **10–11a,b**, are the longest along the series of all the 1-halocycloalkyl cations studied. Generally the trend observed is cyclopropyl < cyclobutyl < cyclopentyl < cyclohexyl. The opposite trend applies to the folding angle between the XCC' and the three or four-membered carbon chain of the cycloalkyl.

Finally, the ^{13}C and 1H NMR chemical shifts for two of the studied species calculated using the GIAO method at the B3LYP level are in good agreement with existing experimental data. The ^{13}C chemical shifts of the carbon atoms and the proton shifts for the olefin-type protons for the 1,4-bridged bromonium ion and 1-chlorocyclohexyl

cation are given in Figure 5, respectively, along with experimental values in parentheses.^{19,20}

3. Hydride affinities, chemical shifts and relative stabilities

The 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, an important question with respect to many practical applications including photoresists and conducting polymers.¹² The calculated values for all the isomers studied are shown in Tables 1–4. According to the calculated hydride affinities, the chloroallyl cation **3a** is found to be the most stable isomer of the $C_3H_4X^+$ cations at B3LYP and MP2 level, whereas in all other cases the bromo isomers are more stable than the chloro ones. On the $C_4H_6X^+$ potential surface, the chlorocyclobutyl cation **4a** is the most stable at B3LYP level. At MP2 level, the bromo analogue **5a** is 2 kcal/mol more stable than the other isomers. The cyclopentene and cyclohexene cations are systematically more stable than cyclopropene and cyclobutene cations. The bromo-cations are more stable than the corresponding chloro-cyclohexene

Table 4. Calculated geometrical parameters (\AA , $^\circ$), relative energies (kcal/mol), zero point energies (kcal/mol), hydride affinities (kcal/mol) and NICS values (ppm) of cyclohexene halonium ions, $\text{C}_6\text{H}_{10}\text{X}^+$

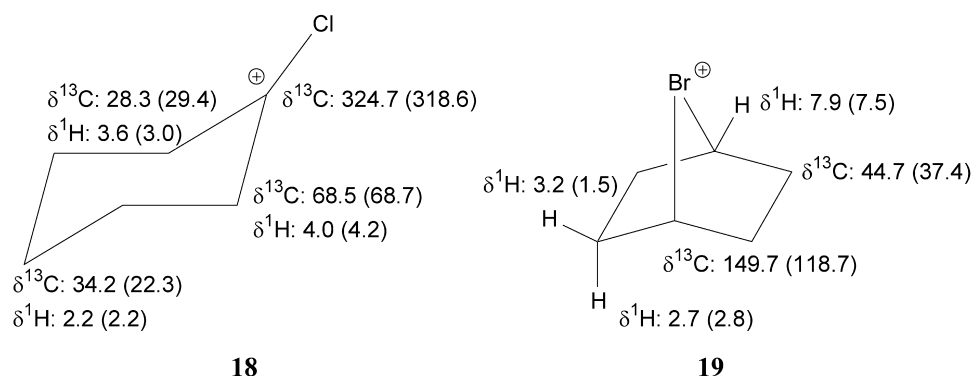
	Method	C–C' ^a	C–X	C'–X	X–C–C'	Folding angle ^b	Rel. energy	ZPE	Hydride affinity	NICS
10a	B3LYP		1.674		119.7		0.0	92.9	239.9	
	MP2		1.653		119.6		0.3		251.5	
11a	B3LYP		1.673		119.5		3.6	92.1	243.5	
	MP2		1.648		120.6		5.6		256.8	
12a	B3LYP	1.462	1.965	1.965	68.2	110.0	14.8	93.0	254.7	–43.5
	MP2	1.463	1.897	1.897	67.3	110.2	13.0		264.2	
13a	B3LYP	1.459	1.973	1.973	68.3	108.2	11.3	92.6	251.2	–42.0
	MP2	1.461	1.901	1.901	67.4	107.9	10.5		261.8	
14a	B3LYP	1.465	1.966	1.978	67.8	106.4	9.2	92.9	249.1	–43.6
	MP2	1.468	1.897	1.900	67.2	105.7	8.0		259.2	
15a	B3LYP		1.980	1.980	51.5	118.4	3.8	93.4	243.7	
	MP2		1.886	1.886	50.2	119.9	0.0		251.3	
16a	B3LYP		2.029	2.029	56.1	97.5	13.7	93.1	253.6	
	MP2		1.929	1.929	54.7	96.9	11.8		263.0	
17a	B3LYP		2.027	2.027	56.1	113.8	14.0	93.0	253.9	
	MP2		1.923	1.923	54.6	115.5	11.9		263.2	
10b	B3LYP		1.833		120.0		0.4	92.5	240.0	
	MP2		1.810		119.9		4.4		252.6	
11b	B3LYP		1.833		120.8		4.0	91.8	243.6	
	MP2		1.804		120.9		9.5		257.7	
12b	B3LYP	1.457	2.120	2.120	69.9	111.4	8.2	92.7	247.7	–45.3
	MP2	1.460	2.060	2.060	69.2	111.2	10.1		258.3	
13b	B3LYP	1.455	2.131	2.131	70.0	109.5	4.8	92.3	244.2	–43.9
	MP2	1.458	2.064	2.064	69.3	109.0	10.5		256.0	
14b	B3LYP	1.459	2.127	2.139	69.6	107.9	3.3	92.5	242.8	–45.6
	MP2	1.464	2.062	2.066	69.1	107.0	8.0		254.0	
15b	B3LYP		2.131	2.131	53.9	117.9	0.0	92.9	239.6	
	MP2		2.039	2.039	52.7	119.4	0.0		248.2	
16b	B3LYP		2.178	2.178	58.2	106.4	10.7	92.7	250.2	
	MP2		2.077	2.077	57.0	105.7	12.6		260.9	
17b	B3LYP		2.176	2.176	58.3	105.1	9.4	92.5	249.0	
	MP2		2.083	2.083	57.0	107.2	11.0		259.3	

^a C' is C2 in **10**–**11a,b** and the second bridged carbon in **12**–**17a,b**.^b The folding angle is this between XCC' and the three or four-membered carbon chain.

cations for all the isomers studied at both levels of theory. The 1,4-bridged bromo cation **9b** is the most stable isomer of $\text{C}_6\text{H}_{10}\text{Br}^+$. Experimental²⁰ and theoretical studies¹⁴ showed the same trend.

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).²¹ 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,^{21,22} cage molecular systems²³ and halonium cations.¹⁵ The values calculated at the B3LYP level NICS for all the isomers found as real minima in the potential energy surfaces of the studied molecules are shown in Tables 1–4. According to NICS values, the bromo cations are more stable than the chloro analogues. The differences between the NICS values of bromo isomers and those of the corresponding chloro isomers (2–4 ppm) show a remarkable stability of the former. As has been stated previously an isomer of

**Figure 5.** Calculated at the B3LYP level and experimental ^{13}C and ^1H NMR chemical shifts for the 1-chlorocyclohexyl cation, **18**, and the 1,4-bridged cyclohexyl bromonium ion, **19** (experimental values in parentheses).

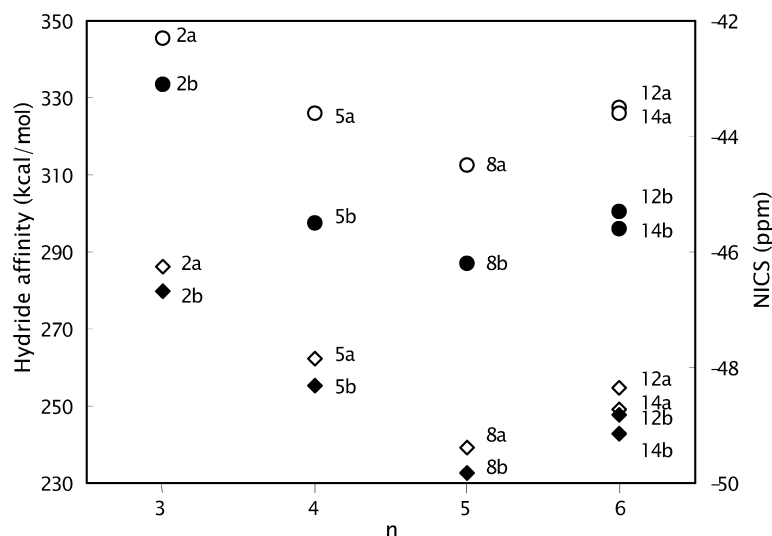


Figure 6. Correlation of ring size (n) and hydride affinities (Cl: ◇, Br: ◆) or NICS values (Cl: ○, Br: ●) calculated at the B3LYP level for the 1,2-bridged chloro- and bromonium ions of the studied cycloalkenes.

enhanced stability shows small hydride affinities and more negative NICS values.¹⁵ As shown in the correlation diagram of Figure 6, there is quite good overall agreement between the stability predictions based on hydride affinities and NICS values, with the stability of the halonium ions of cycloalkenes studied following the trend cyclopentene > cyclohexene > cyclobutene > cyclopropene.

4. Computational details

The electronic structure and geometry of the halonium cations studied were computed within density functional theory, using gradient corrected functionals, at the Becke3LYP computational level.²⁴ The basis set used was 6-311++G(d,p).^{25,26} Full geometry optimizations were carried out without symmetry constraints. Frequency calculations after each geometry optimization ensured that the calculated structure is either a real minima or a transition state in the potential energy surface of the molecule. The optimized structure from the B3LYP level were reoptimized with the frozen core Møller–Plesset perturbation theory, MP2(fc), computational level.^{27,28} The basis set used was the 6-311++G(d,p). The hydride affinities have been calculated using a total energy of H^- equal to 335 kcal/mol at B3LYP level and 317 kcal/mol at MP2 level, respectively. These values are in good agreement with the value of 331 kcal/mol, which has been estimated from the experimental ionization potential and electron affinity of hydrogen.²⁹ 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 1H NMR shielding constants of the B3LYP/6-311++G(d,p) optimized structures were calculated with the gauge-independent atomic orbital (GIAO) method³⁰ 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 1H shieldings of TMS. All calculations were performed using the Gaussian98 package.³¹

5. Conclusions

The potential energy surfaces of halonium cations of cyclopropene $C_3H_4X^+$, cyclobutene $C_4H_6X^+$, cyclopentene $C_5H_8X^+$ and cyclohexene $C_6H_{10}X^+$, where $X=Cl$ and Br were computed at the B3LYP/6-311++G(d,p) and MP2/6-311++G(d,p) levels of theory. For cyclopropene halonium ions the haloallyl cation is the most stable isomer. In the case of cyclobutene cations the 1-halocyclobutene is the most stable for both $X=Cl$ and Br . For the halocyclopentene cations when $X=Cl$ the chlorocyclopentyl cation is the most stable isomer, whereas for $X=Br$ the 1,2-bridged bromonium cation is more stable. On the $C_6H_{10}X^+$ potential energy surface for $X=Cl$ the 1-halocyclohexyl cation is the most stable, whereas for $X=Br$ the most stable form is the 1,4-bridged cation. The calculated hydride affinities serve as a measure of the relative stability of all the cations studied. Bromine is found to stabilize more than chlorine an adjacent carbocation. For bromine too, the bridged isomers are even more stable. NICS values could be used also as stability indexes, as they correlate quite well with hydride affinity values.

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