Relative Stabilities of Isomeric Chlorine-substituted Carbocations: The $C_2H_4Cl^+$ Cation

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Calculations at the MP2/6-31G**//MP2/6-31G** level show that substitution of chlorine for fluorine has little effect on the stabilities of classical and α-halo isomers of $C_2H_4X^+$, but strongly stabilizes the bridged isomer.

The structure and energetics of halogen-substituted cations, particularly bridging halonium ions, have elicited considerable interest since their involvement in halogenation of alkenes was first proposed.[1] Recently, high level *ab initio* calculations were reported for the $C_2H_4F^+$ cation.[2] These calculations predicted that the fluorine bridged **1** and classical **2** cations are much less stable than the isomer in which fluorine is directly adjacent to the cationic centre **3**. The high energy calculated for the fluorine bridged isomer is consistent with the fact that there is no experimental evidence for such a structure, in contrast to the analogous chloronium and bromonium ions. Owing to the general interest halonium ions attract and our specific interest in halogenated carbocations in connection with photoresist applications, semi-empirical and *ab initio* molecular orbital calculations have been carried out for the $C_2H_4Cl^+$ cation.

Unlike the fluorine-substituted analogue, there is considerable evidence[3–5] that chlorine can form a stable bridged ion such as **1b**. Therefore, three possible isomers were computed for $C_2H_4Cl^+$ in order to determine their relative stabilities in the gas phase, and to compare the effects of chlorine and fluorine substitution α and β to carbocations. The $C_2H_4Cl^+$ cation has been examined previously with MINDO/3[6] and *ab initio* methods up to HF/3-21G[7–9] all of which predicted **1b** to be the global minimum.

All stationary points were located using the AM1[10] method. Although AM1 shares the shortcomings of MNDO[11] with respect to underestimating the stability of nonclassical ions,[12] it does provide good starting geometries for subsequent *ab initio* calculations.[13,14] The AM1 geometries were optimized further at the HF/6-31G** level with GAUSSIAN88,[15] and all critical points were tested by computing the Hessian matrix at the same level. There is ample evidence[6,16] that correlation effects are particularly important when studying nonclassical ions, therefore, all stationary points were recomputed at the MP2/6-31G**//MP2/6-31G** level.

The calculated total energies for the chlorides (**1b**–**3b**) are reported in Table 1. The relative hydride affinities (HAs) of **1b**–**3b** are given in Table 2, along with the corresponding fluoride hydride affinities extracted from Ford and Raghuveer's[2] paper. The bridged chloronium ion **1b** is computed to be more stable than the classical isomer **2b** even at the AM1 and HF levels. Inclusion of electron correlation at the MP2 level shifts the relative energies strongly in favour of the α-chloro **3b** and bridged **1b** isomers. The α-chloro isomer **3b** is computed to be more stable than the bridged cation **1b** by 4 kcal mol^{-1} (1 cal = 4.184 J). The classical ion **2b** is least stable of all by a very wide margin. In addition to being high in energy, **2b** possesses one imaginary frequency at the 6-31G** level. Therefore, it is a transition state, not a minimum. Any displacement along the transition vector leads spontaneously to the bridged isomer **1b**.

In order to remove any bias due to the HF geometries, **1b**–**3b** were recalculated at the MP2/6-31G** level. Optimization at the MP2 level has no effect on the relative hydride affinities (Table 2) except for **1a** which is reduced by 3 kcal mol^{-1}. Inclusion of zero point energies has a small, but mostly negligible effect on the relative energies. The ZPEs should be applied with caution, anyway, since these species all exhibit low-frequency vibrations.

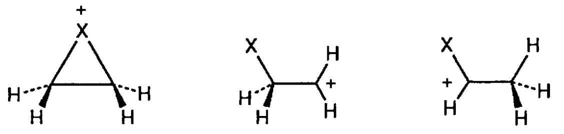
The computed energies for **1b**–**3b** are consistent with experimental work by Berman *et al.*[5] and Holmes *et al.*,[3] who found two distinguishable isomers for $C_2H_4Cl^+$ separated by 5.6 or 2 kcal mol^{-1}, respectively. Both authors assigned the lower energy to isomer **3b** in agreement with the results reported here. The small computed and experimental energy difference between **1b** and **3b** contrasts sharply with the fluorinated derivatives, the bridged isomer of which, **1a**, is computed to be almost 25 kcal mol^{-1} less stable than the α-substituted isomer **3a**.

Calculation of the hydride affinities allows direct comparison of the fluorine- and chlorine-substituted isomers. The computed hydride affinities for the classical and α-halo isomers are virtually identical whether the halogen is fluorine or chlorine (Table 2). By contrast, chlorine substitution stabilizes the bridged isomer by 20 kcal mol^{-1}. Even with this large change, however, the α-chloro cation **3b** remains the global minimum by a small margin. This points to a surprising capacity for fluorine and chlorine to stabilize gas-phase cations directly *via* π-donation. It also shows that while the abilities of fluorine and chlorine to form bridged cations are very different, their π-donating abilities are remarkably similar. The latter result is unexpected since fluorine and chlorine have different electronegativities and reside in different rows of the periodic table.

Table 1 AM1 heats of formation and *ab initio* total energies for **1b**–**3b**

Isomer	AM1	HF/6-31G**	MP2/6-31G**[a]	MP2/6-31G**[b]
1b	216.6	−537.2188533	−537.6202158	−537.641169
2b	217.6	−537.1955914	−537.5765707	−537.5977914
3b	199.9	−537.2290468	−537.6265751	−537.6470521
C_2H_4F	−66.3	−178.0853485	−178.5483950	−178.5489599
C_2H_4Cl	−26.2	−538.1393353	−538.5639144	−538.5843983

[a] Calculated at the HF/6-31G** geometry. [b] Fully optimized at the MP2/6-31G** level, except for C_2H_4F which was calculated using the frozen core approximation at the MP2/6-31G** geometry in order to be consistent with ref. 2.



1a = F
b = Cl

2

3

Fig. 1 Isomers of $C_2H_4X^+$, where X is either fluorine or chlorine

Table 2 Calculated relative hydride affinities for **1**–**3** in kcal mol^{-1}. Values for the fluorides were obtained using the cation energies reported in reference 2

Isomer	AM1	HF/6-31G**	MP2/6-31G**[a]	MP2/6-31G**[b]	+ZPE[c]	Exp
1a	32.7	29.7	28.1	24.8		
2a	23.5	24.4	31.8	31.4		
3a	0.0	0.0	0.2	0.1		
1b	19.4	10.9	4.0	4.0	5.6	2[d]–5.6[e]
2b	20.4	25.5	31.4	31.2	30.2	
3b	2.7	4.5	0.0	0.0	0.0	0.0

[a] Calculated at the HF/6-31G** geometry except for **1a**–**3a** which were calculated at the HF/6-31G* geometry.[2] [b] Fully optimized at the MP2/6-31G** level. [c] MP2/6-31G**//MP2/6-31G** + ZPE. [d] From ref. 3. [e] From ref. 5.

Even though the chlorine bridged isomer is not predicted to be the global minimum, the relative energy *versus* **3b** is down to 4 from 25 kcal mol^{-1} for the fluorine derivative. Extrapolating to bromine, one might argue that the bridged isomer will become the global minimum because of bromine's increased ability to form back-coordinated π complexes[17] such as **1**.

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