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# A Quantum-Chemical Study of the $C_2H_3F_2^+$ and $C_2H_3Cl_2^+$ Isomers and Their Interconversion. CBS-QB3 Proton Affinities of Difluoroethenes and Dichloroethenes

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Potential energy surfaces of the $C_2H_3X_2^+$ isomers and proton affinities of dihaloethenes $C_2H_2X_2$ (X = F, Cl) were computed at the B3LYP/6-31++G(d,p), MP2/6-311++G(d,p), and CBS-QB3 levels. The classical 1,1-dihaloethyl cations $CH_3CX_2^+$ represent global minima for the $C_2H_3X_2^+$ isomers. Other minima located are classical 1,2-dihaloethyl cations, the chloroethylchloronium (Cl-bridged) cation, halogen-protonated *cis*-1,2-, *trans*-1,2-, and 1,1-dihaloethenes, and ion−dipole complexes of the $CH_2{=}CX^+$ cation with the HX molecule. The classical 2,2-dihaloethyl cations, as well as H-bridged cations, are at first-order saddle points. The fluoroethylfluoronium cation is not at a stationary point. Transition states were located and activation energies computed for isomerization (1) of the *trans*-1,2-difluoroethyl cation to the 1,1-difluoroethyl cation, (2) of the *cis*-1,2-difluoroethyl cation to its trans rotamer, (3) of the chloronium cation to the 1,1-dichloroethyl cation, (4) of the *cis*-1,2-dichloroethyl cation to the chloronium cation, and (5) of the halogen-protonated dihaloethenes to carbon-protonated isomers. Protonation of dihaloethenes at carbon is more favorable than protonation at halogen. The best estimates at CBS-QB3 for proton affinities (in kcal/mol) are as follows: 1,1-$C_2H_2F_2$, 171.1; *cis*-1,2-$C_2H_2F_2$, 152.9; *trans*-1,2-$C_2H_2F_2$, 151.9; 1,1-$C_2H_2Cl_2$, 176.0; *cis*-1,2-$C_2H_2Cl_2$, 159.7; *trans*-1,2-$C_2H_2Cl_2$, 162.0.

## 1. Introduction

Halogenated ethyl cations are species of considerable theoretical interest. Partial substitution of hydrogen atoms by halogens in $C_2H_5^+$ increases the number of possible isomers and strongly influences the relative energies of the open classical and bridged nonclassical structures. Monohalogenated ethyl cations have been investigated thoroughly, by means of both experimental[1−13] and computational[12,14−21] methods, and their potential energy surfaces are now well understood. The present contribution addresses potential energy surfaces of the dihalogenated ethyl cations $C_2H_3F_2^+$ and $C_2H_3Cl_2^+$.

Monohalogenated ethyl cations $C_2H_4Br^+$,[1,2] $C_2H_4I^+$,[1−3] and $C_2H_4Cl^+$ [4] have been obtained by Olah et al. in superacid media. Other authors studied the $C_2H_4X^+$ cations in the gas phase[5−12] and in the solid phase.[13] Detailed quantum-chemical calculations at high levels of theory[12,14−18] were performed for X = F, Cl, and Br. References to the earlier calculations can be found in these papers. Most of the authors considered three isomers of $C_2H_4X^+$: the 1-haloethyl cation, the 2-haloethyl cation, and the halonium ion (nonclassical halogen-bridged structure).[22−25] All the 2-haloethyl cations were computed to be much less stable than the isomeric 1-haloethyl cations (by 25−31 kcal/mol).[12,15−18] The higher stabilities of the 1-haloethyl cations with respect to their 2-halo isomers are due to the stabilizing $\pi$-donation from the α-halogen atoms to the carbenium center. The relative energies of halonium cations and isomeric 1-haloethyl cations depend on the halogen. The fluoronium ion is computed to be much less stable than the 1-fluoroethyl cation (by 24−25 kcal/mol).[14,18] The chloronium ion is slightly higher in energy (by 4 kcal/mol)[15,18] than the 1-chloroethyl cation, whereas the bromonium ion is slightly lower (by 3 kcal/mol)[16] than the 1-bromoethyl cation. These values compare favorably with experimental results for isomers of $C_2H_4Cl^+$ and $C_2H_4Br^+$.[5,7]

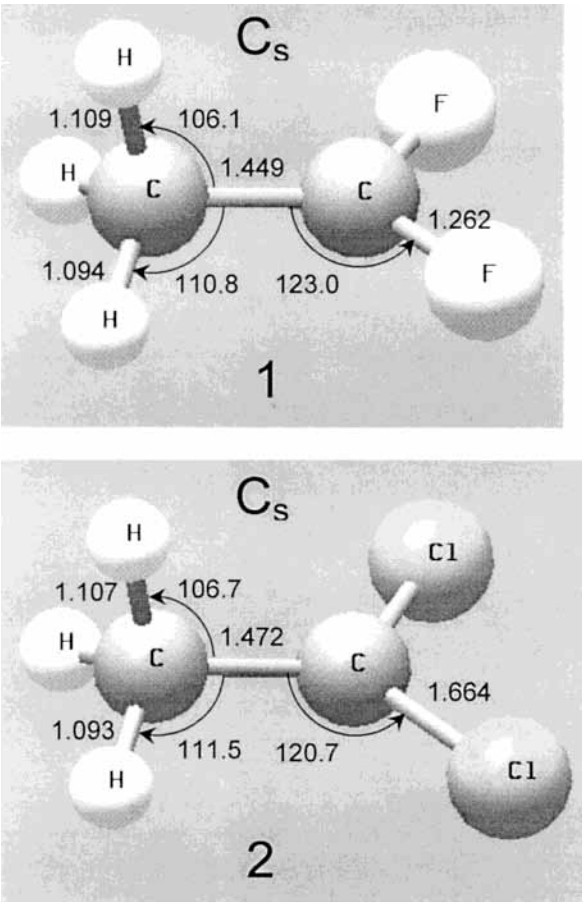

**Figure 1.** 1,1-Difluoroethyl cation (**1**) and 1,1-dichloroethyl cation (**2**).

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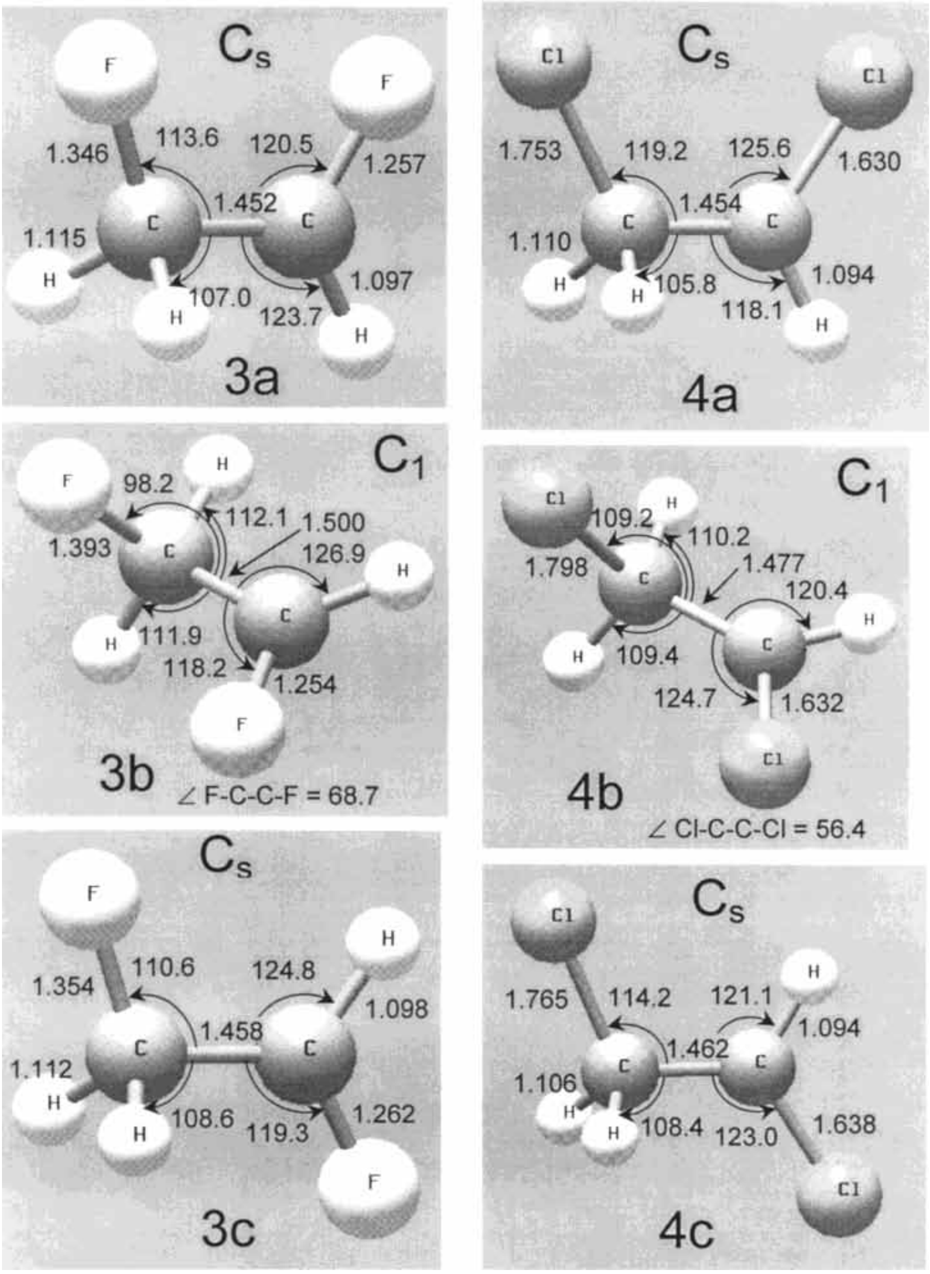

**Figure 2.** *cis*-1,2-Difluoroethyl cation (**3a**), *gauche*-1,2-difluoroethyl cation (**3b**), *trans*-1,2-difluoroethyl cation (**3c**), *cis*-1,2-dichloroethyl cation (**4a**), *gauche*-1,2-dichloroethyl cation (**4b**), and *trans*-1,2-dichloroethyl cation (**4c**).

Experimental results indicate that the iodonium ion[1−3] is the most stable isomer of $C_2H_4I^+$. Calculations for the iodonium ion[19−21] and 2-iodoethyl cation[19] were performed, but the energy gap to the 1-iodoethyl cation was not computed. Along with the above considered three most obvious isomers of $C_2H_4X^+$, Rodriquez et al.[15] computed two additional forms of $C_2H_4Cl^+$, namely the Cl-protonated vinyl chloride and the ion−dipole complex of vinyl cation with HCl.

To date the potential energy surfaces of the dihalogenated ethyl cations were not subjected to similar detailed studies, although some isomers were examined by quantum-chemical methods.[26−35] The heats of formation of the $CH_3CF_2^+$, $CH_2FCHF^+$, and $CHF_2CH_2^+$ cations were calculated at the SCF level.[30] Brum et al.[32] studied the $CH_3CF_2^+$ and $CHF_2CH_2^+$ cations at the SCF, MP2, G1, and G2 levels in connection with a determination of the ionization energies of the corresponding fluoroethyl radicals. They found that the former cation is a stable structure, while the latter one converts spontaneously either to $CH_3{-}CF_2^+$ or to $CH_2F{-}CHF^+$, depending on the starting conformation. Orlova and Minyaev[33] studied orders of the carbon−halogen bonds in a number of haloorganic compounds and computed geometries for the $CH_2FCHF^+$ and $CH_2ClCHCl^+$ species. The carbon−carbon bond stretching energies in the $CH_3$-$CF_2^+$ and H-bridged $HFC{-}(H){-}CHF^+$ cations were considered.[34] Keating et al.[35] computed two conformations of the $CH_2ClCHCl^+$ cation and the H-bridged $HClC{-}(H){-}CHCl^+$ species in the course of studies on the properties of 1,2-dichloroethylidene. Proton affinities of difluoroethenes were experimentally measured,[36,37] while for dichloroethenes we did not find reports on such measurements.

The aim of the present work is to systematically examine the potential energy surfaces of $C_2H_3F_2^+$ and $C_2H_3Cl_2^+$. The relative energies of different isomers have been computed and the type of stationary point (local minimum or saddle point) determined. Finally, the proton affinities of difluoroethenes and dichloroethenes have been calculated.

**TABLE 1: B3LYP/6-31++G(d,p) (Unlabeled), MP2(full)/6-311++G(d,p) (labeled MP2), and CBS-QB3 (Labeled CBS-QB3) Energies for the $C_2H_3F_2^+$ Isomers**[a]

| formula | $E_{\mathrm{el}}$ | ZPE | $E_{\mathrm{therm}}$ | $H_{\mathrm{rel}}$ |
|---|---|---|---|---|
| $CH_3CF_2^+$, **1** | −277.369 52 | 30.0 | 3.4 | 0 |
| MP2 | −276.871 21 | 30.7 | 3.4 | 0 |
| CBS-QB3 | −277.075 91 | 29.7 | 3.4 | 0 |
| *cis*-$CH_2FCHF^+$, **3a** | −277.327 30 | 29.7 | 3.3 | 26.1 |
| MP2 | −276.822 65 | 30.5 | 3.2 | 30.1 |
| CBS-QB3 | −277.029 48 | 29.4 | 3.3 | 28.7 |
| *gauche*-$CH_2FCHF^+$, **3b** | −277.311 65 | 30.2 | 3.0 | 36.1 |
| *trans*-$CH_2FCHF^+$, **3c** | −277.325 15 | 29.5 | 3.4 | 27.3 |
| MP2 | −276.820 23 | 30.3 | 3.3 | 31.0 |
| CBS-QB3 | −277.027 06 | 29.1 | 3.4 | 30.0 |
| $CHF_2CH_2^+$ ($C_s$), **5a** | −277.284 75 | 29.2 | 3.0 | 52.0 |
| $CHF_2CH_2^+$ ($C_1$), **5b** | −277.283 85 | 28.5 | 3.0 | 51.9 |
| *cis*-H-bridged, **8a** | −277.312 94 | 28.4 | 3.0 | 33.5 |
| MP2 | −276.811 38 | 29.0 | 3.0 | 35.4 |
| *trans*-H-bridged, **8b** | −277.309 95 | 28.3 | 3.0 | 35.3 |
| MP2 | −276.807 60 | 28.9 | 3.0 | 37.7 |
| cis-CHF═C(H)FH$^+$, **10a** | −277.287 72 | 28.7 | 3.5 | 50.1 |
| [*cis*-CHF═CHF]H$^+$, **10b** | −277.281 03 | 27.2 | 2.9 | 52.2 |
| *trans*-CHF═C(H)FH$^+$, **12** | −277.282 43 | 28.6 | 3.7 | 53.5 |
| $CH_2$═C(F)FH$^+$, **14a** | −277.293 92 | 27.3 | 4.0 | 45.3 |
| [$CH_2$═$CF_2$]H$^+$, **14b** | −277.251 52 | 26.4 | 3.1 | 70.1 |
| TS (**10a** → **3a**), **16** | −277.245 39 | 26.5 | 3.3 | 74.3 |
| TS (**12** → **3c**), **17** | −277.244 06 | 26.3 | 3.2 | 74.8 |
| TS (**14a** → **1**), **18** | −277.245 10 | 26.0 | 3.1 | 73.8 |
| FC═C(H)HFH$^+$, **22** | −277.289 86 | 25.5 | 4.8 | 46.9 |
| $CH_2$═CF$^+$ + HF | −277.272 93 | 24.5 | 5.0 | 56.7 |

[a] Electronic $E_{\mathrm{el}}$ (in au), zero-point ZPE (in kcal/mol), and thermal $E_{\mathrm{therm}}$ (in kcal/mol). Relative energies $H_{\mathrm{rel}}$ (in kcal/mol, including the ZPE and thermal corrections) with respect to the global minimum $CH_3CF_2^+$.

## 2. Details of Computations

All the calculations were performed with the Gaussian 98 program.[38] The natural charges[39] were computed using the NBO program[40] incorporated in Gaussian 98. The $C_2H_3X_2^+$ potential energy surfaces were investigated using the hybrid density functional/Hartree−Fock method B3LYP[41−43] with the 6-31++G-(d,p) basis set.[44] In addition to B3LYP/6-31++G(d,p), MP2-(full) calculations with the 6-311++G(d,p) basis set[44−46] were performed for the most important structures on the potential energy surfaces. These included the open 1,1- and 1,2-dihaloethyl cations (the most stable $C_2H_3X_2^+$ isomers) and the halogen- or hydrogen-bridged cations (nonclassical structures).

Geometries of the species involved were fully optimized. Analytical calculations of the vibrational frequencies were performed in order to determine the nature of the obtained stationary points (local minima have no imaginary modes and transition states have one). Paths connecting each transition state to the associated minima were checked using the IRC method.[47,48] The obtained relative energies of isomers and proton affinities were corrected for zero-point and thermal (298 K) energies derived from the frequency calculations.

Proton affinities of difluoroethenes and dichloroethenes were computed using the CBS-QB3 method.[49] This method is based on the B3LYP/6-311(2d,d,p) geometry optimization and frequencies, and the MP2/6-311+G(3d2f,2df,2p), MP4(SDQ)/6-31+G(d(f),p), and CCSD(T)/6-31+G(d′) single point energies. The total CBS-QB3 energy is the sum of the MP2/6-311+G-(3d2f,2df,2p) energy extrapolated to the complete basis set limit and the MP4(SDQ), CCSD(T), ZPE, and empirical corrections. The CBS-QB3 method is shown to provide very accurate thermochemical values, with the maximum error of 2.8 kcal/mol and mean average error of 0.87 kcal/mol on the G2 test set.

**TABLE 2: B3LYP/6-31++G(d,p) (Unlabeled), MP2(full)/6-311++G(d,p) (Labeled MP2), and CBS-QB3 (Labeled CBS-QB3) Energies for the $C_2H_3Cl_2^+$ Isomers**[a]

| formula | $E_{\mathrm{el}}$ | ZPE | $E_{\mathrm{therm}}$ | $H_{\mathrm{rel}}$ |
|---|---|---|---|---|
| $CH_3CCl_2^+$, **2** | −998.081 76 | 28.0 | 3.7 | 0 |
| MP2 | −996.891 98 | 28.6 | 3.6 | 0 |
| CBS-QB3 | −997.062 26 | 27.6 | 3.7 | 0 |
| *cis*-$CH_2ClCHCl^+$, **4a** | −998.056 75 | 27.8 | 3.5 | 15.3 |
| MP2 | −996.862 66 | 28.5 | 3.4 | 18.2 |
| CBS-QB3 | −997.035 81 | 27.4 | 3.5 | 16.2 |
| *gauche*-$CH_2ClCHCl^+$, **4b** | −998.048 45 | 28.1 | 3.2 | 20.5 |
| *trans*-$CH_2ClCHCl^+$, **4c** | −998.052 01 | 27.4 | 3.2 | 17.6 |
| MP2 | −996.857 89 | 28.2 | 3.2 | 20.6 |
| CBS-QB3 | −997.030 66 | 27.0 | 3.2 | 18.8 |
| $CHCl_2CH_2^+$ ($C_s$), **6a** | −998.020 72 | 27.8 | 3.3 | 37.7 |
| $CHCl_2CH_2^+$ ($C_1$), **6b** | −998.007 18 | 26.4 | 3.3 | 44.8 |
| chloronium ion, **7** | −998.059 48 | 28.8 | 3.5 | 14.6 |
| MP2 | −996.869 86 | 29.7 | 3.3 | 14.7 |
| CBS-QB3 | −997.040 15 | 28.4 | 3.5 | 14.5 |
| cis-H-bridged, **9a** | −998.039 61 | 26.3 | 3.2 | 24.2 |
| MP2 | −996.849 06 | 26.8 | 3.2 | 24.7 |
| trans-H-bridged, **9b** | −998.036 72 | 26.1 | 3.4 | 26.1 |
| MP2 | −996.845 83 | 26.7 | 3.3 | 26.7 |
| *cis*-CHCl═C(H)ClH$^+$, **11a** | −998.029 65 | 26.0 | 3.6 | 30.6 |
| [*cis*-CHCl═CHCl]H$^+$, **11b** | −998.027 95 | 24.5 | 3.4 | 30.0 |
| *trans*-CHCl═C(H)ClH$^+$, **13** | −998.027 08 | 26.3 | 3.8 | 32.7 |
| $CH_2$═C(Cl)ClH$^+$, **15a** | −998.024 89 | 25.7 | 3.9 | 33.6 |
| [$CH_2$═$CCl_2$]H$^+$, **15b** | −997.995 64 | 23.9 | 3.4 | 49.7 |
| TS (**11a** → **4a**), **19** | −997.995 81 | 24.7 | 3.4 | 50.3 |
| TS (**13** → **7**), **20** | −997.994 78 | 24.5 | 3.7 | 51.1 |
| TS (**15a** → **2**). **21** | −997.984 95 | 24.1 | 3.6 | 56.7 |
| ClC═C(H)HClH$^+$, **23** | −998.021 13 | 22.9 | 5.1 | 34.3 |
| $CH_2$═CCl$^+$ + HCl | −998.012 05 | 22.1 | 5.1 | 39.2 |

[a] Electronic $E_{\mathrm{el}}$ (in au), zero-point ZPE (in kcal/mol), and thermal $E_{\mathrm{therm}}$ (in kcal/mol). Relative energies $H_{\mathrm{rel}}$ (in kcal/mol, including the ZPE and thermal corrections) with respect to the global minimum $CH_3CCl_2^+$.

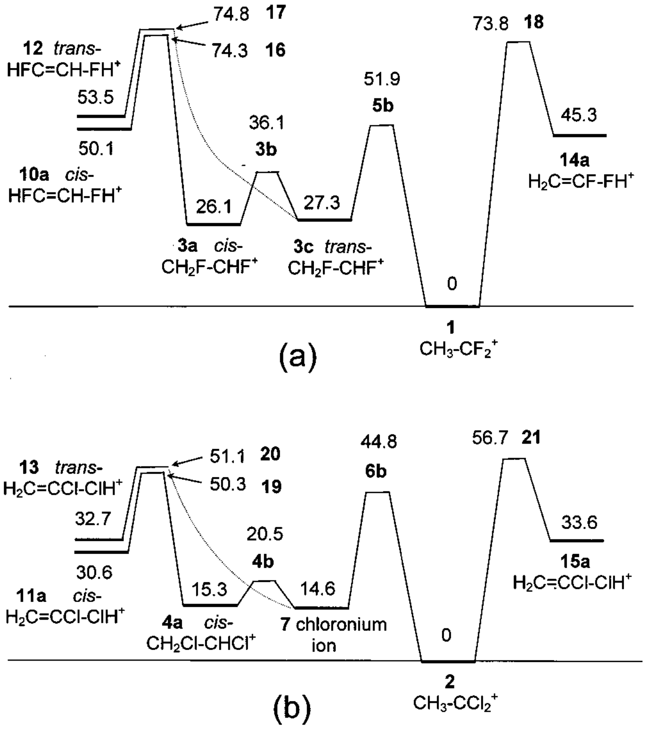

**Figure 3.** Relative energies and pathways to interconversion between the isomers of $C_2H_3F_2^+$ (a) and $C_2H_3Cl_2^+$ (b): (bold figures) structure numbers; (straight figures) relative energies in kcal/mol.

## 3. Results and Discussion

The $C_2H_3X_2^+$ isomers are grouped and considered in the following order: (1) classical dihaloethyl cations; (2) halogen-

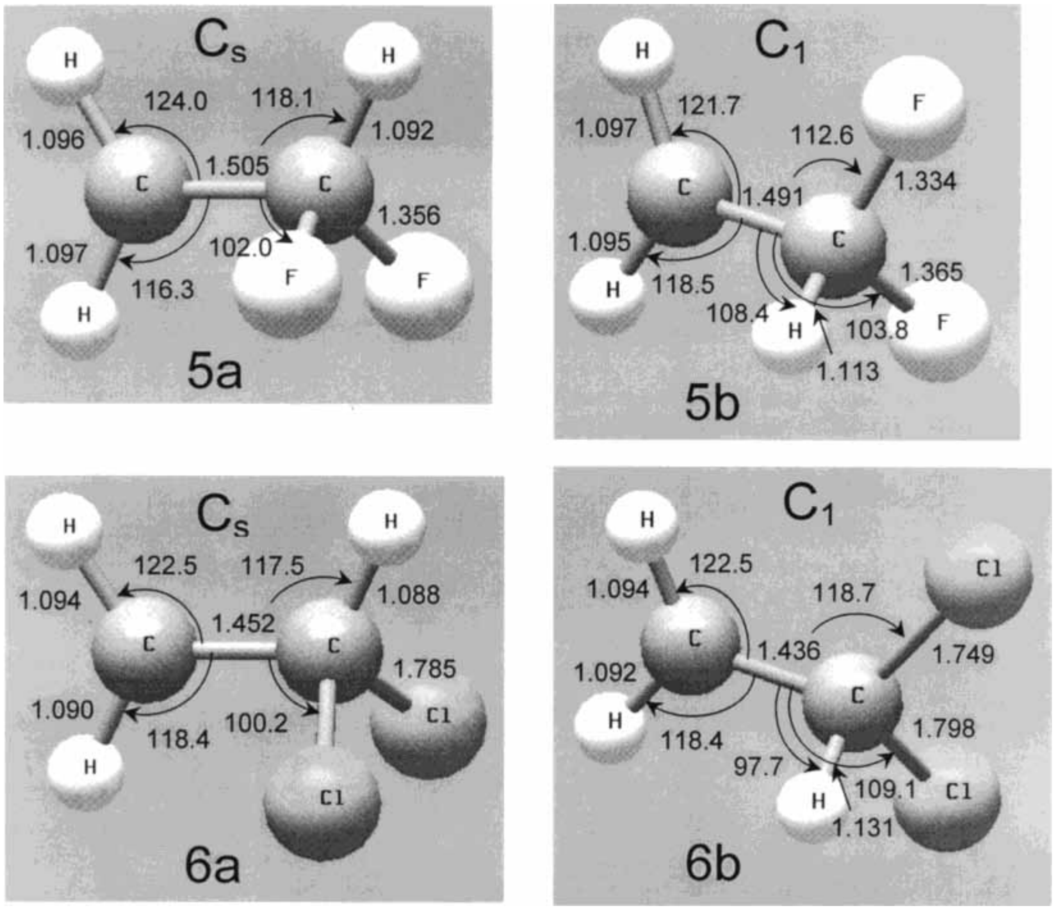

**Figure 4.** 2,2-Difluoroethyl cation, $C_s$ (**5a**); 2,2-difluoroethyl cation, $C_1$ (**5b**); 2,2-dichloroethyl cation, $C_s$ (**6a**); and 2,2-dichloroethyl cation, $C_1$ (**6b**).

bridged cations (halonium cations); (3) hydrogen-bridged cations; (4) protonated dihaloethenes; (5) ion−dipole complexes of the $C_2H_2X^+$ cation with the HX molecule.

In the discussion we will mostly use the B3LYP/6-31++G(d,p) geometric parameters. The MP2/6-311++G(d,p) calculations gave all important $C_2H_3X_2^+$ isomers to be of the same stationary point types as given by B3LYP/6-31++G(d,p). The geometric parameters from both levels of theory for all isomers excluding the chloronium ion (see section 3.2), are also very similar. There are notable, but not crucial, differences in the computed C−X bond lengths, the MP2/6-311++G(d,p) values being shorter by up to 0.018 Å for C−F and by up to 0.029 Å for C−Cl. Other parameters differ even less (the C−C bond lengths agree within 0.007 Å, the C−H bond lengths within 0.004 Å, and the C−C−H and C−C−X angles within 1.5°).

**3.1. Classical Dihaloethyl Cations.** *3.1.1. $CH_3CX_2^+$.* Previous studies of the haloethyl cations indicated that the halogen substituents in the α-position stabilize the carbenium ion.[14−18,27−29,31] This suggests that the 1,1-dihaloethyl cations will be the most stable isomers of the difluoro- and dichloroethyl cations. Indeed, our calculations indicate that the $CH_3CX_2^+$ cations **1** and **2** (Figure 1) are at the global minima on the $C_2H_3X_2^+$ potential energy surfaces for both X = F and X = Cl.

Donation of the electron density from the halogen lone pairs to the empty p-orbitals of the α-carbon atom is evident from the computed values of natural charges and atomic orbital populations.[39] Indeed, the populations on the p-orbitals of X perpendicular to the X−C−X plane are notably lower than 2 (1.791 for X = F and 1.675 for X = Cl). Because of the $\pi$-donation, the Cl atoms in $CH_3CCl_2^+$ bear large positive charges (+0.358 e). Charges on the F atoms in $CH_3CF_2^+$ are negative (−0.197 e), since a strong displacement of the $\sigma$ C−F bond density toward F outweights the effect of $\pi$-donation. The $\pi$-donation causes shortening of the C−X bonds in $CH_3CX_2^+$ with respect to $CH_3CHX_2$, to 1.262 from 1.381 Å for X = F and to 1.664 from 1.809 Å for X = Cl.

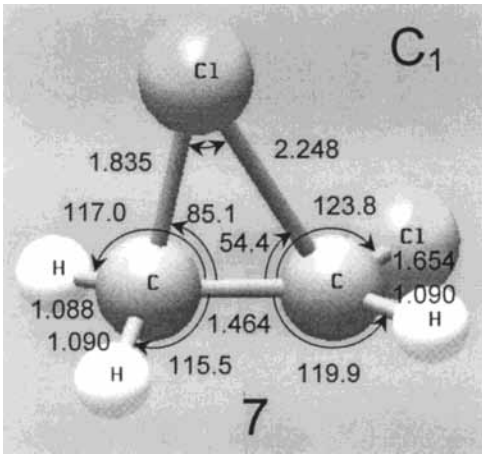

**Figure 5.** Chloroethylchloronium cation.

Hyperconjugation with the methyl group[50] also contributes to stabilization of the cationic carbons in $CH_3CX_2^+$. This causes shortening of the C−C bond in $CH_3CX_2^+$ with respect to that in the corresponding 1,1-dihaloethanes, to 1.449 from 1.506 Å for X = F and to 1.472 from 1.515 Å for X = Cl. In addition, interaction of the empty p-orbital with the coplanar C−H bond causes this bond to be longer than the two others (e.g., 1.109

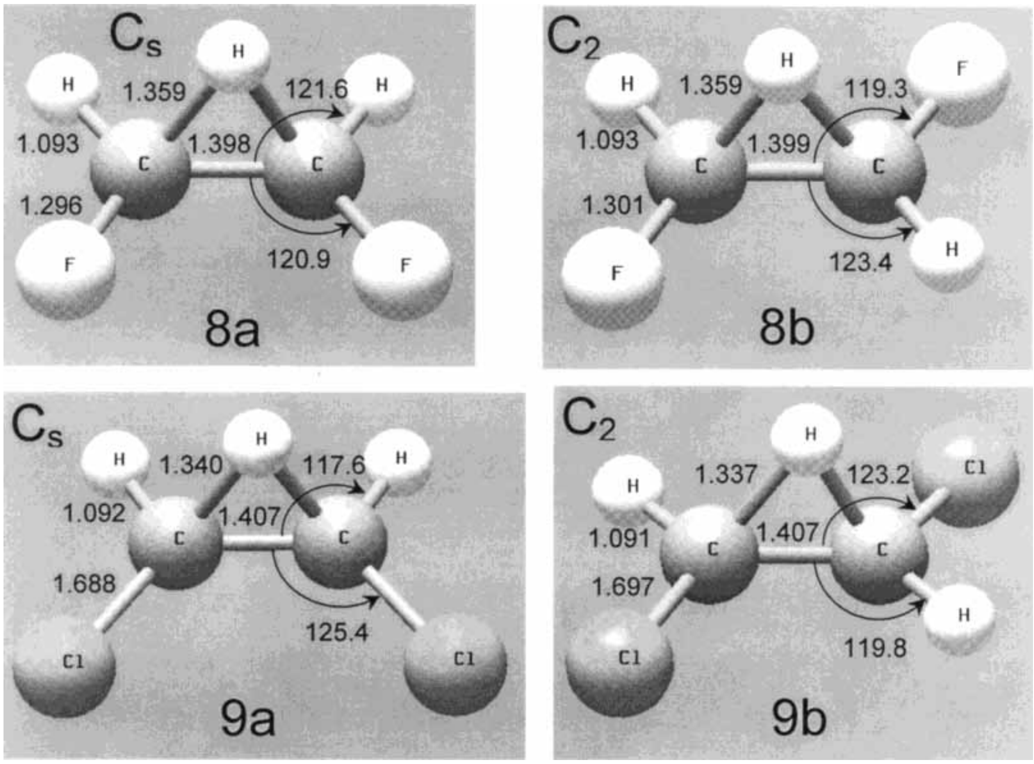

**Figure 6.** Hydrogen-bridged cations: *cis*-$C_2H_3F_2^+$ (**8a**); *trans*-$C_2H_3F_2^+$ (**8b**); *cis*-$C_2H_3Cl_2^+$ (**9a**); *trans*-$C_2H_3Cl_2^+$ (**9b**).

vs 1.094 Å in $CH_3CF_2^+$), and the corresponding C−C−H angle to be smaller than the two others (106.1 vs 110.8° in $CH_3CF_2^+$).

*3.1.2. $CH_2XCHX^+$.* Three stationary point conformations, cis, trans, and gauche, were located for each of the $CH_2FCHF^+$ and $CH_2ClCHCl^+$ cations (Figure 2). Frequency calculations indicate that only the *cis*-$CH_2FCHF^+$, *trans*-$CH_2FCHF^+$, and *cis*-$CH_2ClCHCl^+$ are at the local minima, whereas both gauche cations and *trans*-$CH_2ClCHCl^+$ are at first-order saddle points. Thus, the conformational behavior of $CH_2ClCHCl^+$ resembles that of $CH_3CHCl^+$ and $CH_3CHF^+$, where the structure in which the halogen eclipses a hydrogen is the only minimum.[14,15,17,18]

$\pi$-Donation to the cationic carbon in $CH_2XCHX^+$ occurs from the α- but not from the $\beta$-halogens. Therefore, the α C−X bonds are significantly shorter than the $\beta$ bonds (e.g., 1.247 vs 1.346 Å in *cis*-$CH_2FCHF^+$). Earlier, Orlova and Minyaev[33] reported such an effect for these cations. Because of the $\pi$-donation, the electron densities on α-halogens are smaller than on $\beta$-halogens (e. g., the computed natural charges in *cis*-$CH_2FCHF^+$ are −0.171 e on α-F vs −0.302 e on $\beta$-F). Because of the absence of the second $\pi$-donating α-halogen, 1,2-dihaloethyl cations have higher energies than the isomeric 1,1-dihaloethyl cations (see Tables 1 and 2).

The lowest energy rotamers of the 1,2-dihaloethyl cations are *cis*-$CH_2FCHF^+$ (**3a)** (26.1 kcal/mol above $CH_3CF_2^+$) and *cis*-$CH_2ClCHCl^+$ (**4a**) (15.3 kcal/mol above $CH_3CCl_2^+$). The trans conformations **3c** and **4c** have slightly higher relative energies (+27.3 kcal/mol for X = F, +17.6 kcal/mol for X = Cl). The gauche conformations (**3b**, **4b**) of $CH_2XCHX^+$ are the least stable (+36.1 kcal/mol for X = F, +20.5 kcal/mol for X = Cl). The lower stability of the *gauche*-$CH_2XCHX^+$ is the consequence of unfavorable hyperconjugation between the $\beta$ C−X bond and the empty p-orbital of the cationic carbon.[14,51] A trend toward formation of the fluoriranium ring observed in this rotamer will be discussed in section 3.3.

The predicted energy ordering of the cis and trans conformations is somewhat surprising. Indeed, one could expect that the steric repulsion of the two bulky halogen atoms in *cis*-$CH_2XCHX^+$ would make these isomers less stable than their trans isomers. However, the calculations at all three levels, B3LYP/6-31++G(d,p), MP2/6-311++G(d,p), and CBS-QB3, consistently predict a slightly better energy for the cis conformations. The predicted differences are 0.9−1.3 kcal/mol for the 1,2-difluoroethyl cation and 2.3−2.6 kcal/mol for the 1,2-dichloroethyl cation. Following a suggestion of the reviewer of this paper, we checked whether inclusion of electron correlation is essential to correctly reproduce the cis−trans energy difference in $CH_2XCHX^+$. At HF/6-311++G** the ordering of energy is the same as at the correlated levels, but the magnitude of the differences is even smaller (0.2 kcal/mol for $CH_2FCHF^+$ and 0.4 kcal/mol for $CH_2ClCHCl^+$).

Relative to the 1,1-dihaloethyl cations, the MP2/6-311++G(d,p) energies for the *cis*- and *trans*-1,2-dihaloethyl cations are 3−4 kcal/mol higher, and the CBS-QB3 energies are 1−3 kcal/mol higher than the B3LYP/6-31++G(d,p) values (Tables 1 and 2).

The IRC analysis[47,48] indicates that the gauche conformation of the $CH_2FCHF^+$ cation represents a transition state between its cis and trans conformations. Thus, the barrier for rotation for *cis*-$CH_2FCHF^+$ is 10.0 kcal/mol. Isomerization to the global minimum $CH_3CF_2^+$ requires a higher activation energy of 24.6 kcal/mol and proceeds via the unstable 2,2-difluoroethyl cation (see the diagram in Figure 3). The IRC analysis of the *gauche*-$CH_2ClCHCl^+$ and *trans*-$CH_2ClCHCl^+$ saddle points shows that the former is a transition state between the *cis*-$CH_2Cl{-}CHCl^+$ and the chloronium ion (see section 3.2), whereas the latter rearranges to the chloronium ion in both forward and backward directions along the reaction coordinate.

*3.1.3. $CHX_2CH_2^+$.* The 2,2-dihaloethyl cations do not represent local minima on the potential energy surfaces. Two first-order saddle point structures for each of the $CHF_2CH_2^+$ and $CHCl_2CH_2^+$ cations were located (Figure 4). The $C_s$ structure **5a**, according to the IRC analysis, descends to the *trans*-1,2-

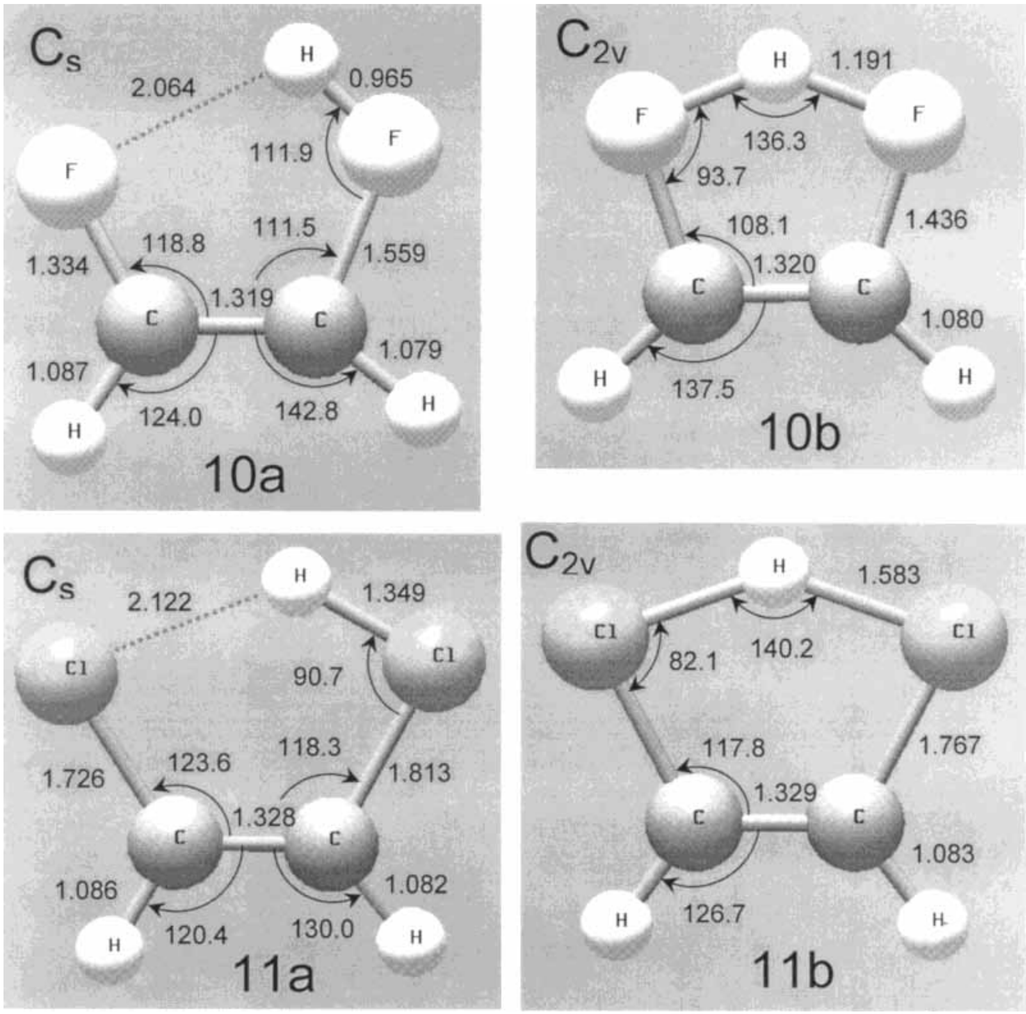

**Figure 7.** Fluorine-protonated *cis*-1,2-difluoroethene (**10a**), transition state for proton shift between two fluorines (**10b**), chlorine-protonated *cis*-1,2-dichloroethene (**11a**), and transition state for proton shift between two chlorines (**11b**).

difluoroethyl cation along both directions of the reaction coordinate. Similarly, the $C_s$ structure **6a** descends to the chloronium ion (see section 3.2). The $C_1$ conformations of $CHF_2CH_2^+$ (**5b)** and $CHCl_2CH_2^+$ (**6b**) are chemically more interesting, as they represent transition states for formation of the 1,1-dihaloethyl cations, the structures at the global minima. The IRC analysis indicates that **5b** is the transition state between the *trans*-$CH_2FCHF^+$ and $CH_3CF_2^+$, while **6b** is the transition state between the chloronium ion and $CH_3CCl_2^+$.

**3.2. Halonium Cations.** The chloroethylchloronium ion **7** (Figure 5) is found to be at a local minimum. It possesses a formally divalent bridging chlorine atom bound to two carbons. The two Cl−C bonds are not equivalent (1.835 and 2.248 Å at B3LYP/6-31++G(d,p)). The longer bond is formed with the carbon atom that is bound to the other chlorine. The asymmetry of the two Cl−C bonds in the chloriranium ring is confirmed at the MP2/6-311++G(d,p) level, but the computed difference (1.829 and 1.989 Å) is much smaller than at B3LYP/6-31++G-(d,p).

According to the natural charge analysis (at B3LYP/6-31++G(d,p)), the positive charge of the chloronium cation is distributed among the bridging Cl atom (+0.226 e), the $CH_2$ group (+0.178 e), and the CHCl group (+0.595 e). The higher positive charge on the CHCl group with respect to the $CH_2$ group seemingly contradicts the high electronegativity of the Cl substituent. This suggests that the chloroethylchloronium ion has a significant contribution from a structure resembling the classical 1,2-dichloroethyl cation ($ClCH_2CHCl^+$). The suggestion is supported by the significant positive charge on the nonbridging chlorine (+0.343 e), as well as the length of the nonbridging C−Cl bond (1.654 Å). The latter is closer to the length of the α C−Cl bond in *cis*-$CH_2ClCHCl^+$ (1.630 Å) than to the $\beta$ C−Cl bond (1.753 Å).

The energy of the chloronium ion is slightly (0.7 kcal/mol) below that of the *cis*-1,2-dichloroethyl cation and 14.6 kcal/mol above the global minimum. The MP2/6-311++G(d,p) and CBS-QB3 values for the energy difference between the chloronium cation and 1,1-dichloroethyl cation are very close (within 0.1 kcal/mol) to that found at B3LYP/6-31++G(d,p) (Table 2).

Isomerization of the *cis*-$CH_2ClCHCl^+$ to the chloronium ion proceeds via the *gauche*-$CH_2ClCHCl^+$ transition state and the activation energy is 5.2 kcal/mol. Isomerization of the chloronium ion to $CH_3CCl_2^+$ proceeds via the unstable 2,2-dichloroethyl cation, and the activation energy for this process is high, 30.2 kcal/mol.

The fluoroethylfluoronium ion, unlike the chloronium ion, does not correspond to a stationary point on the potential energy surface. Ring opening occurs with no activation barrier and the *trans*-$CH_2FCHF^+$ cation is formed. This result was obtained at both B3LYP/6-31++G(d,p) and MP2/6-311++G(d,p). Earlier it was found[14,18] that the fluoronium ion is at a local minimum on the $C_2H_4F^+$ potential energy surface. In the case of $C_2H_3F_2^+$, however, the second fluorine atom apparently facilitates the

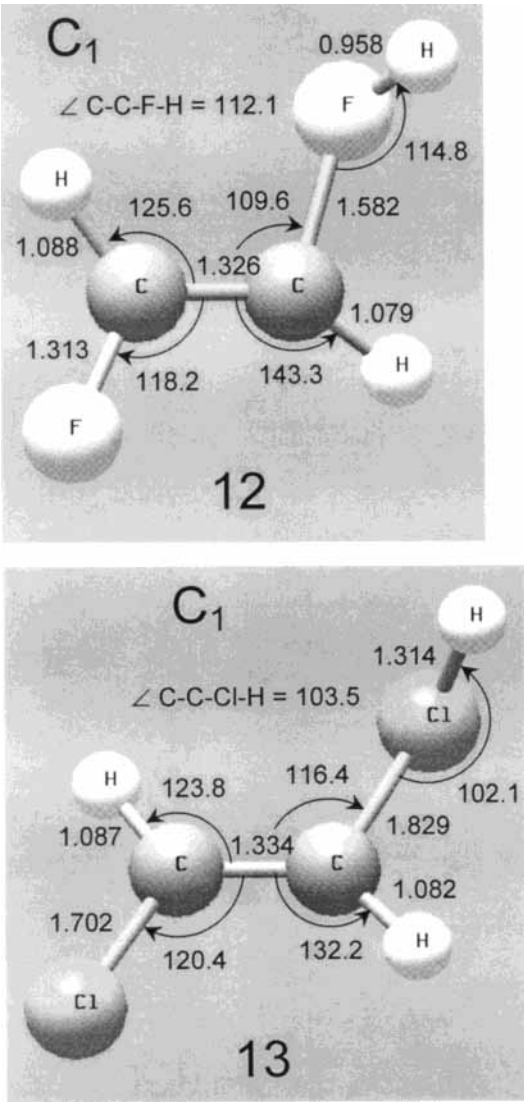

**Figure 8.** Fluorine-protonated *trans*-1,2-difluoroethene (**12**) and chlorine-protonated *trans*-1,2-dichloroethene (**13**).

opening of the fluoriranium ring, because this F stabilizes the product classical carbocation. Thus, the behavior of halonium ions resembles the behavior of oxiranium and thiiranium ions,[52,53] whose stability toward the ring opening depends on the nature of the substituent groups on the ring.

A trend toward formation of the fluoriranium ring is observed in the *gauche*-1,2-$CH_2FCHF^+$ considered in section 3.1.2. Although the gauche rotamer represents a transition state between the cis and trans rotamers, the value of the C−C−$F_\beta$ angle in this transition state (98.2°) is smaller than that in both the reactant (113.6°) and product (110.6°). However, this angle is still larger than 90°, and the distances from $F_\beta$ to the two carbon atoms are very different, 1.393 and 2.188 Å. This implies that *gauche*-1,2-$CH_2FCHF^+$ has to be considered as a classical dihaloethyl cation, rather than as a fluoronium ion.

**3.3. Hydrogen-Bridged Cations.** The H-bridged $C_2H_3X_2^+$ cations are not at a local minima on the potential energy surfaces. First-order saddle points corresponding to the cis and trans isomers of H-bridged $C_2H_3X_2^+$ species **8a**, **8b**, **9a**, and **9b** were located (Figure 6). The bridging hydrogens of all these structures shift toward one carbon atom with no activation barrier. Such a shift transforms the H-bridged *cis*-$C_2H_3X_2^+$ isomers to the *cis*-$CH_2XCHX^+$ species, *trans*-$C_2H_3F_2^+$ to *trans*-$CH_2FCHF^+$, and *trans*-$C_2H_3Cl_2^+$ to the chloronium ion. These rearrangements are exoergic by 7−8 kcal/mol for the H-bridged $C_2H_3F_2^+$ and by 9−12 kcal/mol for $C_2H_3Cl_2^+$ (B3LYP/6-31++G(d,p)). The MP2/6-311++G(d,p) calculations also predict the H-bridged cations to be saddle points and give similar exothermicities for their isomerization (5−7 kcal/mol for X = F and 6−12 kcal/mol for X = Cl).

**3.4. Halogen-Protonated *cis*-1,2-, *trans*-1,2-, and 1,1-Dihaloethenes.** The computed structures of the halogen-protonated difluoro- and dichloroethenes are shown in Figures 7−9. The halogen-protonated *cis*-1,2-dihaloethenes **10a** and **11a** are planar and contain intramolecular hydrogen bonds X−H···X. The halogen-protonated *trans*-1,2-dihaloethenes **12** and **13** and 1,1-dihaloethenes **14a** and **15a**, have $C_1$ symmetry, since the hydrogen atoms bound to the halogen are not located in the CCX plane. The CCXH dihedral angles vary from 103.5° in Cl-protonated *trans*-1,2-dichloroethene to 141.3° in F-protonated 1,1-difluoroethene.

The 1,4-proton migration in the halogen-protonated *cis*-1,2-dihaloethenes occurs very easily and the transition structures **10b** and **11b** (Figure 7) have $C_{2v}$ symmetry. The computed activation energy for this shift for X = F is 2.7 kcal/mol. In the case of X = Cl, inclusion of the ZPE corrections results in an activation energy with a negative value (−0.6 kcal/mol). This is likely to be a computational artifact, since the zero-point energy term corresponding to the movement of the H atom between the two Cl atoms is included in the ZPE of structure **11a** but not in the ZPE of structure **11b**. Given the very small difference in the electronic energies of **11a** and **11b** (1.1 kcal/mol), the proton obviously moves freely between the two Cl atoms of **11a**. The geometry of the halogen-protonated *cis*-1,2-dihaloethenes changes significantly during the hydrogen shift. For example, the C−F distances in **11a** differ by more than 0.2 Å but become equal in **11b** and reverse when the hydrogen shift is complete. It is interesting that such significant geometry changes have only a small effect on the energy.

In contrast, the proton shift between the two halogens of halogen-protonated 1,1-dihaloethenes requires a significant activation energy, 24.8 kcal/mol for X = F and 16.1 kcal/mol for X = Cl. The planar structures of $C_{2v}$ symmetry **14b** and **15b** (Figure 9) represent transition states for this process. Geometry changes in the course of the proton shift are even greater than in the case of *cis*-1,2-dihaloethenes. For instance, in **14a** the C−F distances differ by 0.54 Å and the C−C−F angles differ by 43°. This is the probable origin of the relatively high activation energies for the proton shift in **14a** and **15a**.

Transformation of all the halogen-protonated $C_2H_3X_2^+$ cations to the carbon-protonated isomers is exoergic. The computed transition states for these rearrangements are shown in Figure 10. In the halogen-protonated 1,2-dihaloethenes, according to the IRC analysis, the hydrogen is transferred to the closest carbon atom. This hydrogen is bound simultaneously to C and X in the transition states **16**−**19**. Fluorine-protonated *cis*- and *trans*-1,2-difluoroethenes convert to the *cis*- and *trans*-1,2-difluoroethyl cations, respectively ($\Delta H = -24.0$ and $-26.2$ kcal/mol, $\Delta H^{\ddagger} = 24.2$ and 21.3 kcal/mol). Chlorine-protonated *cis*-1,2-dichloroethene transforms to the *cis*-1,2-dichloroethyl cation, whereas chlorine-protonated *trans*-1,2-dichloroethene rearranges to the chloronium ion ($\Delta H = -16.0$ and $-15.4$ kcal/mol, $\Delta H^{\ddagger} = 19.7$ and 18.4 kcal/mol).

Rearrangements of the halogen-protonated 1,1-dihaloethenes are more complicated. Initially, the hydrogen moves to the closest carbon atom and this would lead to formation of the 2,2-dihaloethyl cations. However, the latter cations are not at local minima and collapse to the 1,1-dihaloethyl cations without

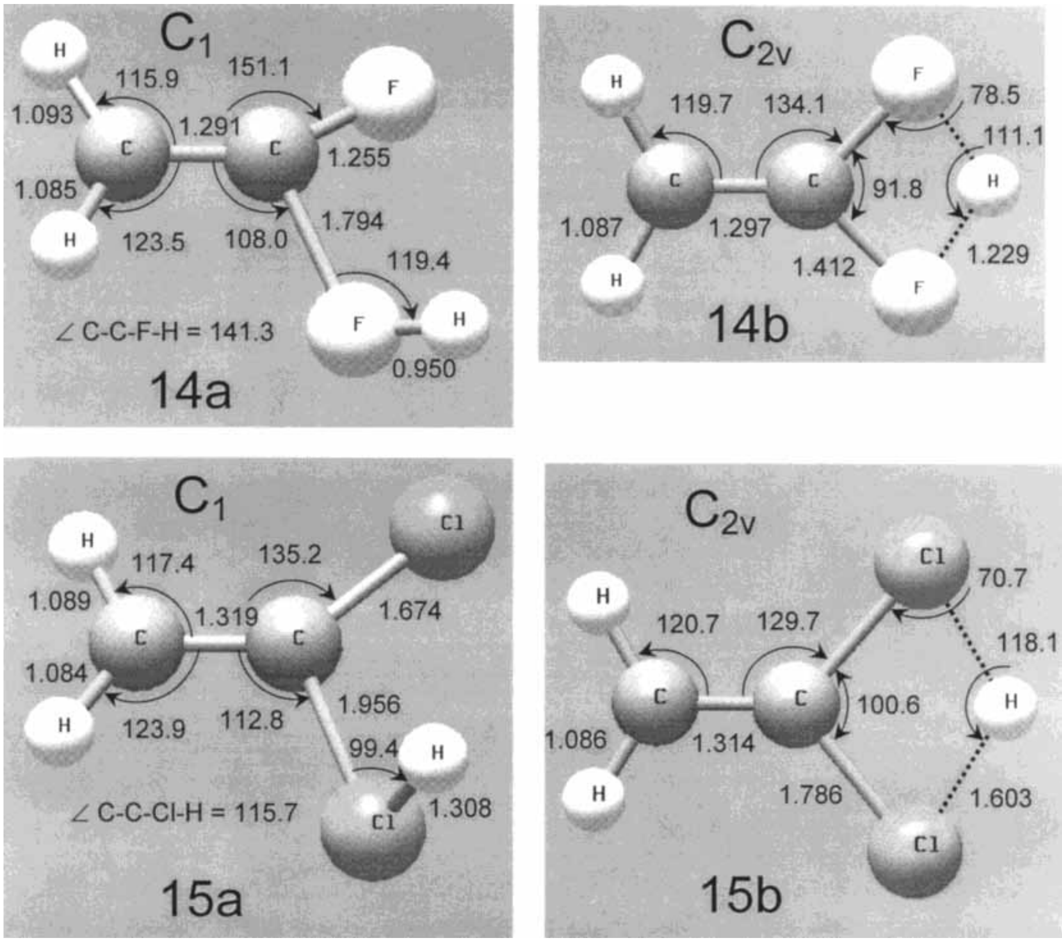

**Figure 9.** Fluorine-protonated 1,1-difluoroethene (**14a**), transition state for proton shift between two fluorines (**14b**), chlorine-protonated 1,1-dichloroethene (**15a**), and transition state for proton shift between two chlorines (**15b**).

**TABLE 3: Computed Proton Affinities (PA, in kcal/mol) of Dihaloethenes for Different Products of Protonation**[a]

| neutral | protonated isomer | B3LYP | MP2 | CBS-QB3 | exptl PA |
|---|---|---|---|---|---|
| $CH_2=CF_2$ | $CH_3CF_2^+$ | 172.0 | 172.1 | 171.1 | 177 ± 3;[b] 174.8[c] |
| | $CH_2=CFFH^+$ | 126.7 | | | |
| *cis*-$CHF=CHF$ | *cis*-$CH_2FCHF^+$ | 154.6 | 152.1 | 152.9 | 164 ± 2[b] |
| | *cis*-$CHF=CHFH^+$ | 130.6 | | | |
| *trans*-$CHF=CHF$ | *trans*-$CH_2FCHF^+$ | 153.8 | 151.5 | 151.9 | 165 ± 2[b] |
| | *cis*-$CH_2FCHF^+$ | 155.0 | 152.9 | 153.1 | |
| | *trans*-$CHF=CHFH^+$ | 127.6 | | | |
| $CH_2=CCl_2$ | $CH_3CCl_2^+$ | 179.2 | 178.3 | 176.0 | |
| | $CH_2=CClClH^+$ | 145.7 | | | |
| *cis*-$CHCl=CHCl$ | *cis*-$CH_2ClCHCl^+$ | 162.4 | 159.9 | 159.7 | |
| | chloronium cation | 163.1 | 163.4 | 161.4 | |
| | *cis*-$CHCl=CHClH^+$ | 147.1 | | | |
| *trans*-$CHCl=CHCl$ | chloronium cation | 163.4 | 163.8 | 162.0 | |
| | *trans*-$CHCl=CHClH^+$ | 145.3 | | | |

[a] Zero-point and thermal (298 K) corrections included. B3LYP stands for B3LYP/6-31++G(d,p), and MP2 for MP2(full)/6-311++G(d,p) [b] Reference 36. [c] Reference 37.

barriers. Therefore, the final products of the halogen-protonated 1,1-dihaloethenes rearrangement are 1,1-dihaloethyl cations, as shown by the IRC analysis. In the transition states **20** and **21** the hydrogen atom is bound to both the X and the halogenated C atom but at the same time has a rather short distance (1.642 Å for X = F, 1.970 Å for X = Cl) to the second C, its ultimate destination. The activation energies for rearrangement of the 1,1-isomers (28.5 kcal/mol for X = F and 23.1 kcal/mol for X = Cl) are somewhat higher than those for the 1,2-isomers. This is probably due to the fact that the transition state structures for rearrangement of the 1,1-isomers show some similarity to the unstable 2,2-dihaloethyl cations. However, the overall reaction heats for rearrangement of the halogen-protonated 1,1-dihaloethenes (−45.3 kcal/mol for X = F and −33.6 kcal/mol for X = Cl) are much greater than those for 1,2-isomers. This is because the halogen-protonated 1,1-isomers are converted to the global minimum 1,1-dihaloethyl cations, whereas the 1,2-isomers rearrange to the higher energy 1,2-dihaloethyl cations or the chloronium ion.

**3.5. Ion−Dipole Complexes of the $C_2H_2X^+$ Cation with the HX Molecule.** The computed structures of the $[FC{=}C(H)H\text{- -}FH]^+$ and $[ClC{=}C(H)H\text{- -}ClH]^+$ complexes **22** and **23** are shown in Figure 11. Earlier it was found[54,55] that the $H_2C{=}CCl^+$ ion is the global minimum on the $C_2H_2Cl^+$ potential energy surface. The polar HX molecule can attach to one of the hydrogens of $H_2C{=}CX^+$. A rather long H- -X bond is

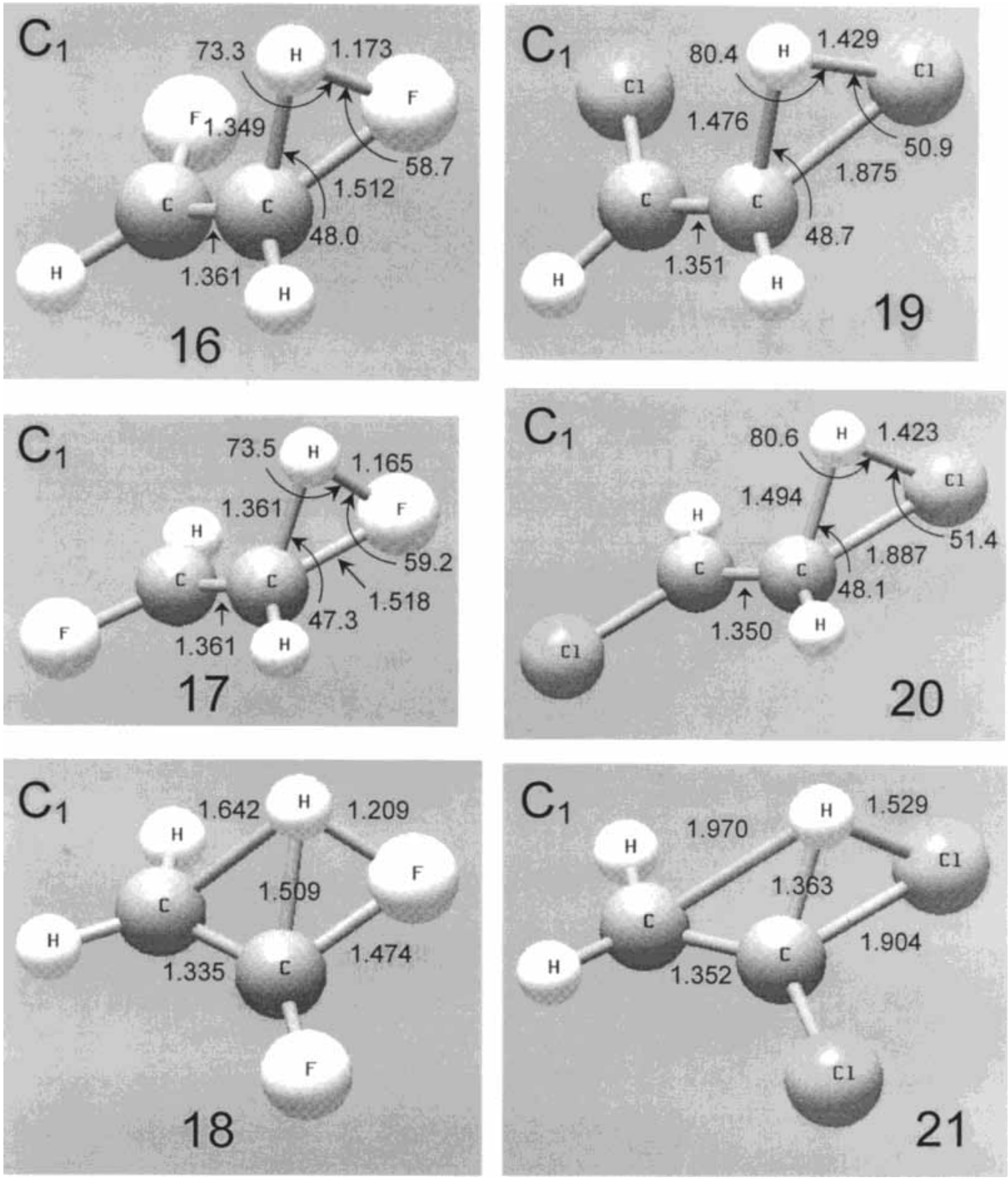

**Figure 10.** Transition states for isomerization of the halogen-protonated difluoro- and dichloroethenes to the carbon-protonated isomers.

formed in these complexes: 1.837 Å for X = F and 2.323 Å for X = Cl. Formation of the hydrogen bond makes the C−H bond with the involved hydrogen slightly longer than the second C−H bond (ca. 1.11 Å versus ca. 1.09 Å). The calculated energy of the ion−dipole complexes with respect to the separated $C_2H_2X^+$ and HX species is −9.8 kcal/mol for X = F and −4.9 kcal/mol for X = Cl. The higher complex formation energy with HF is likely due to its higher dipole moment (the calculated values are 1.99 D for HF versus 1.46 D for HCl). The relative energies of the $[XC{=}C(H)H\text{- -}XH]^+$ cations with respect to the global minimum $CH_3CX_2^+$ isomers are +46.9 kcal/mol for X = F and +34.3 kcal/mol for X = Cl.

The HX molecule can also attach to the cationic carbon of $H_2C{=}CX^+$. This leads to the halogen-protonated 1,1-dihaloethenes considered in the previous section. The computed binding energies of the HX molecules to the α carbon atoms of $H_2C{=}CX^+$ (−11.4 kcal/mol for X = F and −5.6 kcal/mol for X = Cl) are slightly more negative than the energies of binding to the hydrogen atom.

**3.6. Proton Affinities of Difluoroethenes and Dichloroethenes.** Now we can compute the proton affinities (PA) of dihaloethenes $C_2H_2X_2$, using the above results to predict which protonated isomer $C_2H_3X_2^+$ can be produced from each dihaloethene isomer. 1,1-Dihaloethenes can be protonated either at the *β*-carbon, yielding 1,1-dihaloethyl cations, or at a halogen, yielding halogen-protonated dihaloethenes. Protonation at the α-carbon can be ruled out, as it would result in the formation of the unstable 2,2-dihaloethyl cations. Protonation at the *β*-carbon is much more exoergic (ca. 45 kcal/mol for X = F and ca. 34 kcal/mol for X = Cl, see Table 3) than protonation at halogen.

The proton affinities for protonation of 1,1-difluoroethene at the *β*-carbon computed at the three levels agree within 1 kcal/mol (see Table 3). The best estimate of 171.1 kcal/mol (CBS-QB3) is in good agreement with the value of Williamson et al.[37] (174.8 kcal/mol), derived from a thermochemical cycle involving the photoionization products of difluoropropane. Ridge[36] found the proton affinity of $H_2C{=}CF_2$ to be 177 ± 3 kcal/mol using bracketing experiments, and his lower margin is also close to the present computational results.

We did not find reports on experimental measurements of the proton affinities of dichloroethenes. Our calculated values

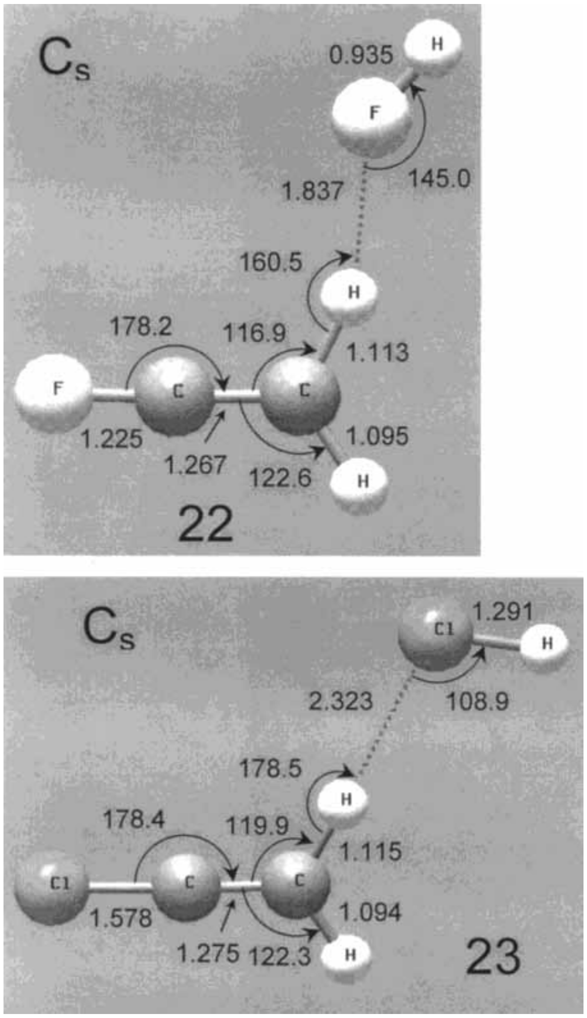

**Figure 11.** Ion-dipole complexes of the 1-fluorovinyl cation with hydrogen fluoride (**22**) and of the 1-chlorovinyl cation with hydrogen chloride (**23**).

for 1,1-dichloroethene from the three levels agree within 3.2 kcal/mol. The best estimate from CBS-QB3 is 176.0 kcal/mol.

1,2-Dihaloethenes can also be protonated either at a carbon or at a halogen. As in the case of 1,1-dihaloethenes, protonation at carbon is more exoergic (24−26 kcal/mol for $X = F$ and 15−18 kcal/mol for $X = Cl$) than protonation at halogen. Protonation at the $\pi$-bond can be ruled out, as it would result in the formation of the unstable H-bridged cations.

Protonation at carbon will transform *cis*- and *trans*-1,2-difluoroethenes to the *cis*- and *trans*-1,2-difluoroethyl cations, respectively. If the temperature is sufficiently high, the *trans*-1,2-difluoroethyl cation may rotate to the more stable cis conformation (activation barrier 8.8 kcal/mol, see Figure 3). This would slightly (1.3 kcal/mol according to CBS-QB3) increase the proton affinity of *trans*-1,2-difluoroethene. Isomerization to the global minimum $CH_3CF_2^+$ would be very exoergic but is unlikely to occur at ambient temperatures because of the high activation barrier (24.6 kcal/mol).

Our best estimates (CBS-QB3) for the proton affinities for *cis*- and *trans*-1,2-difluoroethenes are 152.9 and 151.9 kcal/mol, respectively (Table 3). These values are more than 10 kcal/mol lower than those found by Ridge[36] in bracketing experiments (164 ± 2 kcal/mol for *cis*-1,2-difluoroethene and 165 ± 2 for the trans isomer). It is unlikely that the computational results are in error by 10 kcal/mol or more, given the proven high precision of the CBS-QB3 method and its good agreement with the two other theoretical methods (Table 3). Therefore, we suggest that the proton affinities in the literature[36] are overestimated.

Protonation of *cis*- and *trans*-1,2-dichloroethenes at carbon will lead to the *cis*-1,2-dichloroethyl cation and chloronium ion, respectively. It is possible that the *cis*-1,2-dichloroethyl cation will isomerize to the chloronium ion in the course of protonation, since the activation barrier for this process is small (5.2 kcal/mol, see Figure 3). This would slightly (1.7 kcal/mol according to CBS-QB3) increase the proton affinity of *cis*-1,2-dichloroethene. Isomerization to the global minimum $CH_3CCl_2^+$ would be very exoergic but is unlikely to occur at ambient temperatures because of the high activation barrier (30.2 kcal/mol). Our best estimates (CBS-QB3) for the proton affinities of *cis*- and *trans*-1,2-dichloroethenes are 159.7 and 162.0 kcal/mol, respectively.

The possibility of protonation of dihaloethenes at the halogen atom cannot be excluded. Once formed, the halogen-protonated dihaloethenes will not readily isomerize to the more stable carbon-protonated forms at ambient temperatures, as the activation barriers for such isomerizations are considerable (18−29 kcal/mol, see Figure 3). However, formation of the halogen-protonated dihaloethenes would require much stronger proton donors than formation of the carbon-protonated isomers. Deprotonation energies of the cations that can protonate difluoroethenes on F should be ≤127−131 kcal/mol, and for protonation of dichloroethenes on Cl they should be ≤145−147 kcal/mol.

## 4. Conclusion

1. A quantum-chemical study of the $C_2H_3X_2^+$ ($X = F$, Cl) potential energy surfaces has been performed. The results obtained indicate that the classical 1,1-dihaloethyl cations represent global minima. Other minima located are classical 1,2-dihaloethyl cations (cis and trans conformations of $CH_2FCHF^+$ and only the cis conformation of $CH_2ClCHCl^+$), the chloroethylchloronium (Cl-bridged) cation, halogen-protonated *cis*-1,2-, *trans*-1,2-, and 1,1-dihaloethenes, and ion−dipole complexes of the $CH_2{=}CX^+$ cation with the HX molecule. In contrast, classical 2,2-dihaloethyl cations, as well as H-bridged cations, represent first-order saddle points. No stationary points correspond to the fluoroethylfluoronium cation.

2. Transition states were located and activation energies computed for isomerization of the *trans*-1,2-difluoroethyl cation to 1,1-difluoroethyl cation, of the *cis*-1,2-difluoroethyl cation to its trans rotamer, of the chloronium cation to the 1,1-dichloroethyl cation, of the *cis*-1,2-dichloroethyl cation to the chloronium cation, and of the halogen-protonated dihaloethenes to carbon-protonated isomers.

3. Proton affinities of difluoro- and dichloroethenes were computed. The best estimates at CBS-QB3 for proton affinities (in kcal/mol) are as follows: 1,1-$C_2H_2F_2$, 171.1; *cis*-1,2-$C_2H_2F_2$, 152.9; *trans*-1,2-$C_2H_2F_2$, 151.9; 1,1-$C_2H_2Cl_2$, 176.0; *cis*-1,2-$C_2H_2Cl_2$, 159.7; *trans*-1,2-$C_2H_2Cl_2$. 162.0. Protonation of dihaloethenes at a carbon is more favorable than protonation at a halogen. Formation of the halogen-protonated dihaloethenes might possibly be observed in reactions with very powerful proton donors.

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