The Relative Stability of Some $C_4H_4F^+$ and $C_4H_4Cl^+$ Isomers investigated by *Ab Initio* Quantum Chemical Methods. Are Cyclic Halogenophenium Ions Aromatic?

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Molecules with the general formulae $C_4H_4F^+$, $C_4H_4Cl^+$, and C_4H_4O have been investigated by applying *ab initio* quantum chemical methods. The relative stability and the geometries of a number of isomers were obtained from the calculations. Of special interest are the cyclic fluorophenium and chlorophenium ions. These two structures represent *local* but not *global* minima of their respective potential energy surfaces. Populational analysis and the structural parameters show that these cyclic ions are not aromatic. These findings are discussed in connection with previous results from solution chemistry.

The existence of cyclic halogenophenium ions has been established by several studies.[1] Aryl-substituted chlorophenium, bromophenium, and iodophenium ions have all been well characterised. No evidence for the existence of stable fluorophenium ions (X = F) can be found in the literature. It is therefore of great interest to investigate whether this molecular species is likely to exist. The halogenophenium ions are isoelectronic with the five-membered aromatic ring compounds furan, pyrrole, and thiophene. For this reason the question about the degree of aromaticity of the halogenophenium ions has been raised by Olah and Yamada.[1]

It was decided to investigate these questions by applying quantum chemical methods. In order to get a broader perspective on the question of the stability of the fluorophenium and the chlorophenium ions, several other isomers (I) with the general formulae $C_4H_4F^+$ and $C_4H_4Cl^+$ were also investigated. Because of the important question about aromaticity, an analogous (electrically neutral) molecule, furan, and one of its isomers were also included in the study.

The only isomer of $C_4H_4F^+$ that has been the subject of study by *ab initio* methods before is the 1-fluorobuta-1,3-dien-2-ylium ion (2).[2] To our knowledge no $C_4H_4Cl^+$ ion has been studied so far.

Calculations and Results

The calculations were performed using programs from the program system MOLECULE,[3] using a CDC 170/835 computer. A basis set of contracted gaussian functions $(7s3p/4s)$ contracted to $(4s2p/2s)$ was used. The orbital exponents and contraction coefficients for carbon and fluorine were taken from Roos and Siegbahn.[4] Huzinaga's[5] basis scaled by a factor 1.44 $(= 1.2 \times 1.2)$ was used for hydrogen s-functions.[6]

For optimisation of geometry at the Hartree–Fock (HF) level of theory, the analytical energy gradient was calculated with the MOLFORC[7] program using Pulay's method.[8]

For one single structure (see below), the complete active space SCF (CASSCF)[9] method was used to find out whether a single determinant wave function is adequate for describing the electronic state.

The optimised geometries are (1)—(19). The energy data are given in the Table.

Relative Stabilities.—$C_4H_4F^+$ *Isomers.* It is a little surprising that the most stable structure does not correspond to the fluorophenium ion (1). *A priori* one might expect this ion to possess some degree of aromatic character, a property which should make it lower in potential energy than the open-chain

(I)

X = F, Cl, Br, I
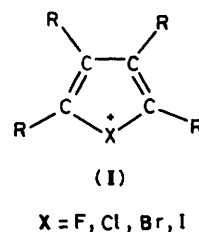
isomers. The lowest energy isomer is the 4-fluorobuta-1,3-dien-2-ylium ion (5), which is allylic. The two isomers (2) and (6) also have allylic structures. However, the position of the fluorine atom in each of these two isomers is unfavourable compared with isomer (5). The geometrical data obtained for (2) are close to those obtained by Go *et al.*[2]

The effect of twisting the methylene group in (5) by 90° is to increase the energy because the allylic stabilisation is lost as can be seen from the results for (11).

The isomer (4) is interesting. Among others Schwarz *et al.*[10] and Jemmis and von R. Schleyer[11] have discussed pyramidal cations quite extensively. However, pyramidal cations with a halogen atom on one apex have not been studied before. The results here suggest that the species is stable, but high in energy compared with the other isomers. This ion can be considered to be a complex between F^+ and cyclobutadiene, or between cyclobutadiene^{2+} and F^-. This problem of a correct description indicated that the single determinant SCF wave function might be inadequate. Therefore a complete active space SCF (CASSF) calculation was carried out.[9] The numbers of doubly occupied orbitals (the inactive space) was for each of the irreducible representations (C_{2v} symmetry): a_1:7, a_2:3, b_1:3, b_2:2. The active space consisted of five orbitals (having a total of six electrons) with the division: a_1:1, a_2:2, b_1:2, b_2:0. This gave rise to 18 configurations (determinants) in the CI part. The results show that the leading configuration (with a coefficient of 0.95) is close to the SCF solution. Furthermore the CASSCF charge on the fluorine is -0.1 compared with -0.3 from the SCF solution. These findings indicate that the original SCF wavefunction is a satisfying description of this unusual ion.

The pyramidal $C_4H_4F^+$ isomer (4) is 360 kJ mol^{-1} less stable than the planar isomer (1). This is about twice as much as the difference in stability between the pyramidal and the planar isomers in the electron-deficient systems $C_5H_5^+$, C_4H_4BH, and C_4H_4Be.[11]

All attempts to optimise the geometry of structure (3) failed. This structure rearranges to (1) without activation energy. From the calculations of (4) it was noticed that there is a

Table. Energy data

Compound	Absolute energy (hartree)	Relative energy (kJ mol^{-1})
(1)	$-252.528\ 14$	74
(2)	$-252.523\ 54$	86
(3)	no minimum, collapses to (1)	
(4)	$-252.390\ 92$	435
(5)	$-252.556\ 42$	0
(6)	$-252.538\ 20$	48
(7)	$-252.511\ 53$	118
(8)	$-252.512\ 05$	117
(9)	$-252.509\ 11$	124
(10)	$-252.522\ 28$	90
(11)	$-252.521\ 76$	91
(12)	no minimum, collapses to (14)	
(13)	$-252.390\ 04$	437
(14)	$-252.477\ 12$	208
(15)	$-612.553\ 40$	39
(16)	$-612.570\ 01$	0
(17)	$-612.525\ 14$	113
(18)	$-228.328\ 62$	0
(19)	$-228.290\ 90$	99

minimum corresponding to (3) is an indication on that the interaction between the 4 π-electrons of the hydrocarbon part and the p-electrons of the fluorine is important for stabilisation of (1).

The open-chain isomer (9) is found to be 50 kJ mol^{-1} higher in energy than the five-membered ring (1). It is therefore a considerable gain in energy upon cyclisation. The results of (8) show that there is a small gain in energy even by forming this four-membered ring from (9). Our results, however, give no indication about the height of the barrier of the cyclisations.

The protonated species (13) is very high in energy. Proton-ation of 1-fluorobut-3-en-1-yne on the fluorine atom is therefore unfavourable. This finding is in line with the results of Jorgensen and his co-workers for vinyl fluoride.[13] Vinyl fluoride prefers to have the proton on carbon. Protonation of 1-fluorobut-3-en-1-yne on C-1, leading to the ion (2), is preferred by 351 kJ mol^{-1} and on C-3, giving (14), by 229 kJ mol^{-1}. In this connection it should be noticed that the cyclic structure (14) comes from geometry optimisation of the starting structure (12)

$C_4H_4Cl^+$ *Isomers.* Of the three $C_4H_4Cl^+$ isomers, structure (16) is the one having lowest energy. This situation is analogue to that found for the $C_4H_4F^+$ ions where isomer (5) is the most stable. The chlorophenium ion (15) is the second most stable $C_4H_4Cl^+$ isomer, while (17) is higher in energy than both (15) and (16).
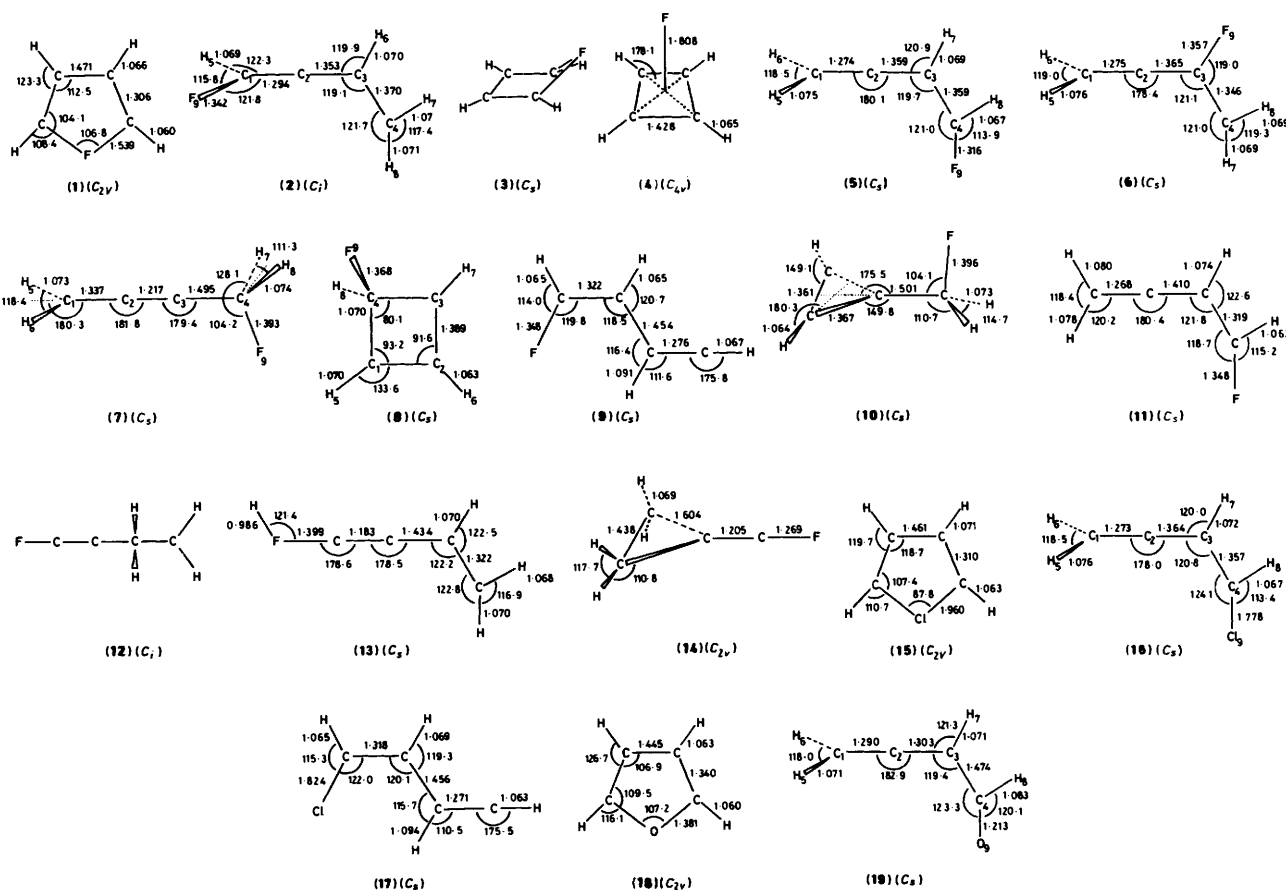
considerable barrier between (4) and (1). A comparison with the $C_5H_5^+$ system is relevant in this connection. In addition to the D_{5h} cyclopentadienyl cation (antiaromatic, 4 π-electrons), there exists a minimum for an out-of-plane C_s symmetry species similar to (3). Depending on the level of approximation, each of the two $C_5H_5^+$ isomers is the more stable.[12] The stability differences are, however, very small. The non-existence of a

C_4H_4O *Isomers.* In contrast to the two analogous positively charged systems, furan (18) is energetically more favourable than the open-chain allene type of structure (19).

Aromaticity.—A precise definition of the term aromaticity which is relevant to all aspects of aromatic chemistry is difficult to give. In the literature a great variety of definitions flourishes.
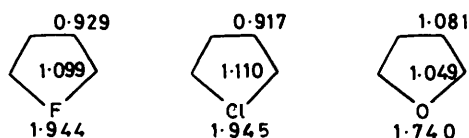
Figure. Mulliken π-atom populations of the three five-membered heterocyclic compounds

In order to have a meaningful discussion we have decided to look at the question of aromaticity from two different points of view. These two ways of approaching the problem are (a) the degree of π-electron density delocalisation and (b) structural features of the molecules.

(a) *Electron density.* Mulliken atomic population analysis is a useful tool for describing the electron distribution within a molecule.[14] This method does not provide a strict physical measure of the electron density, so the numbers obtained should not be taken too literally. The strength of the method lies in comparing populations within a series of structurally related molecules. In the Figure the π-electron populations of the fluorophenium ion (1), the chlorophenium ion (15), and (electrically neutral) furan (18) are given. The results demonstrate that the degree of delocalisation is most pronounced in furan, although it can be seen that even for this compound the degree of delocalisation is far from being complete. This would ideally require a population of 1.2 on each of the five atoms. There has been a long dispute in the chemical literature concerning the degree of aromaticity of furan.[15] Although furan both from experimental experience and numerous theoretical analyses is less aromatic than *e.g.* pyrrole, there are so many similarities between furan and benzene chemistry that use of the term aromaticity is justified.

The two cyclic halogenophenium ions only show a very modest degree of π-electron delocalisation. The best way of describing the situation in these ions is not to speak of delocalisation, but instead consider the ability of the halogen atom to act as a means of polarising the C–C double bonds. The effect of the halogen is to make the β-position more prone to nucleophilic attack than the α-position.

(b) *Structural features.* If the cyclic halogenophenium ions were perfect aromatic molecules of benzene type, then the C–C bonds should be of equal length, somewhere between that of a double bond and that of a single bond. Structures (1), (15), and (18) show the structural parameters of the three cyclic compounds. The C–C bond lengths in furan are 1.340 and 1.445 Å, respectively. In the fluorophenium ion the corresponding numbers are 1.306 and 1.471 Å, and in the chlorophenium ion 1.310 and 1.461 Å. Double bonds are calculated to have lengths of *ca.* 1.31 Å when double zeta basis sets like the one used here are employed. Therefore the C_α–C_β bonds of the cyclic halogenophenium ions have lengths which are typical of that of isolated double bonds. This again illustrates the very low degree of delocalisation in these compounds.

The protonation of furan has recently been studied by *ab initio* methods.[16] It is interesting to notice the close structural resemblance between *O*-protonated furan and the fluorophenium ion. For example, it is seen that protonation on oxygen leads to a significant shortening of the C_α–C_β bond to 1.318 Å. The effect of substituting the oxygen of furan with F^+ is almost the same as that of protonating the oxygen. Therefore it seems that the induction of a positive charge is the most important difference between these systems and furan.

Relevance to Condensed-phase Chemistry.—The following two points about the chemistry of the cyclic halogenophenium ions should be noted. (a) The structures represent local minima of the respective potential energy surfaces. This indicates that they are isolable species, at least in the gas phase. It should however be noted that there exist open-chain isomers of lower energy. From solution chemistry only substituted halogenophenium ions are known. The substituents are usually aromatic rings, which probably stabilise the halogenophenium ions (thermodynamically and kinetically) relative to the other isomers.

(b) The cyclic halogenophenium ions are not expected to possess any degree of aromatic character. The effect of the heteroatoms is to polarise the double bonds so that they are activated for nucleophilic attack in the α-position.

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