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Molecular Orbitals Studies on Two Limiting Structures of Conjugated Vinyl Cation, $C_4H_4F^+$

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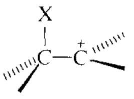
Nonempirical LCAO-MO-SCF calculations employing STO-3G minimal basis set have been carried out to examine the two limiting, open and bridged, structures of a conjugative fluorovinyl cation system and the interconversion of these two structures. The bridged ion is found to be 37.6 kcal/mole higher in energy than the open ion. Three pathways of converting the open ion to bridged ion were investigated. The pathway in which conjugation is preserved along the reaction profile gives the lowest energy barrier and depicts the bridged ion as a transition state.

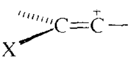
Key word: $C_4H_4F^+$

1. Introduction

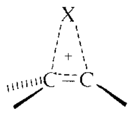
In electrophilic addition of halogens to unsaturated systems, both the open (I) and bridged (II) halonium cationic intermediates have been postulated [1].



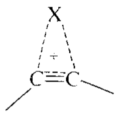
I-a



I-b



II-a



II-b

Theoretical calculations on the $C_2H_4F^+$ carbocation show that both structures are local energy minima with the open ion having a greater stability by 10 kcal/mole [2]. The $C_2H_2F^+$ vinyl cation in the bridged structure is an energy maximum (transition state), 31 kcal/mole above the energy minimum of the open structure [3]. The bridged chloronium ion is more stable than the open by 9.35 kcal/mole [4]; while the bridged $C_2H_2Cl^+$ vinyl cation is found to be an "energy maximum",

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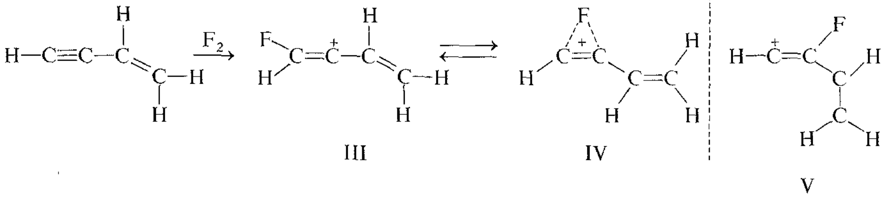
11 kcal/mole above the open structure [5]. The sulfur atom which was considered to be a much better bridging agent was also studied. The open ion $C_2H_4SH^+$ was shown to lack thermodynamic stability and spontaneously interconverts into the bridged structure [6]. On the other hand, the bridged vinyl (thiirenium) cation was 3–5 kcal/mole more stable than the open structure [7]. Therefore, based on these theoretical studies and experimental work, it is suggested that the bridging ability of halogens (and sulfur) across the single bond is greater than across a double bond, and that the halogen bridging ability increases down the periodic table.

Results of an investigation on the effect of conjugation on vinyl cations are given in this paper. The reaction studied is:


III IV V

An ethylenic unit is added to the fluoro-vinyl cation system in conjugation. Due to the size of the molecule involved, only STO-3G minimal basis sets were used for the SCF calculation. The geometries of the two limiting structures – open (III) and bridged (IV) ions – are optimized and their interconversion reaction profiles are examined. The other open structure (V) where the positive charge is not in direct conjugation with the adjacent ethylenic unit is not a realistic reaction intermediate. Furthermore, this intermediate arises from anti-Markovnikov sense of addition of the electrophile. Therefore, it is not included in the study. Intuitively, the open structure should be preferentially stabilized by delocalization of the positive charge into the allylic double bond. Such a delocalization effect due to the adjacent double bond is not expected in the bridged ion as the positive charge is localized in the cyclic three-membered ring. Therefore, in correspondence to the $C_2H_2F^+$ study, the calculations should show the bridged ion to be a transition state, and the energy difference between the open and bridged ions should be greater. This result is indeed found.

2. Method

Non-empirical LCAO-SCF-MO quantum chemical calculations were carried out on an IBM-370/165 computer using the GAUSSIAN 70 computer program [8] and internal STO-3G minimal basis sets with standard exponents are used throughout the calculations.

3. Results

Complete geometry optimization was performed on the two limiting structures. The results are summarized in Figs. 1 and 2. The conformational variation results are presented in Tables 1 and 2 and illustrated in Fig. 3.

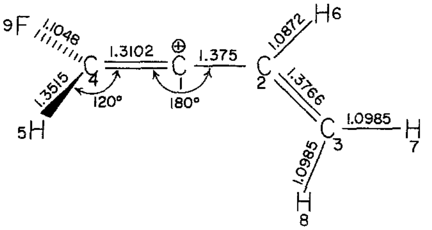


Fig. 1. Geometrical parameters for the most stable open ion (conformer *a*) (units in Å)

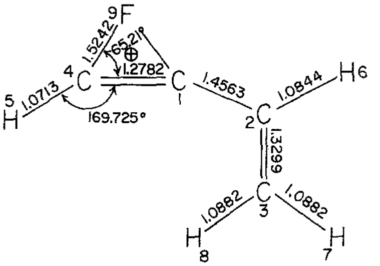


Fig. 2. Geometrical parameters for the most stable bridged ion (conformer *d*) (units in Å)

Since the cationic center and the ethylenic unit are orthogonal to each other in the most stable open ion while the bridged ion attains a planar geometry, three pathways can be envisaged for their interconversion. *The first pathway* is designed such that the F atom approaches the bridging position and at the same time, the molecule rotates giving rise to the planar species. *The second pathway* has the F atom coming in to bridge without the rotation. This gives the "twisted" bridged ion as the product, where the two double bonds are perpendicular to each other. *The third pathway* again involves no rotation, but uses the planar open ion as "reactant" and the planar bridged ion as "product". These three energy profiles were computed along an assumed reaction coordinate corresponding to nominal conversion of 25, 50, and 75 per cent, with extra points to ascertain more clearly the shapes of the profiles. The atomic coordinates are chosen on the assumption that the motion of atoms occurs in a synchronized fashion. The results are listed in Table 3 and illustrated in Fig. 4.

Table 1. Conformational study of the open ion

Conformer	$H_5C_4C_2C_3$ Dihedral angle	Total energy (a.u.)	Relative energy a.u.	Relative energy kcal/mole
a	90°	−249.61489	0.0	0.0
b	45°	−249.59790	0.01699	10.66
b′	135°	−249.59730	0.01759	11.04
c	0°	−249.56883	0.04606	28.90
c′	180°	−249.56937	0.04552	28.56

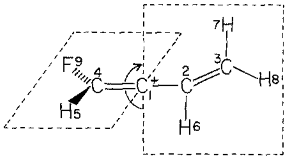
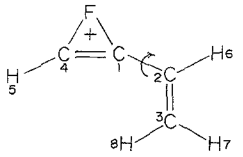


Table 2. Conformational study of the bridged ion

Conformer	$C_4C_1C_2C_3$ Dihedral angle	Total energy (a.u.)	Relative energy a.u.	Relative energy kcal/mole
d	0°	−249.55494	0.0	0.0
e	45°	−249.55458	0.00036	0.23
f	90°	−249.55369	0.00125	0.78
g	180°	−249.55439	0.00055	0.35



4. Discussion

4.1. Open Ion

The molecule can be visualized as a halogen-substituted butadiene moiety less a hydride ion creating a cationic center. The $C_4C_1C_2$ angle is found to be linear, unlike that of butadiene. Both the *cis* and *trans* isomers (about the $C_4{=}C_1$ double bond) are not as stable as the linear geometry. The orbital on C_1 can be thought of as sp-hybridized, with the p_y orbital forming a double bond with C_4 and p_z an empty orbital carrying the positive charge.

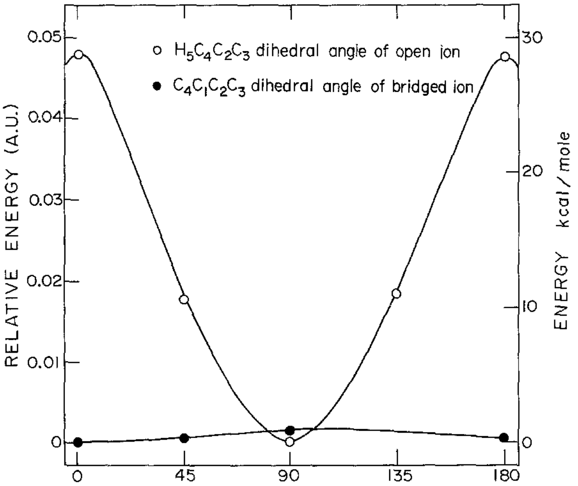


Fig. 3. Conformational variation versus the dihedral angle in the open ion and in the bridged ion

In comparing the optimized geometries for the previously studied $C_2H_2F^+$ ion and the present $C_4H_4F^+$ molecule, it is found that the molecules are not too different in geometry. The vinyl cationic double bonds are of equal lengths. The C_4–H_5 and C_4–F_9 bond lengths are a little bit longer than their counterparts in the simple ion. Presumably, the conjugated system has an extra stabilizing factor from the other double bond. As a consequence, the bonding electrons need not be held as tightly.

The result of the conformational study shows that conjugation between the empty p_z orbital and the adjacent double bond as in conformer *a* is of overriding importance in comparison to the conjugation of the two double bonds. This is expected in terms of the delocalization and therefore, stabilization, of the positive charge. Furthermore, partial delocalization of the charge, as in conformers *b* and *b′* where the dihedral angles are 45° and 135° respectively, is better than the planar conformers *c* and *c′* where the dihedral angle angles are 0° and 180°, respectively. In terms of total energy, conformers *b*'s are about 11 kcal/mole less stable and conformers *c*'s are about 29 kcal/mole less stable than the "orthogonal" arrangement.

On examining the gross orbital charges, it is interesting to note that the $2p_z$ orbitals of C_1 and C_3 have values 0.430 and 0.509 respectively in the most stable open ion. This shows that the positive charge is shared between C_1 and C_3, by conjugation through the C_2=C_3 double bond, in an allylic cationic-like fashion. In contrast, the planar structures have C_1 carrying almost the full charge. Its gross orbital charge is about 0.1 in both cases. Thus, restricting the charge on C_1 results in destabilization of the ion and the planar structures are not as stable.

Table 3

a) Pathway A: Interconversion of Conformers *a* and *f*

Percentage conversion	Nuclear repulsion (a.u.)	Total energy (a.u.)	Relative energy a.u.	kcal/mole
Open	142.51720	−249.61489	0.0	0.0
25	143.60001	−249.59956	0.01533	9.62
50	145.55618	−249.56846	0.04643	29.14
70	147.85799	−249.55031	0.06458	40.53
75	148.54738	−249.54906	0.06583	41.31
80	149.28811	−249.54923	0.06566	41.20
Bridged	150.57229	−249.55494	0.05995	37.62

b) Pathway B: Interconversion of Conformers *d* and *f*

Percentage conversion	Nuclear repulsion (a.u.)	Total energy (a.u.)	Relative energy[a] a.u.	kcal/mole
Open	142.07173	−249.56883	0.04606	28.90
25	142.79856	−249.56245	0.05244	32.91
50	144.27421	−249.54970	0.06872	40.91
70	146.15320	−249.54617	0.06772	43.12
75	146.73857	−249.54717	0.06772	42.50
80	147.37783	−249.54883	0.06606	41.45
Bridged	150.57229	−249.55494	0.05995	37.62

c) Pathway C: Interconversion of Conformers *a* and *i*

Percentage conversion	Nuclear repulsion (a.u.)	Total energy (a.u.)	Relative energy a.u.	kcal/mole
Open	142.51720	−249.61489	0.0	0.0
25	143.31127	−249.60311	0.01176	7.38
50	144.86557	−249.58032	0.03457	21.69
75	147.42178	−249.56183	0.05306	33.30
83.33	148.55207	−249.55901	0.05588	35.07
91.67	149.85745	−249.55702	0.05787	36.31
Bridged	151.36011	−249.55369	0.06120	38.40

[a] Values are compared to the most stable open ion.

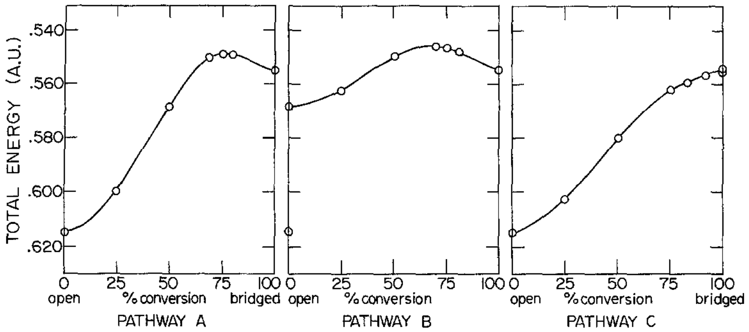


Fig. 4. Reaction profiles of three different pathways for the interconversion of open and bridged conjugated vinyl cation. **A** Conversion from open ion, conformer *a* (cf. Table 1) to bridged ion, conformer *d* (cf. Table 2). **B** Conversion from open ion, conformer *c* (cf. Table 1) to bridged ion, conformer *d* (cf. Table 2). The two points at 0% conversion show the energy difference between conformers *a* and *c*. **C** Conversion from open ion, conformer *a* (cf. Table 1) to bridged ion, conformer *f* (cf. Table 2). The two points at 100% conversion show the energy difference between conformers *d* and *f*

4.2. Bridged Ion

The initial geometrical parameters were obtained from the studies of the $C_2H_2F^+$ cation. Complete optimization reveals that the overall structure is almost the same as that of the simple cyclic ion. The addition of the ethylenic unit does not change the overall geometry at all. The bridged ion is 37.6 kcal/mole higher in energy than the most stable open ion. This value is only 6 kcal/mole higher than the simple ion difference. Since the basis sets used are different, direct comparison cannot be made.

The conformational variation of the bridged ion is also studied. Whether the double bond is in conjugation with the cyclic cationic center is of no significance. The energy differences among these conformers are less than 1 kcal/mole. In others words, there is no large barrier between the conformers. Thus, the interpretation is that there is almost free rotation about the C_1–C_2 single bond, and the double bond introduces no stabilizing effect on the bridged ion. The crucial conjugative effect in the open ion is lost in the bridged ion. The gross orbital charge picture again substantiates this point. The charge resides mainly on C_1 and C_4, and not on C_3.

4.3. Reaction Profiles

4.3.1. Pathway A

An energy maximum is found at 75% conversion to the bridged ion. The barrier is approximately 41 kcal/mole. The bridged ion is sitting in a very shallow "energy well", only about 4 kcal/mole from the transition state. From the gross orbital charge tables, the bulk of the charge is residing at C_1 and C_4. Little charge is accommodated by C_3 at the maximum. Thus the transition state of this hypothetical reaction is very much bridged ion-like.

4.3.2. Pathway B

The energy maximum is again observed at about 70% conversion. The barrier from the planar structure is about 25 kcal/mole. Together with the difference in energy between the planar and the most stable open ion – 18 kcal/mole, the total activation energy for this "reaction" is 43 kcal/mole, of the same magnitude as in pathway A. The bridged "product" is also found in a very shallow "energy well", about 5 kcal/mole from the transition state.

4.3.3. Pathway C

There is no barrier between the two species. The conversion from the open to the bridged ion is all uphill in energy. The "maximum" occurs at the bridged ion itself, implying that the bridged ion is in fact the transition state. The gross orbital charge tables show that C_3 is participating in sharing the positive charge along the reaction profile. Therefore, the positive charge is more diffused in this pathway, and the energy is kept lower than the other two.

In these three reactions pathways, A and B give the impression that the bridged ion is a local "energy minimum", while C is an "energy maximum". Pathways A and B can be regarded as unlikely in reality since the conjugative property of the open ion is lost as soon as the conversion starts. Only in pathway C, as the F atom approaches the bridging position is the positive charge dispersed among not only C_1, C_4 and F, but also C_3. As a result the total energy is kept low all along the reaction coordinate. Reactions generally proceed along the path with the lowest energy barrier. In this instance, the barrier is the bridged ion itself. Therefore, the bridged ion should be regarded as an energy maximum. At this maximum, conjugation from C_3 is no longer feasible since C_1, C_4 and F atoms form an integrated cyclic unit. Nearly free rotation about the C_1–C_2 single bond results in nearly the same total energy for all bridged ion conformers.

If this conclusion is valid, then this investigation parallels those from earlier studies on simpler molecules such as $C_2H_2F^+$, $C_2H_2Cl^+$ and others. Fluorine, commonly labelled as a poor bridging agent, has not been found to participate in any bridged structures, either in experimental work or theoretical calculations. The addition of a conjugative unit can only stabilize any open ion further and raise the energy of the bridged structures.

The results of this study are supported by experimental evidence. An open vinyl cation is postulated in the addition of chlorine to phenylacetylene in acetic acid. Equal amounts of *cis*- and *trans*-dichloro and chloro-acetoxy-styrene products are found [9]. The lack of stereospecificity in the products of bromination of phenylacetylene also points to an open or weakly bridged vinyl cation intermediate [10]. In addition, large Hammett ρ-values are obtained for these reactions. The implication is that the positive charge is developed on the α-carbon on the side chain and a substantial demand is required from electron-donating groups to stabilize this transition state of the addition.

"Minimal basis sets yield SCF energy moderately far to very far above the Hartree-Fock limit" [11]. The inadequacy of the basis set used in this study should be realized. However, energy differences are a different matter. At least, the result that the energy difference between open and bridged ion is larger in a conjugative than a simple vinyl cation system is correct. The bridged ion as an energy maximum seems reasonable also. However, the numerical results should be regarded as qualitative only. Extended basis set calculations may change the values somewhat, as have been shown by many works, especially by the study on the $C_2H_4F^+$ ion [2].

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