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Quantum Chemical Study of the Geometries and Stabilities of the Two Valence-Tautomers of $C_2H_2F^+$

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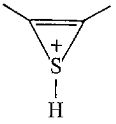
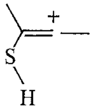
Non-empirical SCF-MO molecular wavefunctions were computed for the two limiting structures of $C_2H_2F^+$ with full geometry optimization using double-zeta quality atomic orbital basis sets. The bridged structure (fluorenium ion) was found to be an energy maximum (transition state) about 31 kcal/mole higher than the open structure (fluoro-vinyl cation). The latter, contrary to the unsubstituted vinyl cation, is slightly (4.5°) bent away from fluorine at the electron deficient centre.

Key words: $C_2H_2F^+$, valence tautomers of ~

1. Introduction

We have recently reported [1] non-empirical calculations on the relative stabilities of the bridged (1) and open (2) structures of $C_2H_2SH^+$. It was found that the two structures are of similar energies ($\Delta E = 3.9$ kcal/mole)[1] and that a fairly low energy barrier ($E_a = 12.8$ kcal/mole) separates the two minima on the potential surface. These results compare very well with the experimental findings of the solvolysis of β-thiovinyl sulphonates [2] as well as of the electrophylic addition of sulphenyl chlorides to alkynes [3].


(1)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Theoretical data on the potential surfaces related to cations of the general type $C_2H_2X^+$ (X = halogens) are totally lacking, whereas experimental data suggest that the properties of halogens, as bridging atoms, change with the atomic number decreasing from iodine to chlorine (almost no data are available for fluorine [2–4].

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[1] This value varies with the basis set. The 31*sp* basis set that was used most extensively, gave 3.9 kcal/mole, the 53*sp* basis set gave 0.8 kcal/mole, while the 77*spd* basis yielded 14.7 kcal/mole.

As part of a long-range investigation [1] on the effect of bridging atom on the relative stabilities of ions related to (1) and (2), we present in this paper the results of non-empirical MO calculations on the ion $C_2H_2F^+$ with full geometry optimization.

2. Method

The non-empirical SCF–MO calculations were carried out on a CDC 6600 computer using a modified [5] POLYATOM II system [6]. The MO basis was obtained by linear transformation of an AO basis, which in turn was generated from a set of primitive Gaussian type functions (GTF) by contraction.

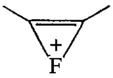
Two double zeta quality basis sets were used throughout this paper. First of all, geometry optimization was performed using Basch *et al.*'s [7] basis set for H, C, and F and in the latter part of the work Dunning's basis set [8] was used in comparison with the previous calculations. The details of these two 34*sp* basis sets are summarized in Table 1.

Table 1. Contracted Gaussian basis sets used in calculations on the $C_2H_2F^+$ species

Chemical	Basis Size		Basis Type		Contraction Scheme	Ref.
system	prim.	contr.	prim.	contr.		
			First 34*sp*			
F	25	10	$(10^S, 5^P)$	$[4^S, 2^P]$	(1 2 3 4) (5 6 7) (8 9) (10)/(11 12 13 14) (15)	[7a]
C	25	10	$(10^S, 5^P)$	$[4^S, 2^P]$	(1 2 3 4) (5 6 7) (8 9) (10)/(11 12 13 14) (15)	[7b]
H	4	2	(4^S)	$[2^S]$	(1 2 3) (4)	[7b]
C_2H_2F	83	34				
			Second 34*sp*			
F	24	10	$(9^S, 5^P)$	$[4^S, 2^P]$	(1 2 3 4 5 6) (7) (8) (9)/(10 11 12 13) (14)	[8]
C	24	10	$(9^S, 5^P)$	$[4_S, 2_P]$	(1 2 3 4 5 6) (7) (8) (9)/(10 11 12 13) (14)	[8]
H	4	2	(4^S)	$[2^S]$	(1 2 3) (4)	
C_2H_2F	80	34				

3. Results

Full geometry optimization was performed on the two limiting structures (3), (4) using Basch *et al.*'s basis set. The results are summarized in Tables 2 and 3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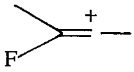

(4)

and graphically illustrated in Figs. 1 and 2. The coordinates associated with the optimized geometries are shown in Table 4.

The SCF calculations on the optimized geometries of (3) and (4) were repeated using Dunning's set and the results are shown in comparison in Table 5.

Table 2. Variation of total energy with molecular geometry as computed with Basch *et al.*, basis set (entries 1–22) and Dunning's basis set (entries 23–27) for fluorenium ion

No.	Bond lengths (Å)			Angles (degrees)		Total energy
	C–C	C–F	C–H	FCC	CCH	(Hartree)
1	1.32264	1.44700	1.14220	62.80	160.18	−175.7474488
2	1.12264			67.17		−175.7118351
3	1.22264			65.01		−175.7519239
4	1.42264			60.55		−175.7165566
5	1.25842	1.44700	1.14220	64.22	160.18	−175.7543196
6		1.34700		62.15		—175.7039102
7		1.54700		66.00		—175.7768762
8		1.69700		68.23		—175.7802487
9		1.84700		70.08		—175.7645121
10	1.25842	1.63567	1.14220	67.38	160.18	—175.7820713
11			0.94220			—175.7569098
12			1.04220			—175.7876897
13			1.24220			—175.7560805
14	1.25842	1.63567	1.07128	67.38	160.18	—175.7889440
15					155.18	—175.7822500
16					165.18	—175.7933243
17					175.18	—175.7950251
18					180.00	—175.7924026
19	1.25842	1.63567	1.07128	67.38	171.98	—175.7955184
20	1.15842			69.26		—175.7710897
21	1.35842			65.46		—175.7833281
22	1.27513	1.63567	1.07128	67.06	171.98	—175.7955282
23	1.27513	1.63567	1.07128	67.06	171.98	—175.8085569
24		1.53567		65.47		—175.8012500
25		1.64934		67.26		—175.8085421
26		1.73567		68.45		—175.8043867
27	1.27513	1.64151	1.07128	67.15	171.98	—175.8085756

The energy profile associated with the interconversion of (3) and (4) was computed with Dunning's basis set along an assumed reaction coordinate corresponding to the nominal 25, 50, 75, and 90% conversion. The atomic coordinates were chosen with the assumption that the motion of all the atoms are occurring in a synchronized fashion. These results are summarized in Table 6 and illustrated in Fig. 3.

4. Discussion

One point that emerges from these calculations is related to molecular geometry. The fluorovinyl cation (open structure) has a normal C–F bond length since in the optimized geometry it is computed to be 1.323 Å which compares favourably with experimental C–F bond length (1.32 Å) of $FHC{=}CH_2$. On the other hand the C–F bond length in the fluorenium ion (cyclic structure) is anomalously long (1.642 Å) which suggests a relatively weak bonding.

Table 3. Variation of total energy with molecular geometry as computed with Basch *et al.*, basis set (eneries 1–27) and Dunning's basis set (entry 28) for *β*-fluorovinyl cation

No	Bond lengths (Å)				Bond angles (deg.)			Total energy
	C_1–C_2	C_1–F	C_1–H_1	C_2–H_2	FC_1C_2	$H_1C_1C_2$	$C_1C_2H_2$	(Hartree)
1	1.34980	1.32500	1.14245	1.14733	127.87	116.68	180.00	—175.8361627
2	1.24980							—175.8344432
3	1.44980							—175.8173178
4	1.30816	1.32500	1.14245	1.14733	127.87	116.68	180.00	—175.8386428
5		1.22500						—175.8281597
6		1.33263						—175.8385629
7		1.42500						—175.8309359
8	1.30816	1.32302	1.14245	1.14733	127.87	116.68	180.00	—175.8386469
9					117.87			—175.8365790
10					122.87			—175.8387953
11					132.87			—175.8361512
12	1.30816	1.32302	1.14245	1.14733	125.06	116.68	180.00	—175.8390196
13			0.94245					—175.8231190
14			1.04245					—175.8400695
15			1.24245					—175.8279030
16	1.30816	1.32302	1.08287	1.14733	125.06	116.68	180.00	—175.8412747
17						111.68		—175.8396892
18						121.68		—175.8408240
19	1.30816	1.32302	1.07287	1.14733	125.06	116.07	180.00	—175.8413550
20				0.94733				—175.8294868
21				1.04733				—175.8442805
22				1.24733				—175.8285353
23	1.30816	1.32302	1.08287	1.07518	125.06	118.07	180.00	—175.8448388
24							175.00	—175.8435937
25							185.00	—175.8452015
26							190.50	—175.8445751
27	1.30816	1.32302	1.07287	1.07518	125.06	118.07	164.55	—175.8452050
28	1.30816	1.32302	1.08287	1.07518	125.06	118.07	184.55	—175.8579897

Table 4. Atomic coordinates (Bohr a.u.) for the optimized geometries of fluorenium ion and *β*-fluorovinyl cation

Fluorenium Ion

	X	*Y*	*Z*
Fluorine	0.0	0.0	−2.858515
Carbon 1	−1.204837	0.0	0.0
Carbon 2	1.204837	0.0	0.0
Hydrogen 1	−3.209481	0.0	0.282615
Hydrogen 2	3.209481	0.0	0.282615

β-Fluorovinyl Cation

	X	*Y*	*Z*
Fluorine	−1.486125	0.0	−2.046567
Carbon 1	0.0	0.0	0.0
Carbon 2	2.472102	0.0	0.0
Hydrogen 1	−0.963075	0.0	1.805558
Hydrogen 2	4.497519	0.0	0.161184

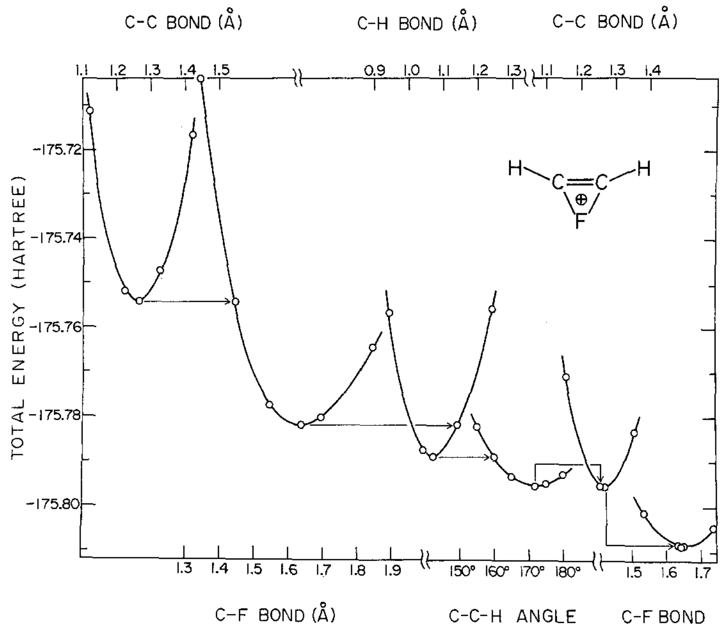


Fig. 1. Geometry optimization of fluorovinyl cation (cf. Table 2 for details on geometry and basis sets)

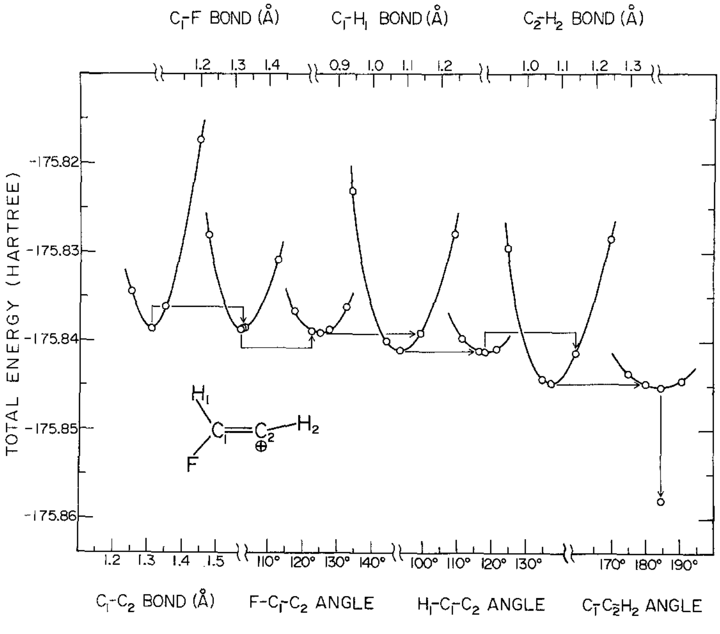


Fig. 2. Geometry optimization of fluorenium ion (cf. Table 3 for details on geometry and basis sets)

Table 5. Computed orbital and total energies of fluorenium ion and β-fluorovinyl cation

No.	Type	Symmetry	Dunning's set		Bush *et al.* set	
		Fluorenium	Fluorovinyl	Fluorenium	Fluorovinyl	Fluorenium
1	1σ	a_1	− 26.60065	− 26.62884	− 26.59431	− 26.62330
2	2σ	a_1	− 11.68785	− 11.69165	− 11.68742	− 11.69122
3	3σ	b_1	− 11.68112	− 11.68929	− 11.68111	− 11.68887
4	4σ	a_1	− 1.92543	− 1.90560	− 1.92589	− 1.90907
5	5σ	a_1	− 1.39658	− 1.40388	− 1.39662	− 1.40388
6	6σ	b_1	− 1.12320	− 1.13353	− 1.12322	− 1.13420
7	7σ	a_1	− 1.04542	− 1.03751	− 1.04518	− 1.03747
8	8σ	b_1	− 1.00800	− 0.93885	− 1.00785	− 0.93969
9	1π	b_2	− 0.97270	− 0.98392	− 0.97256	− 0.98573
10	9σ	a_1	− 0.88212	− 0.90726	− 0.88199	− 0.90831
11	2π	b_2	− 0.73473	− 0.74552	− 0.73438	− 0.74468
12	$10\sigma^*$	a_1	− 0.28133	− 0.21064	− 0.28085	− 0.20836
13	$3\pi^*$	a_2	− 0.14513	− 0.16888	− 0.14483	− 0.16861
14	$11\sigma^*$	b_1	− 0.01461	− 0.08581	− 0.01474	− 0.08453
15	$12\sigma^*$	b_1	0.06428	− 0.02585	0.06336	− 0.02651
16	$13\sigma^*$	a_1	0.08801	0.06310	0.08813	0.06335
17	$14\sigma^*$	b_1	0.14457	0.11656	0.14232	0.11602
Total energy (Hartree)			− 175.85799	− 175.80858	− 175.84521	− 175.79553
ΔE (kcal/mole)			31.01		31.17	

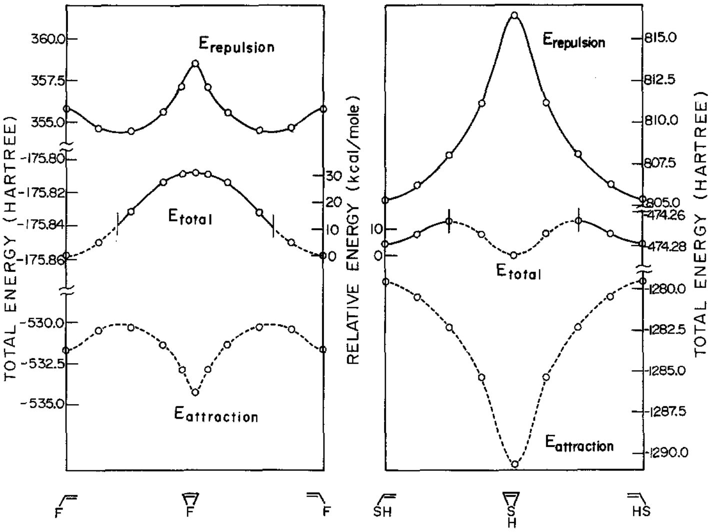
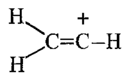


Fig. 3. Reaction profiles for the interconversion of fluorenium ion-β-fluorovinyl cation and thiirenium ion-β-thiovinyl cation

Table 6. Energy components of the various $C_2H_2F^+$ species as computed with the Dunning's basis set

	0%	25%	50%	75%	90%	100%
	Vinyl cation	$\frac{3}{4}$ Vinyl + $\frac{1}{4}$ Fluor.	$\frac{1}{2}$ Vinyl + $\frac{1}{2}$ Fluor.	$\frac{1}{4}$ Vinyl + $\frac{3}{4}$ Fluor.	$\frac{1}{10}$ Vinyl + $\frac{9}{10}$ Fluor.	Fluorenium
V_{nn}	61.0815035	60.4727440	60.4191272	61.0381922	61.8221472	62.5597416
T	175.9051121	175.7928376	175.7081417	175.6542753	175.6727464	175.7322074
V_{ee}	118.8238125	118.3943999	118.3936230	118.9161121	119.5860083	120.2366852
V_{ne}	−531.6684179	−530.5105721	−530.3530380	−531.4227334	−532.8900102	−534.3372098
E_{nuclear}	61.0815035	60.4727440	60.4191272	61.0381922	61.8221472	62.5597416
$E_{\text{electronic}}$	−236.9394932	−236.3233346	−236.2512733	−236.8523460	−237.6312555	−238.3683172
$E_{\text{repulsion}}$	355.8104281	354.6599815	354.5208919	355.6085796	357.0809019	358.5286342
$E_{\text{attraction}}$	−531.6684179	−530.5105721	−530.3530380	−531.4227334	−532.8900102	−534.3372098
E_{total}	−175.8579897	−175.8505906	−175.8321461	−175.8141538	−175.8091083	−175.8085756
Virial Coeff.	− 1.9997321	− 2.0003285	− 2.0007057	− 2.0009102	− 2.0007762	− 2.0004345
ΔE(kcal/mole)	0.0	4.64	16.22	27.51	30.67	31.01

Another interesting feature is associated with the non-linear geometry of the electron deficient centre. This observation is particularly interesting when compared with the related systems as shown below.



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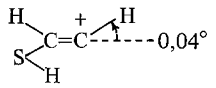

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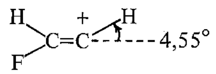
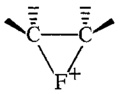


(7)

However, the point of major interest lies in the relative stabilities of the cyclic and open structures. As reported in the previous section the bridged structure appears to be at an energy maximum some 30 kcal/mole above the open structure.

This may be compared with the previous calculations on the saturated analogues (8) and (9) as reported by Clark [9] and Hehre [10]. Although these authors did not state explicitely they seemed to assume that the two limiting structures are thermodynamically stable intermediates, i.e. both points correspond to energy minima on the conformational energy surface.



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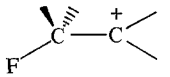

(9)

The former author found, using a 22*sp* basis set, that $\Delta E = E\,(\text{cyclic}) - E\,(\text{open})$ is equal to -3.58 kcal/mole. The latter author found, using a 19*sp* (STO-3G) basis set, that $\Delta E = -19.66$ kcal/mole while the more extensive, (split valence shell) 23*sp* (4-31 G), basis set gave $\Delta E = +11.49$ kcal/mole. These results clearly indicate that the relative stability depends on the quality of the basis set. However, the basis set used in this work, is extensive enough, (double zeta quality corresponding to 34*sp*) to allow us to be confident concerning the reliability of the computed results.

The large instability of the fluorenium ion (3) is possibly related to the greater steric constrain when the carbons are sp^2 hybridized. However, electronic factors may play an important role since the fluorenium ion, but not the saturated analogue (8), could suffer of non-bonding electron repulsion between the electrons of the carbon-carbon double bond and lone electron pairs of fluorine.

In this respect it is worth to compare this result with those recently reported for $C_2H_2SH^+$ ion with similar basis set. It was found that the thiirenium ion (1) and the thiovinyl cation (2) are of comparable stability (see Fig. 3). Quite clearly the longer C–S bond with respect to the C–F bond partially relases the steric strain. Moreover the pyramidal structure at sulfur in (1) will reduce the electron-electron repulsion associated with the sulfur lone pair and the π-electron pair. The detailed analysis of electron-electron repulsion can quantitatively be evaluated in terms of localized molecular orbitals which is now under investigation.

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