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An *ab initio* Molecular Orbital Study of the C_2F_2 Species: The Difluorovinylidene → Difluoroacetylene Rearrangement

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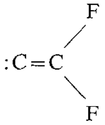
An *ab initio* MO study, using medium size Gaussian basis sets has been made of vinylidene carbene, acetylene and the isomeric cyclic intermediate presumed to represent the transition state of their interconversion reaction, along with their perfluorinated analogs. The total energies of the acetylenes are lower than the vinylidenes and the estimated activation energy of their interconversion is considerably higher for the fluorinated molecules. The results are in line with experimental observations.

The difluorovinylidene carbene, $F_2C=C:$, has been shown to be the principal primary product of the triplet mercury photosensitization of trifluoroethylene [1]. Thermodynamically, it is likely to be less stable than its structural isomer difluoroacetylene, nonetheless its unimolecular isomerization to acetylene is slow at room temperature and consequently the carbene can be readily scavenged. It reacts with the C–H bonds of paraffins to give a 1,1-difluoro-1-alkene and with the π-bonds of olefins to give a difluoromethylene cyclopropane or its secondary fragmentation or rearrangement product.

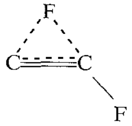
In order to gain an understanding of the cause of the stability of difluorovinylidene and to elucidate details of the hypothetical reaction path leading to acetylene formation, non-empirical MO calculations were performed on three C_2F_2 species including the vinylidene (I) and acetylene (II) structures and the cyclic intermediate (III) assumed to be the transition state of the expected isomerization reaction:



(I)

$F-C\equiv C-F$

(II)



(III)

Table 1. Computed energy values for the three C_2F_2 species

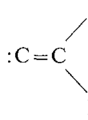
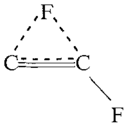
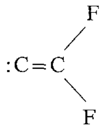
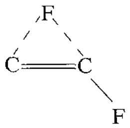
Energy (hartree)			$F-C \equiv C-F$
Electronic attraction	−374.269680	−279.957668	−365.535053
Nuclear repulsion	+102.667484	+108.572154	+ 93.874888
Total molecular	−271.602196	−271.385514	−271.660165
Relative energy (kcal/mole)	0.00	$E_a = +135.96$	$\Delta E = -36.37$

Table 2. Computed molecular orbital[a] energy values (in Hartree a.u.) for the C_2F_2 species

Species							$F-C \equiv C-F$	
MO	$a_1(\sigma)$	$b_1(\sigma)$	$b_2(\pi)$	$a_2(\pi)$	σ	π	σ	π_x and π_y
1	−26.4752	−26.4751	−0.7426	−0.6341	−26.6128	−0.8579	−26.5007	−0.7064
2	−11.4790	− 1.7037	−0.3781	+3.7010	−26.5074	−0.6919	−26.5001	−0.6784
3	−11.3391	− 0.7588	+0.2083		−11.4684	−0.3236	−11.4153	−0.3930
4	− 1.7674	− 0.6145	+1.5526		−11.3359	+0.1866	−11.4136	+0.2746
5	− 1.1030	+ 0.0467			− 1.9665	+1.5592	− 1.7245	+1.5680
6	− 0.8990	+ 0.5879			− 1.7352		− 1.7224	
7	− 0.6535				− 1.0956		− 1.1081	
8	− 0.4411				− 0.9453		− 0.8100	
9	+ 0.4470				− 0.8071		− 0.7507	
10	+ 0.6689				− 0.6999		+ 0.2591	
11					− 0.6120		+ 0.5263	
12					− 0.3962		+ 1.0204	
13					+ 0.2252			
14					+ 0.3989			

[a] The broken line indicates the occupancy limit.

Because of the relatively large size of the molecule only a "medium" Gaussian basis set could be used to expand the molecular orbitals. It consisted of five *s* and two *p* Gaussian type functions [2] (GTF), for both carbon and fluorine, resulting in a total of 44 GTF. This basis set has been used successfully by Clark [3] for studying fluoro hydrocarbons and related molecules and it should be suitable for the present case as well. The calculations were carried out on an IBM 7094-II computer using the POLYATOM system [4].

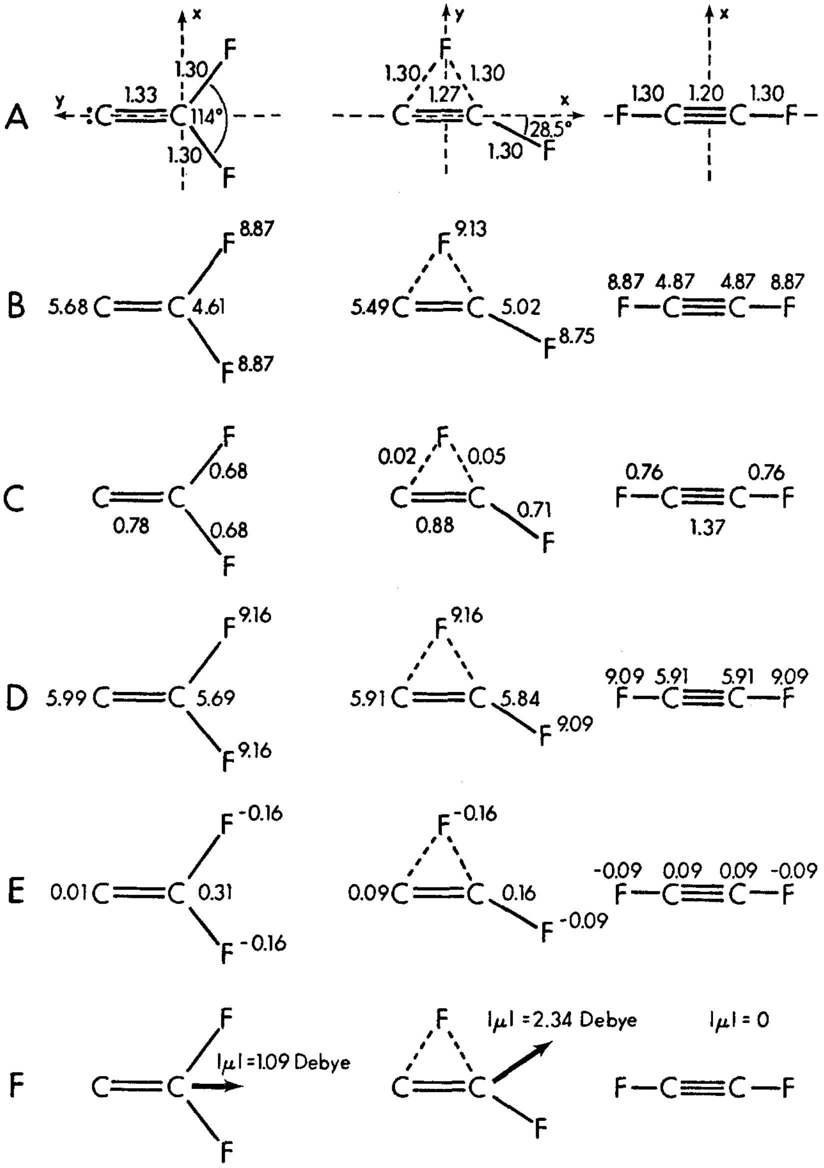
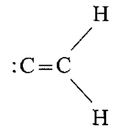
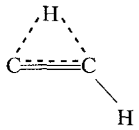


Fig. 1. Geometries and electron distributions for C_2F_2 species. A Bond length (Å) and bond angles. B Net atomic electron populations. C Overlap electron populations. D Gross atomic electron populations. E Net atomic charges. F Dipole moments

The electronic attraction, nuclear repulsion as well as the total energy values computed for the species I to III are summarized in Table 1. The results show that the carbene is indeed less stable than the acetylene as anticipated on the grounds that the former contains one less π bond and the same number of σ bonds as the latter. The energy value computed for the transition state III of the hypothetical unimolecular isomerization is prohibitively large.

Table 3. Computed energy values for the three C_2H_2 species

Energy (hartree)			$H-C\equiv C-H$
Electronic attraction	-100.19584	-102.58358	-101.49828
Nuclear repulsion	23.59257	26.10265	24.83465
Total molecular	-76.60327	-76.48093	-76.66363
Relative energy (kcal/mole)	0.00	$E_a = +76.79$	$\Delta E = -37.89$

In addition to total energies the orbital energies, given in Table 2, the dipole moments and electron populations, presented in Fig. 1, were also calculated. The latter data clearly indicate that the properties of III lie intermediate between I and II. However, the binding of the bridged fluorine to the two carbon atoms, as measured by the overlap populations, is diminishingly small.

For comparison the corresponding calculations were also carried out on the unfluorinated species, vinylidene, acetylene, and the cyclic intermediate representing the transition state for their interconversion. In order to ensure that the two sets of calculations are directly comparable their quality must be commensurate and this requires the use of basis sets of approximately identical sizes.

The basis set used for the C_2F_2 species consisted of 5^s, 2^p GTF on both C and F, which resulted in a total of 44 basis functions. On going from C_2F_2 to C_2H_2 the number of carbon atom orbitals was increased because for the description of hydrogen atoms one normally needs fewer orbitals than for the description of fluorine atoms. In this set of calculations the carbon atoms were represented by 7^s, 3^p GTF while the hydrogen atoms were described [2] by a set of 3^s GTF. This yielded a total of 38 GTF in the basis set, which is comparable to the previous basis set size of 44.

The results, computed for the C_2H_2 species, are given in Table 3. It is seen that the enthalpy changes of the two reactions are very similar but the activation energy associated with the rearrangement of the fluoro compound is nearly twice the value of the unfluorinated molecule. This is in line with expectation since H-atom migration is known to be more facile than F-atom migration while the enthalpy change would be expected to be affected only slightly [1].

Since no literature report exists on the detection or trapping of vinylidene it is quite probable that the isomerization to acetylene is very rapid and features a very low activation energy. Even if we take the activation energy as being zero the estimated value of the activation energy for the fluoro analog is still about 59 kcal/mole, which would adequately explain the reluctance of difluorovinylidene to isomerize.

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