

The Photoelectron Spectrum of 1,1-Difluoroallene. On π Electron Donation and Withdrawal by Fluorine

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Abstract: The photoelectron spectrum and ab initio 4-31G calculations on 1,1-difluoroallene provide unique data on the donor and acceptor properties of fluorine operating on the mutually perpendicular π orbitals in a single molecule. The spectrum has been assigned by correlative analyses, by analysis of the vibrational structure in the first two bands, and by comparison with ab initio 4-31G calculations on allene, 1,1-difluoroallene, and tetrafluoroallene. Because fluorines have only a minor influence on the π and π^* orbitals of the double bond to which they are directly attached, but have a profound energy lowering effect on the orbitals with which they "negatively hyperconjugate", 1,1-difluoroallene has one electron-rich and one electron-deficient double bond, and should provide a valuable probe of electronic characteristics and mechanisms of cycloaddition reactions.

Introduction

1,1-Difluoroallene is a useful addend for the study of cycloaddition mechanisms. Concerted [4 + 2] reactions of electron-rich species occur at the nonfluorinated double bond of difluoroallene, while nonconcerted [2 + 2] cycloadditions occur at the fluorinated double bond.² In order to elucidate more fully the electronic structure of this species, and to gain greater insight into the electronic mechanism of the "perfluoro effect",³ we have carried out photoelectron spectral studies and ab initio calculations on this molecule.

In 1,1-difluoroallene, symmetry factors cause only one π orbital to be influenced by the conjugative electron-donating properties of the fluorine lone pairs, and only the other π orbital to be influenced by the "negative hyperconjugative" electron-accepting properties of the low-lying $\sigma^*_{CF_2}$ orbital (Figure 1). Thus, the C_1C_2 π and π^* orbitals can interact with fluorine lone pairs, while the orthogonal C_2C_3 π and π^* orbitals can interact with the σ_{CF_2} and $\sigma^*_{CF_2}$ orbitals, and only weakly with an antisymmetric combination of fluorine lone pairs. The former interaction will destabilize the C_1C_2 π and π^* orbitals, while the latter will stabilize the C_2C_3 π and π^* orbitals. In addition, polarization of σ electrons, commonly called inductive electron withdrawal, by the electronegative fluorines will lead to a stabilization of both C_1C_2 and C_2C_3 π and π^* orbitals.

Empirically, the π -donating and σ -withdrawing influence of fluorine upon π orbitals appear to cancel. Thus, when the photoelectron spectra of planar unsaturated hydrocarbons and those of the perfluorinated analogues are compared, the perfluoro compound generally has very slightly increased π , but much higher σ , ionization potentials than the hydrocarbon. This phenomenon has been named the "perfluoro effect" by Brundle et al.^{3a} The large increase of the σ ionization potentials has been interpreted as the result of strong mixing of the σ orbitals of the carbon skeleton with orbitals of the electronegative fluorine atoms, while the small change in π ionization potentials is believed to result from near cancellation of π donation and σ withdrawal by fluorine substituents.³ In spite of the apparently satisfactory nature of such qualitative descriptions, the fluorine substituent effect remains of theoretical interest.³⁻⁵ The photoelectron spectrum of 1,1-difluoroallene, reported and analyzed here, reveals certain quantitative aspects of the influence of fluorine upon π orbital energies.

The Photoelectron Spectrum and Ionization Potential Assignments

The photoelectron spectrum of 1,1-difluoroallene^{6,7} is shown in Figure 2, and the ionization potentials and vibrational splittings are given in Table I. The first two bands are rich in

vibrational structure with adiabatic ionization potentials of 9.79 and 11.26 eV, respectively. The vertical ionization potentials cannot be estimated simply in such an asymmetric band, but the weighted average position has been estimated by rough integration to be 10.1 eV for the first band and 11.6 eV for the second. By comparison, allene^{8,9} and tetrafluoroallene⁹ have adiabatic IPs of 9.69 (vertical Jahn-Teller split ionization bands of 10.1 and 10.6 eV) and 10.88 eV (vertical IP of 11.24 eV), respectively. Figure 3 relates the adiabatic IPs of 1,1-difluoroallene and various related molecules. Owing to uncertainties in vertical IPs for some of these compounds, the adiabatic IPs have been compared. The first IP of difluoroallene is slightly decreased relative to that of allene, while the second IP is considerably increased, and is somewhat higher than that of tetrafluoroallene. Evidence detailed below leads to assignment of the first ionization potential to ionization from the π MO of the difluorinated double bond of difluoroallene.

As is known for a variety of planar hydrocarbons, π IPs are only slightly affected by perfluorination.³ Thus, the vertical IP of tetrafluoroethylene (10.58 eV) is very close to that of ethylene (10.51 eV).^{3a} However, the substitution of fluorine for hydrogen in planar hydrocarbons does not always lead to a negligible effect. Thus, fluoroethylene and 1,1-difluoroethylene have vertical π IPs of 10.58 and 10.72 eV, respectively, the latter significantly higher than that of ethylene. On the other hand, the adiabatic IP of difluoroethylene is somewhat lower than that of ethylene (Figure 3). Nevertheless, the influence of substitution of fluorine for hydrogen directly on a π system is invariably quite small, so that there is no doubt that the first IP of 1,1-difluoroallene arises from the difluorinated double bond.

Allylic substitution of fluorine leads to a large increase of π ionization potentials. Thus, 3,3,3-trifluoropropene has a first IP of 10.9 eV,¹⁰ 0.4 eV higher than that of ethylene. The monofluoro compound, 3-fluoropropene, has an IP of 10.56 eV,¹¹ essentially identical with that of ethylene, but considerably higher than that of propene (IP (vert) = 9.91, IP (ad) = 9.55 eV).¹² Thus, allylic fluorine strongly destabilizes the radical cations, or in Koopmans' theorem language,¹³ fluorine strongly stabilizes the π orbitals. The effect can be rationalized simply as the result both of elimination of the hyperconjugative influence of hydrogen (via the π_{CH_2} orbitals) and stabilization of the π orbital due to mixing of the acceptor $\pi^*_{CF_2}$ orbital with the π orbital. In terms of the radical cation, the fluorine is destabilizing because the positive charge is delocalized onto the very electronegative fluorines. In 1,1-difluoroallene, the fluorines are ideally situated to "negatively hyperconjugate"

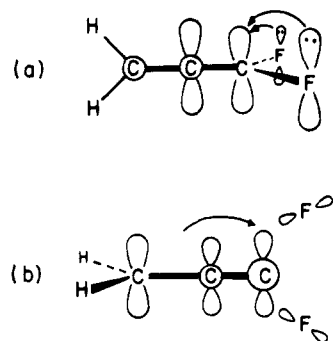


Figure 1. Schematic representation of (a) π conjugation between the lone pairs of fluorine and the π and π^* orbitals of the substituted double bond, and (b) π conjugation between the π and π^* orbitals of the unsubstituted double bond and the σ_{CF_2} and $\sigma^*_{CF_2}$ orbitals.

Table I. Ionization Potentials (± 0.03 eV) and Vibrational Spacings (± 30 cm^{-1}) in the Radical Cations of 1,1-Difluoroallene^b

band	IP	radical cation	ground state (IR) ¹⁵
1	9.79 (ad)	1832	3038 ν_{12}
	10.1 (vert)	1360	3012 ν_1
		897	2026 ν_2
2	11.26 (ad)	1215	1474 ν_3
	11.6 (vert)	980	1326 ν_4
		710	1237 ν_8
		410	925 ν_9
3	15.84 (vert)		799 ν_5
			597 ν_{10}
			528 ν_{14}
			499 ν_6
4	17.06 (vert)		167 ^a ν_{15}
			151 ^a ν_{11}

^a Observed only in Raman. ^b The ground-state fundamentals from Durig et al.¹⁵ are given for comparison.

with the remote double bond, and the increase of the IP arising from the C_2C_3 π MO is very high.

The IPs of tetrafluorobutatriene provide an interesting comparison to the IPs of 1,1-difluoroallene. In the former molecule, the IPs due to the MOs of the terminal double bonds are essentially unchanged, while the IP due to the central π MO, which experiences only hyperconjugative interaction with the terminal fluorines, is raised by about 2 eV,¹⁴ approximately twice that of the C_2C_3 π MO in 1,1-difluoroallene.

The rich vibrational structure in the first and second bands (Figures 4 and 5) provides further evidence for the nature of the first two ionizations. The measured vibrational spacings are listed in Table I. The first band has two strong vibrational progressions with splittings of 1360 and 1832 cm^{-1} and a weak progression with a splitting of 897 cm^{-1} . The second band has a strong progression of 1215 cm^{-1} and three weak progressions of 410, 712, and 983 cm^{-1} . Durig and co-workers have recently analyzed the Raman and infrared spectra of 1,1-difluoroallene;¹⁵ the observed fundamentals in the IR are recorded in Table I.

The prominent 1832- cm^{-1} spacing in the first band of the PE spectrum can be assigned to the antisymmetric CCC stretching frequency, which is 2026 cm^{-1} in the IR. It is notable that this strong 1832- cm^{-1} progression is present only in the first band of difluoroallene, and no similar spacing is observed in the PE spectrum of tetrafluoroallene, which has a single observable vibrational spacing of about 1450 cm^{-1} , or in that of allene, which has no resolved vibrational structure in the π bands.⁸ Upon fluorination, the antisymmetric CCC ground state vibrational frequency increases. The values are 1957 cm^{-1} for allene, 2026 cm^{-1} for 1,1-difluoroallene, and

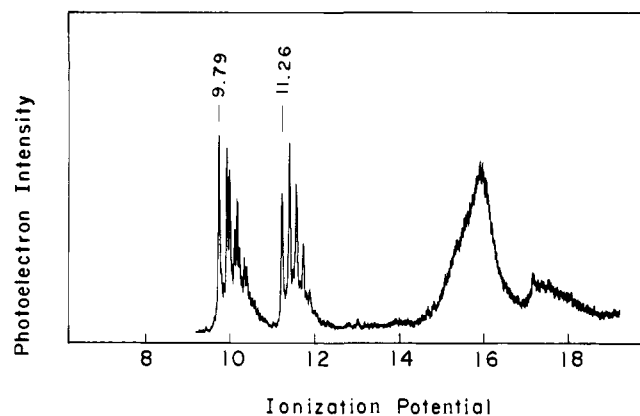


Figure 2. Photoelectron spectrum of 1,1-difluoroallene.

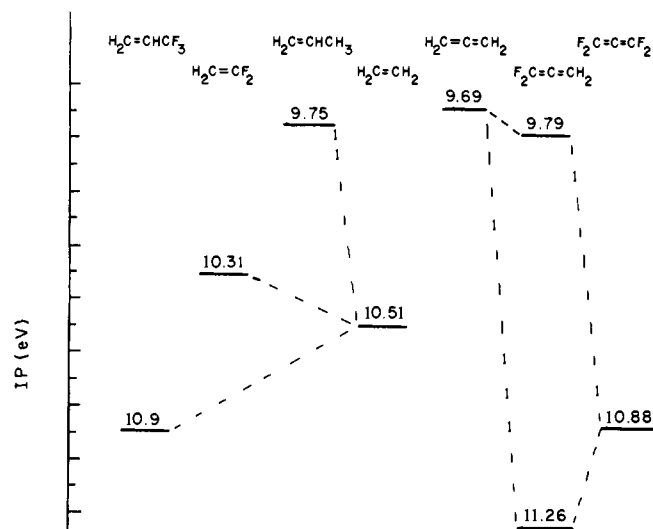


Figure 3. Comparison of adiabatic IPs of 1,1-difluoroallene and related molecules.

2050 cm^{-1} for tetrafluoroallene. As shown later, the highest π orbital in 1,1-difluoroallene is C_1C_2 bonding and C_2C_3 antibonding. It is quite plausible that the antisymmetric stretching vibration is heavily C_1C_2 stretching in character, and that this vibration is strongly excited upon removal of an electron from the orbital described above.

The symmetric CCC stretch of allene (1076 cm^{-1}) is strongly coupled with CF_2 scissoring and stretching vibrations in the fluoroallenes.¹⁵ The 1360- and 897- cm^{-1} spacings in the first band correspond rather well to the 1326- and 799- cm^{-1} frequencies in the ground state, which Durig et al. have analyzed as 24 and 43% CCC symmetric stretching, respectively.¹⁵ The second band also has spacings (1215 and 712 cm^{-1}) which are quite close to the 1326- and 799- cm^{-1} frequencies in the ground state.

As shown in Figure 4, there are several very weak peaks leading the first strong peak which has been assigned as the adiabatic IP. The first of these is 950 ± 30 cm^{-1} lower in energy than the first strong band. We feel that this weak band and the unassigned weak bands within the main vibrational envelope are hot bands, arising from ionizations observed from low concentrations of vibrationally excited ground-state species. The spacing between the first "hot band" and the adiabatic IP is approximately that of the 925- cm^{-1} band observed in the IR spectrum.¹⁵

In addition to the π bands at low ionization energies, the photoelectron spectrum of 1,1-difluoroallene has two higher ionization energy bands with maxima of 15.84 and 17.06 eV.

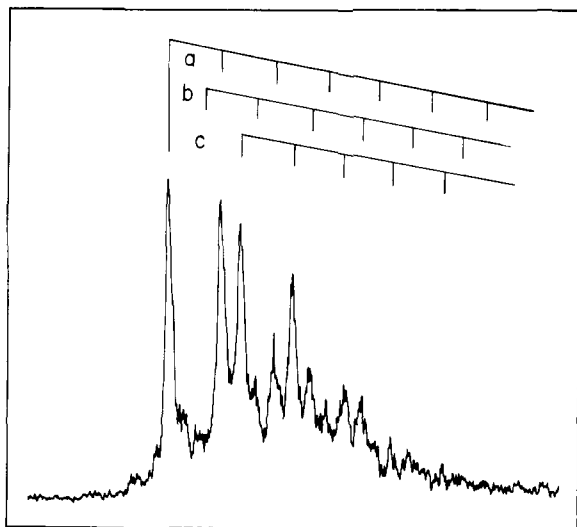


Figure 4. First band and vibrational analysis of the photoelectron spectrum of 1,1-difluoroallene.

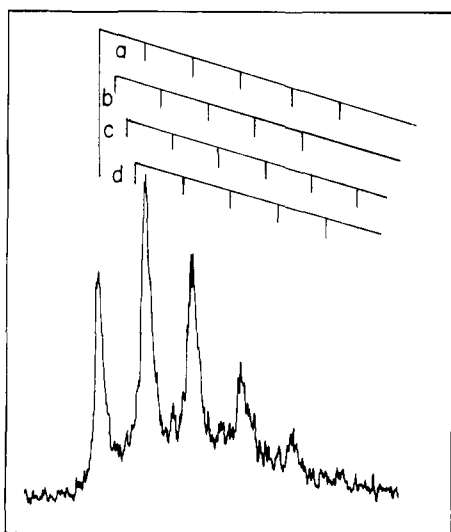


Figure 5. Second band and vibrational analysis of the photoelectron spectrum of 1,1-difluoroallene.

Both are broad and relatively structureless. The more intense band(s) at 15.84 eV corresponds in shape to that at 16.26 eV in tetrafluoroallene⁹ and at 15.7 eV in tetrafluorobutatriene.¹⁴ These have been assigned to in-plane fluorine lone pair IPs in those molecules.¹⁴ This band may also contain several overlapping bands involving ionizations from π_{CH_2} and σ_{CCC} combination orbitals. The corresponding π_{CH_2} ionization potentials for ketene and thioketene fall at 16.28 and 15.5 eV, respectively.¹⁶ The weak band at 17.06 eV corresponds in position to that at 17.3 eV in allene and that at 17.00 eV in tetrafluoroallene, and is assigned to an ionization from a π_{CH_2} and σ_{CCC} combination orbital of a_1 symmetry. The corresponding orbital gives ionization potentials of 18.06 eV for ketene and 17.1 eV for thioketene.¹⁶

4-31G Calculations on Allene and Fluorinated Allenes

SCF calculations on 1,1-difluoroallene and, for comparison, allene and tetrafluoroallene have been carried out using the split valence 4-31G basis set.¹⁷ The highest and second highest π orbital energies and shapes are shown schematically in Figure 6.

The highest occupied molecular orbital (HOMO) of 1,1-difluoroallene at -10.48 eV is predominantly a C_1C_2 π MO

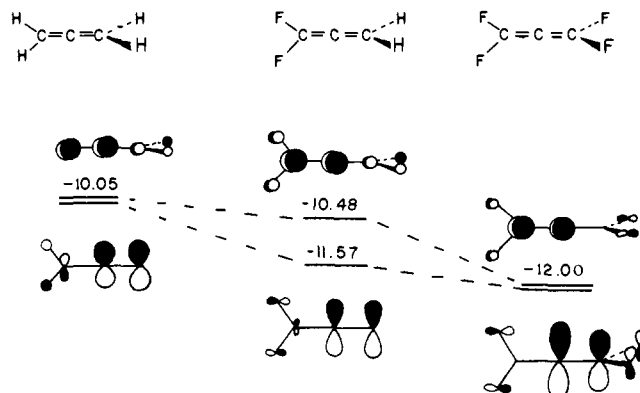


Figure 6. Orbital energies and shapes from ab initio 4-31G calculations on allene, 1,1-difluoroallene, and tetrafluoroallene.

mixed in an antibonding fashion with the lower lying fluorine lone pair orbitals. A hyperconjugative interaction with the remote π_{CH_2} orbital, identical with that in allene, is also present. The donor effect of the CH_2 group results from the much closer proximity of the donor " π_{CH_2} " orbital than the acceptor " $\pi^*_{\text{CH}_2}$ " orbital to the alkene π_{CC} orbital.

The second highest occupied molecular orbital (SHOMO) falls at -11.57 eV, approximately 1 eV below the HOMO, and consists of the C_2C_3 π MO stabilized by a bonding interaction with a $\pi^*_{\text{CF}_2}$ orbital. This orbital is lowered with respect to that of allene due both to this stabilizing interaction and to the loss of the destabilizing interaction with the π_{CH_2} orbital. The π_{CF_2} orbital is much lower in energy than the π_{CH_2} (-18.7 and -15.2 eV, respectively, in 4-31G calculations of CF_2 and CH_2), while the $\pi^*_{\text{CF}_2}$ orbital should be lower in energy than the $\pi^*_{\text{CH}_2}$ orbital. The CF_2 group is an acceptor while the CH_2 is a donor when both interact in a π sense with alkene π bonds.

These effects also appear in the energies of the two π^* orbitals of 1,1-difluoroallene. The lowest unoccupied MO (LUMO) falls at 3.28 eV, separated from the second lowest (SLUMO) by 1.44 eV. The LUMO is concentrated on C_2 and C_3 , here $\pi^*_{-C_2C_3}$, and is strongly stabilized by hyperconjugation with the electron-accepting $\pi^*_{\text{CF}_2}$ orbital. The SLUMO, like the HOMO, is concentrated on C_1 and C_2 and is destabilized by interaction with the π -like donor fluorine lone pair orbital.

Conclusion

In 1,1-difluoroallene, the electron-donating and -withdrawing characters of fluorine operate at the same time on different π orbitals of the molecule. The lack of significant orbital energy, or IP, change upon direct attachment of fluorine to a π system, in spite of the antibonding mixture of fluorine lone pairs with the π orbital, requires a compensating stabilizing effect, and a " σ inductive" effect which both lowers σ orbital energies and lowers the effective electronegativity of the attached carbons appears to account for this in a qualitatively correct way. Allylic fluorine, by contrast, lowers π orbital energies by "negative hyperconjugation", that is, by admixture of the $\pi^*_{\text{CF}_2}$ orbital into the π in a bonding fashion.

The dramatically different effect of fluorines on the two π bonds of difluoroallene confers on the molecule certain unique properties: the C_1C_2 π orbitals are influenced little by fluorine, so that C_1C_2 is, like allene, an electron-rich double bond; the C_2C_3 π orbitals are strongly stabilized, making this bond, like that of trifluoropropene, very electron deficient. Selectivities in attack at one or the other bond should prove diagnostic of the nature of the attacking reagent and the mechanism of the reaction.

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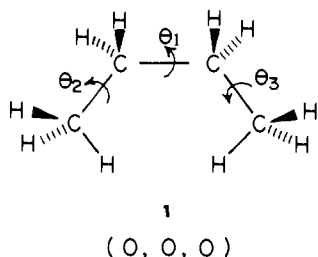
Analysis of the Topological Features of the Conformational Hypersurface of *n*-Butane[†]

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Abstract: An analytic conformational hypersurface was fitted to a total of 63 SCF energy points for *n*-butane. The location of the two minima and two maxima were determined by direct extremization while the positions of the four saddle and four super-saddle points were obtained by minimizing the Euclidean norm of the gradient vector. While the anti conformation was exactly at the point predicted by intuitive stereochemical arguments, the gauche conformation was very sensitive to CH₃ group torsional relaxations.

In recent years, much work has been done regarding conformational and reactive surfaces, but there have been few studied involving hypersurfaces (surfaces of more than two coordinates).¹ We wish to report the determination of the complete torsional hypersurface for *n*-butane (**1**), including the determination of the geometries of all critical points.



This triple-rotor hypersurface is of interest for several reasons. First, it serves as an example of a conformational hypersurface of three coordinates. It also allows the accurate determination of the interaction effects of the nonbonded methyl groups, a crucial parameter (as a model for a "gauche interaction") in empirical force-field calculations such as molecular mechanics. Finally, it is a prelude to ab initio hypersurfaces of molecules containing heteroatoms which empirical methods may not be able to treat properly.

As *n*-butane is one of the simplest molecules capable of ex-

isting in two stable conformations, anti and gauche, it has been well studied experimentally (see Table I). Also summarized there are the previous empirical results and ab initio calculations. All previous ab initio studies and even some of the much less costly empirical calculations have fixed the methyl groups in the staggered conformation (that is, not allowed for methyl rotation) and have also assumed that the saddle point for the anti-to-gauche conversion occurs at the eclipsed conformer ($\theta_1 = 120^\circ$). Some have even assumed that the gauche conformation has a torsional angle (θ_1) of 60° , despite accumulated experimental and theoretical data to the contrary.

Hendrickson, in the course of his molecular-mechanics calculations on the conformations of cycloalkanes, reported² that the gauche minimum occurred at ($63^\circ, 55^\circ, 55^\circ$). The A(anti) \rightarrow G(gauche) saddle point was found at the point predicted by simple stereochemical arguments about eclipsed and staggered bonds, namely ($120^\circ, 60^\circ, 60^\circ$). The bond lengths were fixed at 1.533 and 1.09 Å for C-C and C-H, respectively, for all conformers studied. His barrier-height values (see Table I, ref 2), however, are lower than the experimental values.

Scheraga and co-workers determined³ the critical points of the *n*-butane hypersurface, using rigid rotation. The gauche conformer was located at ($65^\circ, 52^\circ, 52^\circ$), and the A \rightarrow G saddle point at ($121^\circ, 60^\circ, 60^\circ$). Note the large G \rightarrow G barrier (see Table I, ref 3) of nearly 14 kcal/mol, compared to the experimental value of 6 kcal/mol.

Bartell calculated^{4,5} the gauche minimum to be at ($66.8^\circ, 56.7^\circ, 56.7^\circ$), optimizing all internal coordinates. All of these

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