# Electronic States of Difluoroacetylene, Difluorodiacetylene, and Perfluoropentadiyne-1,3 Radical Cations. A Photoelectron Spectroscopic Investigation

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**Abstract**: The He(I$\alpha$) photoelectron spectra of the title compounds have been recorded and assigned. The photoelectron spectra of difluoroacetylene and of difluorodiacetylene terminate the series of dihaloacetylenes (XC≡CX) and dihalodiacetylenes (XC≡C—C≡CX) with X = Cl, Br, I, described previously, so that the complete correlation diagrams are now available, which confirm and extend the previous assignments. For difluoroacetylene and difluorodiacetylene this assignment is unambiguously confirmed by the calculation of vertical ionization energies by a many-body Green function method, which is in perfect agreement with the experimental findings. In turn these results vindicate the simple LCBO treatment proposed previously for halogenated acetylenes and diacetylenes. The latter model is used to interpret the photoelectron spectrum of perfluoropentadiyne-1,3.

For the photoelectron spectroscopist, acetylene,[2] polyacetylenes,[2-4] and their halogenated derivatives (e.g., dihaloacetylenes **1**,[5] dihalodiacetylenes **2**[6]) hold many attractions.

$$\begin{array}{ll} \mathbf{1}(\mathrm{X}) & \mathrm{XC{\equiv}CX} \\ \mathbf{2}(\mathrm{X}) & \mathrm{XC{\equiv}C{-}C{\equiv}CX} \end{array} \quad \mathrm{X = F, Cl, Br, I}$$

To begin with, these molecules, which belong to the symmetry group $D_{\infty h}$, represent ideal cases of $\sigma/\pi$ separation, where the symbols $\sigma$ and $\pi$ retain their original meaning. They are associated with orbital angular momenta (relative to the molecular $z$ axis) of size $|l_z| = 0$ or $\hbar$, respectively. Disregarding smaller corrections to be discussed below, the $^2\Pi$ states of the radical cations $\mathbf{1}^+$(X) and $\mathbf{2}^+$(X) derived from **1**(X) and **2**(X) by ejection of an electron from a $\pi$-orbital differ significantly in energy. This leads to photoelectron spectra with widely spaced, nonoverlapping $\pi$-bands, disregarding obvious cases, such as the near degeneracy of the bands 3 and 4 of **2**(F) (see Figure 1). Secondly, the molecules **1**(X) and **2**(X) and their radical cations $\mathbf{1}^+$(X), $\mathbf{2}^+$(X) are rather rigid systems possessing high-frequency normal modes, mainly of the C≡C stretching type. Therefore the individual $\pi$ bands in the photoelectron spectra of **1**(X) and **2**(X) exhibit well resolved vibrational fine structure.[2-7] Thirdly, two $^2\Pi_\Omega$ states of the radical cations $\mathbf{1}^+$(X), $\mathbf{2}^+$(X) having the same configuration but belonging to the total angular momentum quantum number $\Omega = 3/2$ or $1/2$ are split significantly by spin-orbit coupling, the $^2\Pi_{3/2}$ state of a given configuration being more stable than the $^2\Pi_{1/2}$ state (inversion), The corresponding band separations

$$\Delta_{\mathrm{SOC},j} = E_j(^2\Pi_{3/2}) - E_j(^2\Pi_{1/2}) = I^{\mathrm{v}}_{j,3/2} - I^{\mathrm{v}}_{j,1/2} \quad (1)$$

which have been found to obey simple sum rules,[6,8] provide welcome additional information concerning the electronic structure of the particular state, especially if the halogen atoms X are X = Br or I. Finally, as might have been anticipated from the simple structure of the photoelectron spectra, the $\pi$ systems of **1**(X) and **2**(X) are amenable to a description in terms of extremely simple and transparent LCBO models (= linear combination of (localized) bond orbitals) using a basis of localized two-center $\pi$ orbitals $\pi_{\lambda,\mu}$ ($\lambda = \pm 1$; orbital angular momentum quantum number). In particular, the effect of spin-orbit coupling, i.e., the observed $\Delta_{\mathrm{SOC}}$ can be dealt with by a first-order treatment,[9] in contrast to the more involved higher order calculations necessary for other systems.[10]

The results of such strongly simplified treatments suggest that the energies

$$E_j(^2\Pi) = \frac{1}{2}(E_j(^2\Pi_{3/2}) + E_j(^2\Pi_{1/2})) = \frac{1}{2}(I^{\mathrm{v}}_{j,3/2} + I^{\mathrm{v}}_{j,1/2}) = \overline{I^{\mathrm{v}}_j} \quad (2)$$

(i.e., averaged for the effect of spin-orbit coupling) of corresponding $\pi$ states of the radical cations $\mathbf{1}^+$(X) or $\mathbf{2}^+$(X) with X = F, Cl, Br, I should be linear functions of basis energies $A_{\mathrm{X}}$, and thus of the ionization energies $I$(X) of the free atoms X.[5,6] This has been verified so far only in the case of the haloacetylenes XC≡CH,[11] for which the complete series with X = F, Cl, Br, and I was available.

Although the compounds **1**(X) and **2**(X) are thus ideal for photoelectron spectroscopic investigations, attention must be drawn to their extreme instability. Improper handling may lead to shattering explosions. This is particularly true of **1**(F) and **2**(F).

In the present contribution we discuss the photoelectron spectra of **1**(F) and **2**(F), the first of which had been prepared previously but was not spectroscopically characterized,[12] whereas the second compound has only recently been prepared for the first time,[13] by fragmentation of hexafluorobenzene in an electrodeless discharge. These two molecules are obviously of prime interest in connection with our previous investigations of the photoelectron spectra of **1**(X)[5] and **2**(X)[6] (with X = Cl, Br, I) because their inclusion in the analysis almost triples the energy range of the basis energies $A_{\mathrm{X}}$ of the halogen np$_\lambda$ atomic orbitals and consequently allows a meaningful and much more reliable interpretation of the whole body of data in terms of simple molecular orbital models. In addition, ab initio calculations have been performed on the molecules **1**(F) and **2**(F) as well as calculations taking into account the effect of electronic correlation and reorganization on the values of the ionization energies.

## Experimental Results

In Figure 1 are shown the He(I$\alpha$) photoelectron spectra of difluoroacetylene **1**(F), difluorodiacetylene **2**(F), and perfluoropentadiyne-1,3 (**3**).

$$\mathrm{FC{\equiv}C{-}C{\equiv}CCF_3}$$

**3**

The spectra of **1**(X) and **2**(X) with X = Cl, Br, I have been published previously.[5,6] More precise values for the band po-

Table I. Ionization Energies of the Dihaloacetylenes XC≡CX (**1**(X))[a]

| X | | $j = 1$<br>$\tilde{X}$ | | | $j = 2$<br>$\tilde{A}$ | | | $j = 3$<br>$\tilde{B}$ | | | $j = 4$<br>$\tilde{C}$ | $j = 5$<br>$\tilde{D}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $^2\Pi_{3/2,u}$ | | $^2\Pi_{1/2,u}$ | $^2\Pi_{3/2,g}$ | | $^2\Pi_{1/2,g}$ | $^2\Pi_{3/2,u}$ | | $^2\Pi_{1/2,u}$ | $^2\Sigma_g^+$ | $^2\Sigma_u^+$ |
| F | $I_j^a$ | | 11.18 | | | | | | | | | |
| | $I_j^m$ | | 11.26 | | | | | | | | | |
| | $I_j^v$ | | $11.6_0$ | | | ~17.7 | | | ~18.5 | | (~20.6) | |
| Cl | $I_j^a$ | | 10.09 | | 13.37 | | 13.44 | | | | | |
| | $I_j^m$ | 10.05 | | 10.09 | 13.37 | | 13.44 | | $\sim 14.4_5$ | | 16.76 | 17.81 |
| | $I_j^v$ | | $10.2_5$ | | | $13.4_5$ | | | $14.5_0$ | | | |
| Br | $I_j^a$ | 9.67 | | 9.86 | 12.12 | | 12.42 | | | | | |
| | $I_j^m$ | 9.71 | | 9.90 | 12.12 | | 12.42 | | ~13.5 | | 15.65 | 16.90 |
| | $I_j^v$ | | $9.9_5$ | | | $12.3_0$ | | | $13.4_5$ | | | |
| I | $I_j^a$ | 9.03 | | 9.47 | 10.63 | | 11.24 | | | | | |
| | $I_j^m$ | 9.03 | | 9.47 | 10.63 | | 11.24 | $\sim 12.2_0$ | | $\sim 12.4_5$ | 14.22 | 15.48 |
| | $I_j^v$ | | $9.3_5$ | | | $10.9_5$ | | | $12.3_0$ | | | |

[a] All values are in eV. $I_j^a$ = adiabatic, $I_j^v$ = vertical ionization energy; $I_j^m$ = position of band maximum. The values for $I_j^a$ are those of ref 14. $I_j^m$ and $I_j^v$ (computed according to formula 3, have been deduced from the originals of the spectra shown in ref 14).

Table II. Ionization Energies of the Dihalodiacetylenes XC≡C—C≡CX (**2**(X))[a]

| X | | $j = 1$<br>$\tilde{X}$ | | | $j = 2$<br>$\tilde{A}$ | | | $j = 3$<br>$\tilde{B}$ | | | $j = 4$<br>$\tilde{C}$ | | | $j = 5$<br>$\tilde{D}$ | $j = 6$<br>$\tilde{E}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $^2\Pi_{3/2,g}$ | | $^2\Pi_{1/2,g}$ | $^2\Pi_{3/2,u}$ | | $^2\Pi_{1/2,u}$ | $^2\Pi_{3/2,g}$ | | $^2\Pi_{1/2,u}$ | $^2\Pi_{3/2,u}$ | | $^2\Pi_{1/2,u}$ | $^2\Sigma_g^+$ | $^2\Sigma_u^-$ |
| F | $I_j^m$ | | | | | | | | | | | | | | |
| | $I_j^v$ | | $10.3_5$ | | | 12.9 | | | $17.7_5$ | | | $18.2_5$ | | 19.3 | |
| Cl | $I_j^m$ | | 9.34 | | | 11.68 | | | 13.75 | | | 14.14 | | 16.9 | 17.3 |
| | $I_j^v$ | | $9.5_5$ | | | $11.8_0$ | | | $13.8_0$ | | | $14.2_0$ | | | |
| Br | $I_j^m$ | 9.20 | | 9.29 | 11.22 | | 11.40 | 12.63 | | 12.85 | 13.27 | | 13.36 | 15.9 | 16.2 |
| | $I_j^v$ | | $9.4_0$ | | | | $11.4_0$ | | | $12.7_5$ | | | $13.3_0$ | | |
| I | $I_j^m$ | 8.76 | | 9.05 | 10.25 | | 10.78 | 11.40 | | 11.79 | 12.5 | | 12.61 | 14.6 | 14.9 |
| | $I_j^v$ | | $9.0_0$ | | | $10.5_5$ | | | $11.6_0$ | | | $12.5_5$ | | | |

[a] All values are in eV. $I_j^v$ = vertical ionization energy; $I_j^m$ = position of band maximum. The values $I_j^m$ are those of ref 6. The $I_j^v$ have been computed according to formula 3, using the originals of the spectra shown in ref 6.

sitions in the photoelectron spectra of the systems **1**(X) have recently been obtained by Allan, Kloster-Jensen, and Maier.[14] Characteristic values for the band positions, derived from the photoelectron spectra of Figure 1 and those given in ref 14 and 6 are summarized for **1**(X) in Table I and for **2**(X) in Table II.

Traditionally the positions of the individual bands $j$ in each spectrum are characterized by the adiabatic ($I_j^a$) and/or the vertical ($I_j^v$) ionization energies. In those cases where the vibrational fine structure of the band is well resolved, i.e., where the splits $\tilde{\nu}$ between the individual components are dominated by a high-frequency mode of the radical cation, it is possible to assess the position $I_{j,v'}$ of each of the fine-structure components of band $j$ and their (relative) intensities $i_{j,v'}$ for $v' = 0$ up to a limiting value $v' = k$. This is the case for band 1 of **1**(F) and bands 1, 2 of **2**(F) as can be seen from Figure 1 and from the spectra given in references 5 and 14 for **1**(X) and in ref 6 for **2**(X) with X = Cl, Br, I. Under these conditions we have $I_j^a \equiv I_{j,0}$ and to a good approximation

$$I_j^v \approx \left(\sum_{v'=0}^{k} I_{j,v'} \cdot i_{j,v'}\right) \Big/ \left(\sum_{v'=0}^{k} i_{j,v'}\right) \tag{3}$$

The situation is somewhat more ambiguous if the fine structure of a band $j$ is poorly resolved or unresolved. In such cases the vertical ionization energy is usually assumed to correspond to the position $I_j^m$ of the maximum of the Franck-Condon envelope ($I_j^v \approx I_j^m$) if the band is not too asymmetric. We have used this rough approximation for the bands 2, 3 of **1**(X) and 3, 4 of **2**(X). Finally it has to be mentioned that the vertical ionization energies $I_j^v$ given in Tables I and II have been av-

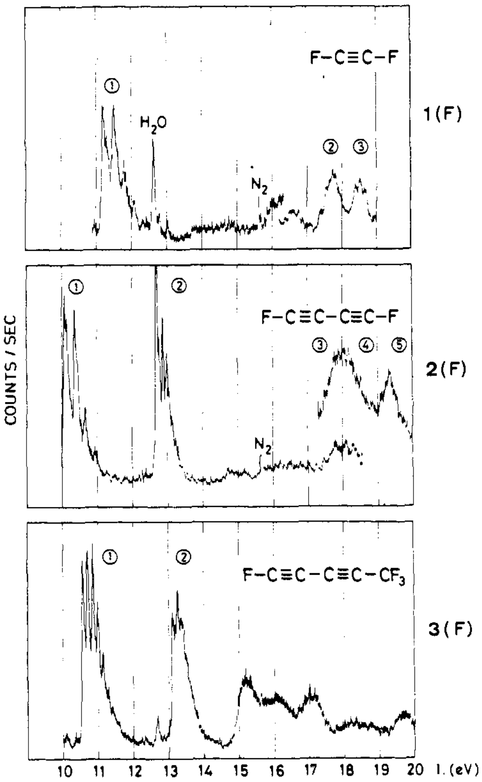


Figure 1. He(Iα) photoelectron spectra of difluoroacetylene **1**(F), difluorodiacetylene **2**(F), and perfluoropentadiyne-1,3 **3**.

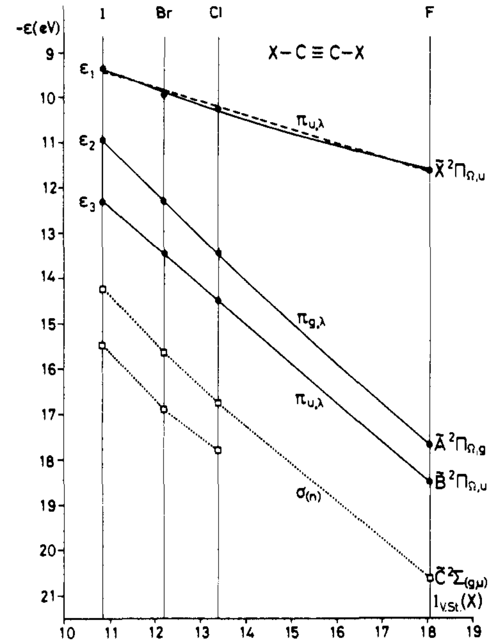


**Figure 2.** Correlation diagram for the "observed" orbital energies of the dihaloacetylenes **1**(X): ●, π-orbital energies; □, σ-orbital energies. The dashed lines represent the linear, the solid lines the parabolic regression functions (7), using the parameters of Table III. The dotted lines indicate simply the proposed correlation of the σ orbitals.

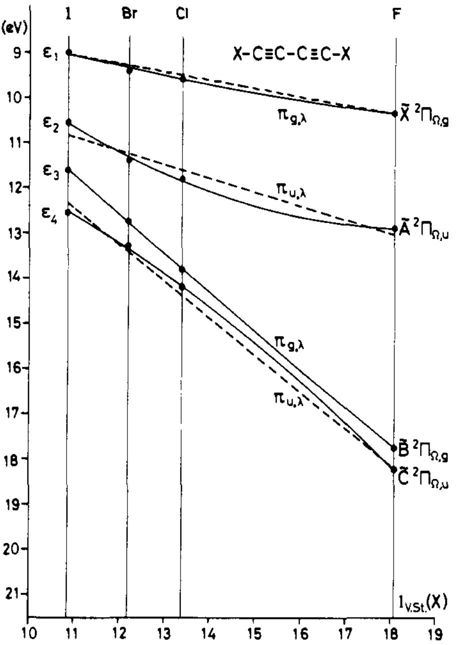


**Figure 3.** Correlation diagram for the "observed" orbital energies of the dihalodiacetylenes **2**(X). For added explanation, see legend to Figure 2.

eraged to eliminate the effect of spin-orbit coupling, as indicated in formula 2.

For the ensuing discussion it is of advantage to introduce the following, traditional simplifications. The vertical ionization energy $I_j^{\mathrm{v}}$ is by definition

$$I_j^{\mathrm{v}} = E_v(^2\tilde{\Psi}_j) - E(^1\Psi_0) \qquad (4)$$

where $E_v$ is the energy of the radical cation in the doublet state $^2\tilde{\Psi}_j$ and with a geometry which fits exactly the structure of the neutral molecule in its electronic singlet ground state $^1\Psi_0$. If the "frozen orbital" approximation underlying Koopmans' theorem is introduced into the calculation of $E_v(^2\tilde{\Psi}_j)$, then one finds that

$$I_j^{\mathrm{v}} = -\epsilon_j \qquad (5)$$

with $\epsilon_j$ being the SCF orbital energy of the canonical orbital $\varphi_j$ vacated in the ionization process. According to previous experience it is expected that the orbital energies $\epsilon_j$ for corresponding states $^2\tilde{\Psi}_j$ of the radical cations $\mathbf{1}^+$(X) and $\mathbf{2}^+$(X) with different substituents X are simple, smooth functions of the basis energies $A_X = \langle p_{\lambda,\mu}(X)|\mathcal{H}|p_{\lambda,\mu}(X)\rangle$ of the halogen $np_\lambda$ atomic orbitals, which in turn have been found to be linear functions (with slope unity) of the ionization energies of the free atoms X.[11,15]

Previously, we have used[5,6,11,16] the atomic ionization energies $I$(X) corresponding to the process $X(^2P^0{}_{3/2}) \rightarrow X^+(^3P_2) + e^-$,[17] but it is preferable to use instead the valence state ionization energies $I_{\mathrm{v.st}}$(X) corresponding to $I_{\mathrm{v.st}}(X) = (3/4)E(^3P) + (1/4)E(^1D)$ with spin-orbit coupling averaged to zero,[18] as has been done in the correlation diagrams of Figures 2 and 3. For the purpose of a regressional analysis it is of advantage to use the deviations $\Delta I_{\mathrm{v.st}}(X) = I_{\mathrm{v.st}}(X) - \bar{I}_{\mathrm{v.st}}$ of the valence state ionization energies relative to their mean $\bar{I}_{\mathrm{v.st}}$ = 13.62 eV. The numerical values (in eV) of all these quantities are

| | F | Cl | Br | I | |
|---|---|---|---|---|---|
| $I$(X) | 17.42 | 13.01 | 11.84 | 10.45 | (ref 17) |
| $I_{\mathrm{v.st}}$(X) | 18.07 | 13.37 | 12.18 | 10.85 | (ref 18) |
| $\Delta I_{\mathrm{v.st}}$(X) | 4.45 | −0.25 | −1.44 | −2.77 | |

(6)

Both parabolic and linear regression lines have been adjusted by standard least-squares techniques to the experimental data $I_j^{\mathrm{v}}$ of Tables I and II. The parameters of the regression functions

$$\begin{aligned} \epsilon_j(X) &= a_j + b_j\Delta I_{\mathrm{v.st}}(X) + c_j(\Delta I_{\mathrm{v.st}}(X))^2 \\ \epsilon_j(X) &= a_j' + b_j'\Delta I_{\mathrm{v.st}}(X) \end{aligned} \qquad (7)$$

are given in Table III together with their standard errors. The resulting regression lines are shown in the correlation diagrams of Figures 2 and 3.

**LCBO Model for Haloacetylenes.** For the rationalization of the experimental results we make use of the LCBO model proposed previously.[3,6] The basis functions are the bonding and antibonding two-center π orbitals $\pi_{\lambda,\mu}$ and $\pi^*{}_{\lambda,\mu}$ ($\lambda = \pm 1$) of the μth triple bond and the np atomic orbitals $p_\lambda$(X) of the terminal halogen atoms X. The empirical basis energies of $\pi_{\lambda,\mu}$ and $\pi^*{}_{\lambda,\mu}$ are[6]

$$\begin{aligned} A_{CC} &= -11.4\ \mathrm{eV} + \delta A(R_1) + \delta A(R_2) \\ A_{CC^*} &= -6.0\ \mathrm{eV} \end{aligned} \qquad (8)$$

where $\delta A(R_1)$ and $\delta A(R_2)$ are corrections depending on the left ($R_1$) and right ($R_2$) substituent of the particular triple bond. If $R_1$ and/or $R_2$ are halogen atoms X, the $\delta A$(X) depend on the electronegativity of X. Using the $\delta A$(X) values (with X = Cl, Br, I) given in ref 6 together with the standard Pauling electronegativities $\chi$(X) we predict $\delta A(F) = -0.5$ eV. The basis orbitals have been shown[11] to follow the simple rule $A_X = -I(X) + 0.04$ eV which yields $A_F = -17.38$ eV. On the other hand the values $A_X$ (X = Cl, Br, I) deduced from the spectra of previously investigated halogen substituted acetylenes are related to the valence state ionization energies of the halogen atoms by $A_X = -I_{\mathrm{v.st}}(X) + 0.41$ eV, which yields $A_F = -17.66$ eV. For the purpose of the present analysis we have chosen a mean value of $A_F = -17.5$ eV.

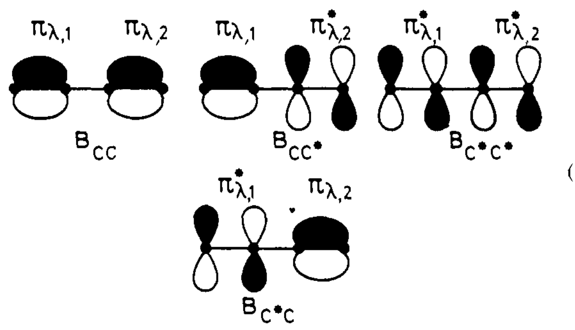
The interaction matrix element between (a) two consecutive bonding ($\pi_{\lambda,1}$; $\pi_{\lambda,2}$), (b) a bonding and an antibonding ($\pi_{\lambda,1}$; $\pi^*{}_{\lambda,2}$), or (c) between two antibonding ($\pi^*{}_{\lambda,1}$; $\pi^*{}_{\lambda,2}$) basis π orbitals is assumed to be of same size, the sign being determined by the following convention for the relative phases of

Table III. Parameters of the Regression Functions (7)[a]

| $j$ | $-a_j$ | $-b_j$ | $-c_j$ | $-a_j'$ | $-b_j'$ |
|---|---|---|---|---|---|
| | | | **1**(X): XC≡CX | | |
| 1 | 10.378 | 0.328 | −0.012 | 10.288 | 0.302 |
| | (0.078) | (0.025) | (0.009) | (0.0053) | (0.019) |
| 2 | 13.694 | 0.955 | −0.012 | 13.602 | 0.929 |
| | (0.008) | (0.003) | (0.001) | (0.044) | (0.016) |
| 3 | 14.710 | 0.864 | −0.003 | 14.690 | 0.858 |
| | (0.011) | (0.004) | (0.001) | (0.010) | (0.004) |
| | | | **2**(X): XC≡C—C≡CX | | |
| 1 | 9.641 | 0.198 | −0.009 | 9.575 | 0.179 |
| | (0.071) | (0.022) | (0.008) | (0.042) | (0.015) |
| 2 | 11.954 | 0.387 | −0.039 | 11.663 | 0.302 |
| | (0.095) | (0.030) | (0.011) | (0.143) | (0.052) |
| 3 | 14.001 | 0.859 | −0.004 | 13.977 | 0.851 |
| | (0.013) | (0.004) | (0.002) | (0.015) | (0.006) |
| 4 | 14.352 | 0.741 | 0.030 | 14.577 | 0.807 |
| | (0.054) | (0.017) | (0.006) | (0.108) | (0.040) |

[a] Values in parentheses are the standard errors. The parameters refer to $\epsilon_j$ and $I_{v,st}(X)$ (in eV).

the basis orbitals



(9)

This yields: $B_{CC} = B_{CC^*} = -B_{C^*C} = -B_{C^*C^*} = -1.22_5$ eV.[3-5] Those between $p_\lambda(X)$ and $\pi_{\lambda,\mu}$ or $\pi^*_{\lambda,\mu}$ have been found to depend on the nature of X, increasing in absolute value with increasing electronegativity of X: $B_{CI} = B_{IC^*} = -B_{C^*I} = -0.97_5$ eV; $B_{CBr} = B_{BrC^*} = -B_{C^*Br} = -1.27$ eV; $B_{CCl} = B_{ClC^*} = -B_{C^*Cl} = -1.46$ eV. (Note that the sign of the matrix elements involving the antibonding orbitals $\pi^*_{\lambda,\mu}$ is due to the choice of the relative phases as indicated in (9)). Thus it is expected that $B_{CF} = B_{FC^*} = -B_{C^*F}$ will be larger than ~1.5 eV in absolute value. As we shall see, this is indeed the case.

To calibrate the LCBO paramaters representative for the fluorine substituents we use the spectrum of **1**(F). With $\delta A(F) = -0.5$ eV we obtain from (8) $A_{CC} = -12.4$ eV to be used as a basis energy for the $\pi_\lambda$ orbitals in the molecule **1**(F). That this is a reasonable estimate is shown by the independent assessment based on the relationship $\epsilon_1 + \epsilon_3 = A_F + A_{CC}$ derived from the LCBO model. With $\epsilon_1 = -11.6$ eV, $\epsilon_3 = -18.5$ eV and $A_F = -17.5$ eV we obtain $A_{CC} = -12.6$ eV, in good agreement with the above-mentioned value. It should be noted that a similar calibration of $A_F$, using the observed ionization energies $I_j^v$ of the monohaloacetylenes XC≡CH (X = F, Cl, Br, and I),[11] yielded $A_F = -17.7$ eV, i.e., a value only marginally lower. It is perhaps remarkable that there does not seem to be any significant influence of the second fluorine atom in **1**(F) on the $A_F$ value.

Finally we calculate from

$$B_{CF}^2 = \left(\frac{\epsilon_1 - \epsilon_3}{2}\right)^2 - \left(\frac{A_{CC} - A_F}{2}\right)^2 \tag{10}$$

the value $B_{CF} = -1.72$ eV, which concludes the calibration of our LCBO model for fluorine substituted acetylenes. Note that $\epsilon_2$ of **1**(F) is found to lie below $A_F$, which is due to the interaction of the even linear combination $p_{\lambda,g} = (p_{\lambda,1}(F) - p_{\lambda,2}(F))/\sqrt{2}$ with the antibonding $\pi$ orbital $\pi_\lambda^*$. However, it should be mentioned that the depression computed on the basis of the above $B_{CF}$ value is somewhat too large (~ −0.2 eV). We believe that this is within the limits of error that can reasonably be expected from such a simple model which neglects, apart from everything else, the effects of electron rearrangement and of electron correlation.

As a result of this calibration the previously proposed set of parameters for the LCBO model of halogen-substituted acetylenes[6] can now be completed to include fluorinated systems (cf. formula 8 for the definition of $A_{CC}$ and $A_{CC^*}$; values in eV)

| R = | C≡C | F | Cl | Br | I | |
|---|---|---|---|---|---|---|
| $\delta A(R)$ | 0.27 | −0.50 | −0.09 | 0.02 | 0.15 | |
| $A_X$ | (see (8)) | −17.5 | −12.96 | −11.79 | −10.43 | |
| $B_{CX}$ | $(-1.22_5)$ | −1.72 | −1.46 | −1.27 | $-0.97_5$ | (11) |

A reliable check of the fluorine parameters contained in (8) is provided by the LCBO-model predictions for **2**(F) and their comparison to the observed band positions. Solving the corresponding secular determinant of sixth order yields the following orbital energies $\epsilon_j$ for the bonding $\pi$ orbitals of **2**(F), to be compared to the observed vertical ionization energies $I_j^v$

FC≡C—C≡CF

$$\begin{array}{ll} \epsilon_1 = -10.12 \text{ eV} & I_1^v = 10.35 \text{ eV} \\ \epsilon_2 = -12.78 & I_2^v = 12.90 \\ \epsilon_3 = -18.18 & I_3^v = 17.9 \\ \epsilon_4 = -18.22 & I_4^v = 18.1 \end{array} \tag{12}$$

As can be seen the correspondence is quite satisfactory and there is no doubt that the assignment given in Table II is the correct one.

The interpretation of the photoelectron spectrum of **3** is slightly more complicated because of the influence of the trifluoromethyl group. However, it is presumably safe to assume that the semilocalized pseudo-$\pi$-orbitals of this group have orbital energies around −16 eV,[19] i.e., rather far removed in energy from the $\pi$ orbitals of the triple bond to which the $CF_3$ group is attached. Furthermore, the interaction term $B_{CCF_3}$ is in all probability small. Thus the main influence of the substituent can be absorbed into an "inductive" $\delta A(CF_3)$ parameter to be inserted into expression (8) for the computation of $A_{CC}$. To determine the size of $\delta A(CF_3)$ we compare the $\pi$-ionization energy of acetylene,[2] trifluoromethylacetylene and bis(trifluoromethyl)acetylene[20]

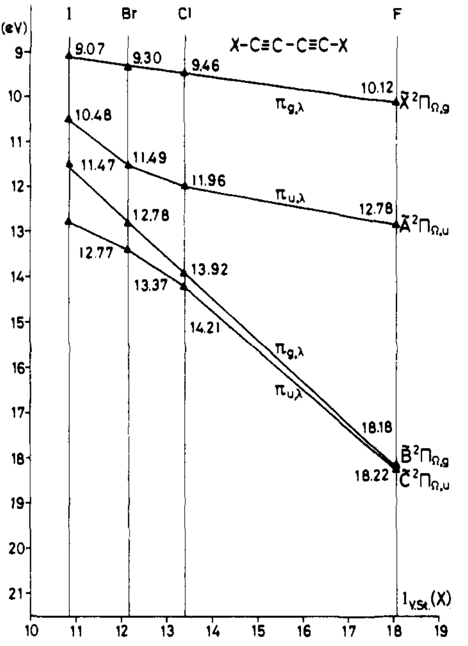


**Figure 4.** Correlation diagram for the orbital energies of the dihalodiacetylenes **2**(X), computed on the basis of the parameters given in (8) and (11).

**Table IV.** Total SCF Energies (in au) and Orbital Energies (in eV) of **1**(F) and **2**(F). The Numbering of the Orbitals Starts with the First Valence Orbital.

| | FC≡CF | | FC≡C—C≡CF |
|---|---|---|---|
| $\sigma_g$ | −718.09 | $\sigma_g$ | −718.25 |
| $\sigma_u$ | −718.09 | $\sigma_u$ | −718.25 |
| $\sigma_g$ | −309.44 | $\sigma_g$ | −309.99 |
| $\sigma_u$ | −309.32 | $\sigma_u$ | −309.99 |
| $1\sigma_g$ | − 45.54 | $\sigma_g$ | −308.17 |
| $1\sigma_u$ | − 45.49 | $\sigma_u$ | −308.14 |
| $2\sigma_g$ | − 29.35 | $1\sigma_g$ | − 45.87 |
| $2\sigma_u$ | − 23.58 | $1\sigma_u$ | − 45.87 |
| $3\sigma_g$ | − 22.51 | $2\sigma_g$ | − 30.88 |
| $1\pi_u$ | − 20.86 | $2\sigma_u$ | − 29.37 |
| $1\pi_g$ | − 20.36 | $3\sigma_g$ | − 24.00 |
| $2\pi_u$ | − 11.93 | $3\sigma_u$ | − 22.88 |
| | | $4\sigma_g$ | − 22.02 |
| | | $1\pi_u$ | − 20.79 |
| | | $1\pi_g$ | − 20.74 |
| | | $2\pi_u$ | − 14.41 |
| | | $2\pi_g$ | − 11.08 |
| | Virtual orbitals | | Virtual orbitals |
| $3\sigma_u$ | 5.32 | $3\pi_u$ | 3.61 |
| $2\pi_g$ | 6.71 | $4\sigma_u$ | 4.79 |
| $4\sigma_g$ | 7.25 | $5\sigma_g$ | 6.29 |
| $4\sigma_u$ | 10.23 | $5\sigma_u$ | 8.89 |
| $3\pi_u$ | 11.32 | $6\sigma_g$ | 9.04 |
| | | $3\pi_g$ | 9.33 |
| $E_{tot}{}^{SCF}$ = −274.431791 au | | $E_{tot}{}^{SCF}$ = −349.970545 au | |

$$\begin{array}{lc} & I_1{}^v(\pi) \\ HC{\equiv}CH & 11.4\ \text{eV} \\ HC{\equiv}CCF_3 & 12.1\ \text{eV} \\ CF_3C{\equiv}CCF_3 & 12.8\ \text{eV} \end{array} \tag{13}$$

From these we deduce that $\delta A(CF_3) = -0.7$ eV should be a good guess. If this value is used in conjunction with the parameters given in (11) one obtains, by solving the corresponding fifth-order secular determinant, the following orbital energies for those bonding $\pi$ orbitals of **3** which are centered mainly on the FC≡C—C≡C moiety

$$\begin{array}{ll} \multicolumn{2}{c}{FC{\equiv}C{-}C{\equiv}CCF_3} \\ \epsilon_1 = -10.47\ \text{eV} & I_1{}^v = 10.8_5\ \text{eV} \\ \epsilon_2 = -13.07 & I_2{}^v = 13.3_0 \\ \epsilon_3 = -18.20 & \quad ? \end{array} \tag{14}$$

Comparison with the vertical ionization energies of the first two bands in the photoelectron spectrum of **3** indicates that the latter are a bit larger than the computed values. This may be due to the neglect of the transmission of the inductive effect due to the $CF_3$ group which would also lower the energy of the basis $\pi$ orbitals of the first triple bond in **3**. Indeed such a transmission has been observed in trifluoromethyl-haloacetylenes, where the halogen basis orbitals are moved to lower energies relative to the $A_X$ values given in (11).[20]

The location of the band corresponding to $\epsilon_3 = -18.2$ eV is uncertain. The series of overlapping bands in the region of 15 to 18 eV of the spectrum of **3** are due to the removal of an electron from one or another of the semilocalized orbitals of the $CF_3$ group. This is supported by the photoelectron spectra of fluoromethanes[19] which exhibit strongly overlapping bands in the region 13 to 19 eV.

To conclude this section we wish to show that our model, i.e., the set of LCBO parameters (8), (11), accounts rather nicely for some of the observed features in the photoelectron spectra of the dihalodiacetylenes **2**(X). From Figure 3 and from the entries in Table III it is obvious that the orbital energies $\epsilon_1$ and $\epsilon_3$ are essentially linear functions of $I_{v,st.}(X)$, whereas $\epsilon_2$ and $\epsilon_4$ exhibit significant positive and negative quadratic components, respectively. In Figure 4 are shown the computed orbital energies $\epsilon_1$ to $\epsilon_4$ for the four compounds in question, i.e., those derived from the LCBO model using the parameters (8) and (11). As is obvious by inspection, the correlation diagram of Figure 3 is faithfully reproduced, including the type of dependence of the $\epsilon_j$ on the valence state ionization energies $I_{v,st}(X)$ of the halogen substituents.

**Nonempirical Calculations on $C_2F_2$ and $C_4F_2$.** For a theoretical assignment of the photoelectron spectrum of **1**(F) and **2**(F) and to gain information on at least some of those $\Sigma$ states which are difficult to study experimentally in the case of the ions **1**(F)$^+$ and **2**(F)$^+$, the vertical ionization energies have been computed nonempirically. The ionization energies are calculated by an ab initio many-body Green's function method.[21] The effects of electronic correlation and reorganization are taken into account in this approach. The SCF calculations were performed with the program system MUNICH[22] using basis sets of Cartesian Gaussian functions. Since the experimental geometry of both **1**(F) and **2**(F) is unknown the geometry was determined by ab initio calculations for **1**(F) and pieced together from theoretical and experimental results for **2**(F). For **1**(F) the geometrical parameters are: $r(C{\equiv}C) = 2.218$ au and $r(C\text{-}F) = 2.464$ au, and for **2**(F) they are $r(C{\equiv}C) = 2.218$ au, $r(C\text{-}F) = 2.464$ au (both as in **1**(F)) and $r(C\text{-}C) = 2.600$ au (taken from diacetylene). The agreement with the results of the INDO calculations on **1**(F) is only moderate: Gordon and Pople determined the geometrical parameters to $r(C{\equiv}C) = 2.249$ au and $r(C\text{-}F) = 2.494$ au.[23] It must be noted that the use of geometries determined from SCF calculations in the Green's function calculation is inconsistent as the latter include electron correlation both in the ground and in the ionic states. Thus either experimental geometries or geometries determined from configuration interaction calculations should be used. These additional computations have, however, not been performed. The basis set employed in the calculation on the molecule **1**(F) consists of 9 s-, 5 p-, and 1 d-type functions, on each center contracted to 4 s-, 2 p-, and 1 d-type functions. For **2**(F) only the s-p basis has been used. The exponential parameters and contraction coefficients of the s- and p-type functions were taken from the work of Huzinaga.[24] The parameters of the d-type functions were: $\alpha_d(F) = 1.0$,

**Table V.** Ionization Energies of $C_2F_2$ (**1**(F)) in Different Orders of the Perturbation Expansion (All Values in eV)

| Symmetry | $-\epsilon_i$ | $I^{(2)}$ | $I^{(3)}$ | $I^{(R)}$ | $P^{(R)}$ | $I^v$(exptl) |
|---|---|---|---|---|---|---|
| $2\pi_u$ | 11.93 | 11.10 | 11.44 | 11.31 | 0.93 | $11.6_0$ |
| $1\pi_g$ | 20.36 | 16.10 | 19.13 | 18.14 | 0.90 | ~17.7 |
| $1\pi_u$ | 20.86 | 16.94 | 19.57 | 18.62 | 0.90 | ~18.5 |
| $3\sigma_g$ | 22.51 | 19.19 | 21.54 | 20.74 | 0.91 | ~20.6 |
| $2\sigma_u$ | 23.58 | 20.00 | 22.63 | 21.70 | 0.89 | |
| $2\sigma_g$ | 29.35 | 26.23 | 26.47 | 26.38 | 0.86 | |

**Table VI.** Ionization Energies of $C_4F_2$ (2(F)) in Different Orders of the Perturbation Expansion (All Values in eV)

| Symmetry | $-\epsilon_i$ | $I^{(2)}$ | $I^{(3)}$ | $I^{(R)}$ | $P^{(R)}$ | $I^v$(exptl) |
|---|---|---|---|---|---|---|
| $2\pi_g$ | 11.08 | 10.29 | 10.51 | 10.36 | 0.92 | 10.35 |
| $2\pi_u$ | 14.41 | 12.83 | 13.40 | 13.14 | 0.91 | $12.9_0$ |
| $1\pi_g$ | 20.74 | 16.15 | 19.30 | 18.20 | 0.89 | ~17.9 |
| $1\pi_u$ | 20.79 | 16.30 | 19.33 | 18.25 | 0.89 | ~18.1 |
| $4\sigma_g$ | 22.02 | 18.40 | 20.53 | 19.76 | 0.90 | ~19.3 |
| $3\sigma_u$ | 22.88 | 19.00 | 21.86 | 20.87 | 0.89 | |
| $3\sigma_g$ | 24.00 | 19.95 | 22.45 | 21.49 | 0.88 | |

$\alpha_d(C) = 0.6$. The total SCF energies and orbital energies are listed in Table IV for both molecules.

The many-body calculations have been performed by including all orbitals except for the core orbitals. The results are given in Table V for **1**(F) and in Table VI for **2**(F). The following data are listed: symmetry identification of the ionization energies, the values according to Koopmans' theorem, the results in second and third order of the perturbation expansion (denoted by $I^{(2)}$ and $I^{(3)}$), the final results including renormalization terms which incorporate the effects of higher orders in the perturbation expansion, the final pole strengths, and the experimental values. It must be noted that the vertical ionization energies computed here should be compared to the centroids of the bands.[25] The pole strengths, $P_i$, have a physical significance too. In the Hartree–Fock approximation the pole strength is unity for the simple ionization process and zero for the process of ejection of one electron and simultaneous excitation of another electron to an unoccupied orbital. When many-body effects are included, the $P_i$ are less than unity for the simple ionization process and $1 - P_i$ gives the probability for satellite lines due to excitations accompanying photoionization. All pole strengths are between 0.86 and 0.93 for **1**(F) and between 0.88 and 0.92 for **2**(F). Thus one may expect satellite lines in the spectra of these molecules with about 10% of the intensity of the principal valence lines.

The first three bands in the spectrum of **1**(F) are due to removal of an electron from one of the $\pi$ orbitals, $2\pi_u$, $1\pi_g$, $1\pi_u$ (listed according to increasing binding energy). The ionization energies which correspond to the removal of an electron from one of the orbitals $3\sigma_g$, $2\sigma_u$, and $2\sigma_g$ are found between 20 and 30 eV and cannot be seen in the experimental spectrum. The higher ionization energies are not very accurate if intense satellite lines are lying in their energy range. The present renormalization method is not applicable then and the more general theory of ref 26 should be used in the calculations.

All first four ionization energies of **2**(F) are due to removal of an electron from a $\pi$ orbital similar to the situation in **1**(F). The values agree nicely with those obtained from experiment and from the LCBO calculations. The $1\pi_g$ and $1\pi_u$ ionization energies lie close together. This is due to the fact that the vacated orbitals are essentially lone pairs on the F atoms. The charge clouds of the two F atoms have, however, very little overlap and their interaction becomes very small. The first ionizations which correspond to ejection of an electron from $\sigma$ orbitals appear at somewhat lower energy than in **1**(F) and are found in the energy range 19.5 to 22 eV. The $4\sigma_g$ ionization potential is associated with band 5 at 19.3 eV in Figure 1.

The ordering of ionic states as supplied by Koopmans' theorem is seen to be correct for both molecules, although the Koopmans values for the ionization potentials are too high. The many-body calculations introduce shifts between about 0.5 and 3 eV and are very nonuniform as is typically found also in other molecules.[27] The agreement of the final results with experiment is very satisfactory and is typical for calculations with basis sets as employed here (see ref 27 and references contained therein).

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# Proton and Carbon-13 Nuclear Magnetic Resonance Studies of Substituted Pyrimidines. 2. Monoprotonation of Methyl- and Aminopyrimidines

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**Abstract:** The monoprotonation of methyl- and aminopyrimidines has been studied by carbon-13 NMR spectroscopy. The chemical shift parameters associated with the protonation of methylpyrimidines have been determined for the aromatic and methyl group carbons from the salts of certain symmetric compounds. The results indicate that a significant difference exists for certain parameters for a given carbon, depending on whether a hydrogen atom or a methyl group is attached to it. The study of the influence of the medium on the protonated forms shows that an especially large solvent effect exists for carbons bearing a methyl group in the position para to the site of protonation. The percentages of the forms monoprotonated at sites N-1 or N-3 of pyrimidines have been evaluated from their chemical shifts in trifluoroacetic acid and dimethyl sulfoxide solutions. The results for methylpyrimidines indicate a higher percentage (ca. 71%) of the form where the protonated nitrogen is in the para position to the methyl group. In the case of the 4-amino-6-methylpyrimidines the influence of the amino group is greater than that of the methyl group and the percentage reaches about 94% for the form where the protonated nitrogen is in the para position to the amino group.

## I. Introduction

In connection with our research on pyrimidines,[1,2] we have undertaken the study of protonation, a phenomenon which is of considerable interest as has been demonstrated by numerous publications on nitrogen heterocycles.[3-20]

Carbon-13 nuclear magnetic resonance spectroscopy ($^{13}$C NMR) has been used since carbon-13 chemical shifts are very sensitive to the effects of protonation.[14]

We have determined first the protonation parameters and then the relative populations of the monoprotonated species, N(1)H or N(3)H, for the methyl and amino derivatives of pyrimidine.

In the case of the protonation parameters there have been relatively few detailed studies.[14,21] It was of interest therefore to evaluate the influence of substitution and solvent on the protonation parameters and to compare their values with those of some similar heterocycles (2-methyl- and 4-methylpyridines).

In the case of the site of protonation of nitrogen heterocycles however, a number of different spectroscopic techniques have been employed, namely UV,[4,18,19] NMR,[7-12,16,17] calorimetry,[20] and potentiometry.[18] There have been some investigations of the protonation of pyrimidines using $^1$H NMR[3,5,6,9-11] and $^{13}$C NMR,[13-15] but no quantitative evaluation has yet been made of the relative percentages of the tautomeric forms.

The problem of carrying out such a determination on the pyrimidine hydrochlorides is that they may undergo partial deprotonation in the convenient media used for neutral materials, i.e., dimethyl sulfoxide ($Me_2SO$) and water. This led us to use trifluoroacetic acid ($CF_3CO_2H$) as solvent for pyrimidines in the study of their monoprotonation.

## II. Experimental Section

**A. Products.** The sources of the compounds **1–21** have been previously reported.[1] The hydrochlorides of pyrimidines **1**, **3**, **7**, **8**, and methylpyridines, and the hydrobromide of pyrimidine **7**, were prepared by passing a current of dry hydrochloric or hydrobromic acid gas through a stirred ether solution of the appropriate product. The perchlorate of pyrimidine **7** was prepared by the action of aqueous perchloric acid on the 4,6-dimethylpyrimidine, and the 1,5-dimethylpyrimidine hydroiodide by treating 5-methylpyrimidine with methyl iodide. $CF_3CO_2H$ was distilled together with $(CF_3CO)_2O$ prior to use.

**B. Instrumentation.** Carbon-13 spectra were recorded at 25.2 MHz on a Varian XL-100-12 (ENSCP, laboratoire de spectrographie RMN, Université de Paris VI) and at 20 MHz on a Varian CFT-20. Solutions were made up in $Me_2SO$, $H_2O$, and $CF_3CO_2H$ in the concentration range 0.3–1.8 M; in this range, the variation of chemical shifts was verified to be negligible. Chemical shifts were measured with respect to internal dioxane. The chemical shift of dioxane with respect to $Me_4Si$ is 68.3 ppm in $CF_3CO_2H$ solution. The accuracies of the chemical shifts and of the coupling constants are 0.05 ppm and 0.5 Hz, respectively. Typical conditions for noise decoupled spectra were: acquisition time: 1.0 s, flip angle: 30°.

## III. Results and Discussion

The carbon-13 chemical shifts of pyrimidines **1–21** in $Me_2SO$ solutions have been published previously.[2] The chemical shifts of these pyrimidines in $CF_3CO_2H$ solutions are summarized in Table I.

The assignments of the spectra of the symmetric pyrimidines were made with the help of off-resonance decoupling and comparison of the signal intensities. For the nonsymmetric pyrimidines and the methylpyridines, it was necessary to use selective decoupling and long-range coupling constant data. Some assignments were based on the following results (Table II): in neutral and acidic media, one has, for pyrimidines, $^1J(C_2H_2) > {}^1J(C_6H_6)$ and, for aromatic carbons $C_i$ of both pyrimidines and pyridines,[22] $^3J(C_iH) > {}^2J(C_iH)$; protonation increases the values of the $^1J$(CH) coupling constants, with the largest effect on the carbon adjacent to the protonation site.