

Photoelectron Spectrum and Electronic Structure of Triazadienyl Fluoride, N₃F

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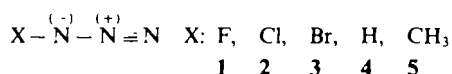
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The He(I) PE spectrum of the title compound **1** has been obtained. Based on quantum mechanical calculations, the ionization potentials have been assigned to molecular orbitals. Good correlation was obtained with the corresponding ionization potentials of chlorine azide (**2**), bromine azide (**3**), hydrazoic acid (**4**), and methyl azide (**5**). The low stability of **1** is apparent from its electronic structure.

The highly explosive triazadienyl fluoride (**1**) recently has been synthesized in pure form¹⁾ and its structure was determined by microwave spectroscopy combined with ab initio calculations²⁾. Due to the extraordinary properties of **1**, an investigation of the electronic structure seemed to be desirable. We now want to report on the UV photoelectron spectrum of **1** and its comparison with compounds **2** to **5**.



The PE spectrum of **1** is shown in Figure 1, the ionization potentials are summarized in Table 1 together with the results of AM1³⁾, MNDO⁴⁾, and ab initio calculations. In the spectrum six strong ionization bands are easily recognized. In addition, some weaker bands are present. Some lines undoubtedly are caused by impurities. The latter are decomposition products of **1**, namely molecular nitrogen^{5,6)} and difluorodiazene⁷⁾, and a trace of carbon dioxide^{5,6)}. Ionization bands of **1** are numbered in the spectrum and peaks assigned to impurities are indicated by vertical lines.

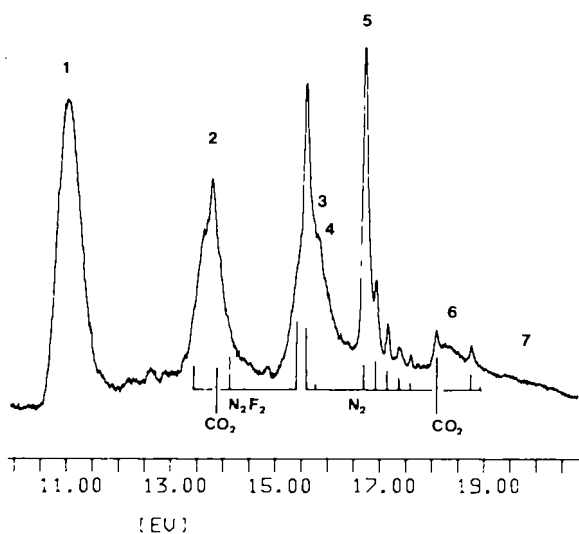


Figure 1. PE spectrum of N₃F (**1**)

Table 1. Ionization potentials IP [eV], vibrational splittings Δν [cm⁻¹] and calculated orbital energies ε[eV] of compound **1**

No	IP	Δν	-ε			Assignment ^{b)}
			AM1	MNDO	MP2/ 6-31G* ^{a)}	
1	11.01	800	10.21	10.36	11.54	3a'' π
2	13.72	1800	13.17	13.72	14.78	8a' n _N , n _F
3	15.6		15.39	16.15	17.22	7a' n _F
4	15.9		15.80	16.51	18.15	2a'' π _F
5	16.67		17.71	18.11	19.69	6a' n _N , σ
6	18.2		18.55	18.77	20.34	1a'' π
7	(19.7)		18.94	19.26	20.32	5a' σ

^{a)} Unpublished results from ref.²⁾. — ^{b)} Valence orbital numbering.

Due to appreciable amounts of decomposition products, identification of IPs belonging to **1** is not quite unequivocal. In particular, this concerns the broad band between 15.0 and 16.2 eV. The peak at 15.55 eV on top of this band is caused by the strongest line of N₂^{5,6)}. After subtraction of this peak a rather broad band remains, that probably is attributable to two ionization events. Therefore, two IPs of **1**, ca. 15.6 and 15.9 eV, are assigned to this band. This interpretation is supported by quantum chemical calculations and comparison with the spectra of compounds **2** and **3** (see below).

The sharp line 5 at 16.67 eV within 0.02 eV coincides with a peak of molecular nitrogen^{5,6)} and therefore at first sight might be assigned to this impurity. From its intensity, however, it is obvious that it does not originate from N₂. The bands 6 and 7, due to experimental reasons, appear with low intensity in the spectrum.

Vibrational structure has been resolved for the first two ionization bands. Progressions of about 800 and 1800 cm⁻¹, respectively, were found. These frequencies most likely are to be assigned to ν₂ = ν_s(N₃) and ν₁ = ν_{as}(N₃) of the respective radical cation. The parent molecule **1** has the following frequencies¹⁾: ν₁ = 2037, ν₂ = 1090 cm⁻¹.

Quantum mechanical calculations for **1** have been performed by the AM1³⁾ and the MNDO⁴⁾ method; the results are summarized in Tables 1 and 2. Results of an ab initio study²⁾ on the MP2/6-31G* level are included. Compared with the ab initio data, which are in excellent agreement with the experimental ones²⁾, the structure parameters from MNDO and AM1 are less accurate. In particular, the F–N bond length and the F–N–N angle deviate appreciably (Table 2).

Excellent linear correlation (r = 0.96–0.98) is obtained for IPs and computed orbital energies ε (Table 1). ε values for the experimental structure²⁾ deviate up to 0.4 eV from the data given in Table 1 and correlation with ionization potentials is slightly less satisfactory. All calculations, except for one, give the same orbital sequence and therefore, based on Koopmans theorem⁸⁾, lead to the same

assignments of the ionization bands to ionic states or molecular orbitals. Only the ab initio calculation would give an inverted assignment of the sixth and seventh IP. Average deviations of orbital energies ϵ from IPs amount to 0.40, 0.61, and 1.61 eV for AM1, MNDO and ab initio calculations, respectively.

Table 2. Structure parameters [pm, °] of compound 1

	MW ^{a)}	AM1	MNDO	MP2/ 6-31G* ^{b)}
F-N	144.4	135.0	128.1	143.2
N _α -N _β	125.3	128.4	129.7	128.2
N _β -N _ω	113.2	113.2	112.5	115.4
F-N-N	103.8	114.9	113.5	103.8
N-N-N	170.8	171.9	165.4	171.6

^{a)} r_s values from ref.²⁾. — ^{b)} From ref.²⁾.

As has been observed for monohaloacetylenes⁹⁾, halogen isocyanates¹⁰⁾, and other compounds¹¹⁾, the ionization energies are a linear function of the ionization potentials of the free halogen atoms⁶⁾. This is illustrated in Figure 2 for the halogen azides 1–3. The correlation for all IPs is linear within experimental error limits. The gradient of each line is an indication of halogen involvement in the particular orbital.

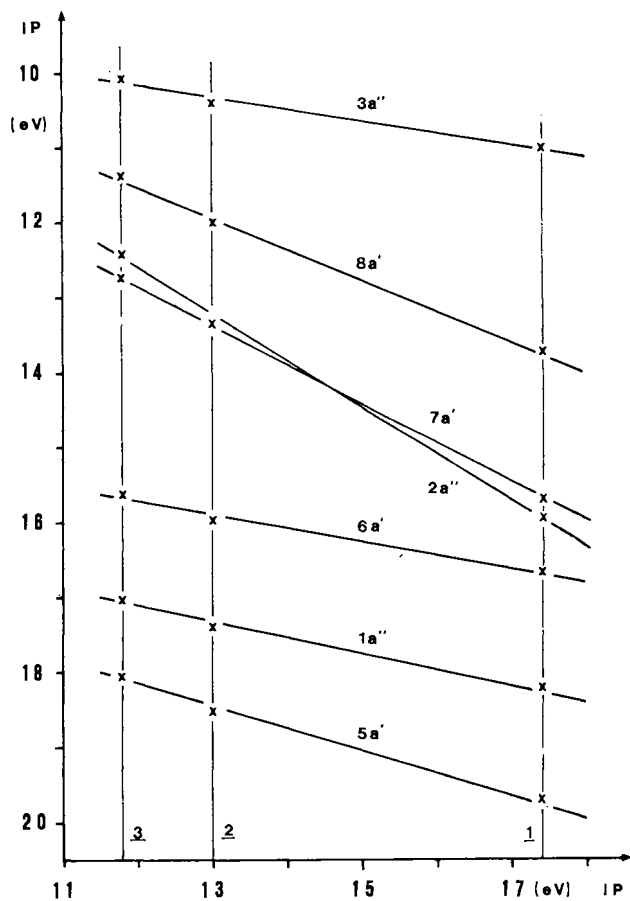


Figure 2. Ionization potentials of azides 1–3 plotted versus the ionization potentials of the free halogen atoms (IPs of 2 and 3 from ref.¹⁰⁾)

It is quite instructive to compare the IPs of 1 with those of hydrazoic acid¹²⁾ (4) and methyl azide¹³⁾ (5). A correlation diagram is given in Figure 3. The first IP of 1 (11.01 eV) and 4 (10.74 eV) are very close to each other while that of 5 (9.81 eV) is about 1 eV smaller. The HOMO of these molecules, the essentially non-bonding π MO ($2a''$ of 4, $3a''$ of 1 and 5), is destabilized through hyperconjugation by the methyl group while the fluorine atom leads only to a small inductive stabilization. The latter is a result of the "perfluoro effect"^{11,14)} which in certain cases allows to distinguish σ and π MOs. Substitution of fluorine for hydrogen in an unsaturated molecule has a much larger stabilizing effect on the σ MOs (2–3 eV) than on the π MOs (<0.5 eV). The different behaviour of σ (and n) and π MOs is clearly perceptible from Figure 3.

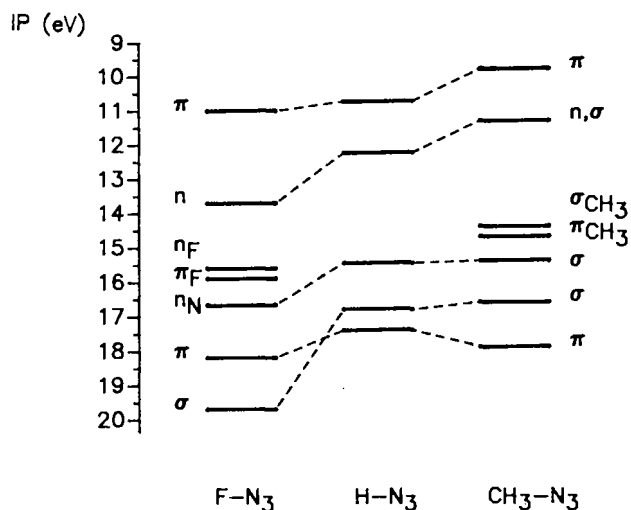


Figure 3. Correlation diagram of ionization potentials of compounds 1, 4, and 5

Molecular orbitals of 1, calculated by the MNDO method⁴⁾, are presented graphically in Figure 4. In accordance with Figure 2, MOs $8a'$, $7a'$, and $2a''$ show large coefficients on the fluorine atom, while the fluorine atomic orbitals contribute only little to MOs $3a''$, $6a'$, and $1a''$.

The instable molecule N_3F is characterized by very weak N–F and $N_\alpha N_\beta$ bonds²⁾. This is consistent with considerable stabilization of the MOs $8a'$, $7a'$, and $2a''$ compared to 2 and 3 (see Figure 2). These orbitals are either N–F ($8a'$) or $N_\alpha N_\beta$ antibonding ($7a'$, $2a''$). Accordingly, the X–N bond is weakened on going from bromine to fluorine azide. While 2 has a quite normal Cl–N bond¹⁵⁾, an unusual long F–N distance was found for 1²⁾. This correlates well with the relative stabilities of these molecules. 1 is not only thermally less stable than 2 and 3 but is one of the least stable of all known covalent azides.

Experimental

N_3F was prepared from HN_3 and F_2 as described elsewhere¹⁾. During transport from Hannover to Essen and during measurement the gaseous sample (20 mg) was kept at dry-ice temperature. The compound was introduced to the target chamber through a needle valve at room temperature. The PE spectrum was recorded with a UPG 200 spectrometer of Leybold-Heraeus equipped with a He(I) lamp (21.21 eV) as radiation source. The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 eV and of argon at

15.759 and 15.937 eV. The accuracy of the measurements is approx. ± 0.03 eV for ionization potentials, for broad or overlapping signals

it drops to ± 0.1 eV. The small amount of substance and its decomposition under measurement did not permit full resolution of vibrational fine structure of all ionization bands.

MO plots (Figure 2) were drawn with the program PERVAL¹⁶.

CAS Registry Numbers

1: 14986-60-8 / 2: 13973-88-1 / 3: 13973-87-0 / 4: 7782-79-8 / 5: 624-90-8

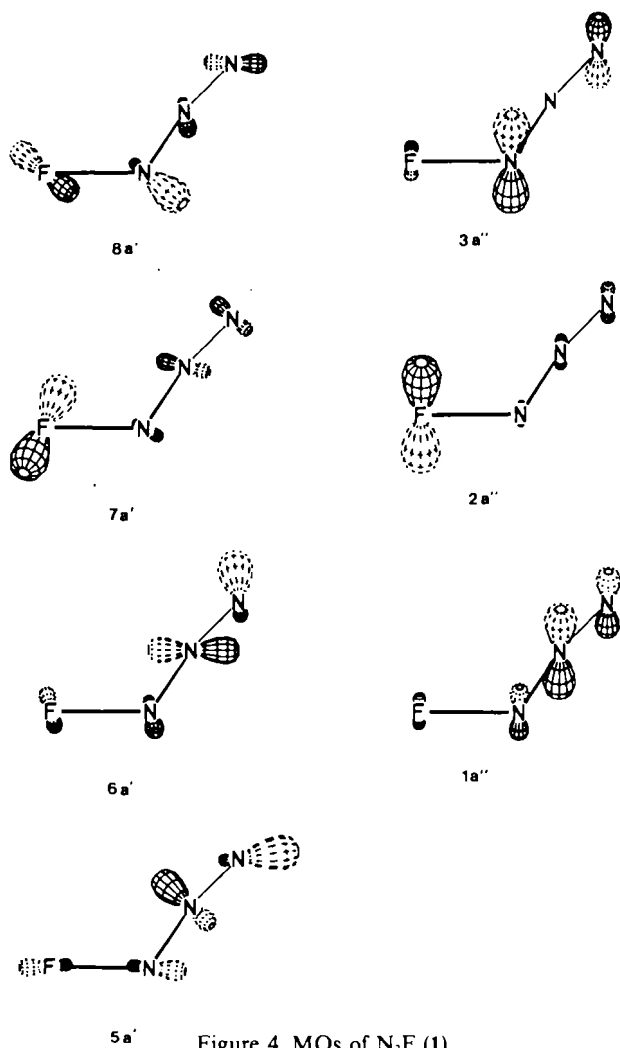


Figure 4. MOs of N₃F (1)

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[266/87]