Photoelectron-Spectrum and Electronic Structure of Perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane) $(CF_3)_2N–O–N(CF_3)_2$

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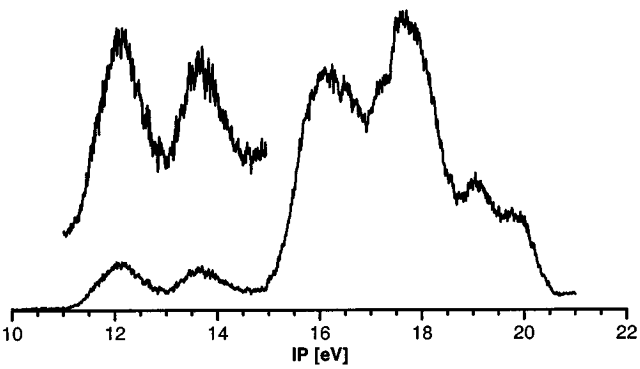
The electronic structure of the title compound **1** has been investigated by UV photoelectron spectroscopy and quantum chemical calculations. **1** has two nearly degenerate n_N lone-pair orbitals which form the two highest occupied MOs. The third highest occupied MO is mainly localized at the oxygen atom (n_0). All calculations indicate that the molecule has a twisted C_2 conformation.

We have recently reported a synthesis and gas-phase electron-diffraction structure analysis of perfluoro(2,4-dimethyl-3-oxa-2,4-diazapentane), $(CF_3)_2N-O-N(CF_3)_2$ (**1**).[1] This compound consists of an N−O−N chain that is substituted by four CF_3 groups. The structure analysis indicated that the molecule has C_{2v} symmetry and an sp,sp conformation in which both nitrogen electron lone-pairs are synperiplanar to the vicinal N−O bond. The electronic structure of this molecule is characterized by electron lone-pairs on three neighbouring (directly bound) atoms which makes it an ideal candidate to study the mutual interactions of such orbitals. We have investigated the electronic structure of **1** by photoelectron (PE) spectroscopy and quantum chemical calculations. The measured ionization potentials are summarized in Table 1 together with the relevant results of the calculations. The PE spectrum of **1** is depicted in Figure 1. In Figure 2 plots of the three highest occupied molecular orbitals are shown.

Figure 1. PE spectrum of $(CF_3)_2N-O-N(CF_3)_2$ (**1**)



The PE spectrum consists of two broad bands with minor intensities, centred at about 12.2 and 13.7 eV, and several broad bands with larger intensities between 15 and 21 eV. Since the intensity of the first band is somewhat larger than that of the second, two ionization events contribute to it although it is not possible to assign different *IP* values to them. For the first band beginning ionization corresponding to the adiabatic ionization energy can be localized at 11.0 eV while the vertical *IP* is at 12.15 eV. For the second band the adiabatic value can be estimated to 12.7 eV.

For analysis of the electronic structure of **1** and the interpretation of the PE spectrum quantum chemical calculations on different levels of theory were performed. Semiempirical methods like AM1[2] and PM3[3] are known to be superior to simple ab initio methods, in particular for the

Table 1. Ionization potentials *IP* [eV] and orbital energies ε [eV] of $(CF_3)_2N-O-N(CF_3)_2$ (**1**)

		B3LYP/6−31+G*		B3LYP/ 3−21+G*	HF/ 6−31+G*	AM1	PM3	Assignment	
IP_v exp.	IP_v	IP_a	$-\varepsilon$	$-\varepsilon$	$-\varepsilon$	$-\varepsilon$	$-\varepsilon$		
12.15[a]	11.90	10.82	9.76	10.62	13.90	12.91	12.83	$n_N{}^+$	(A)
			9.74	10.79	14.26	12.99	12.92	$n_N{}^-$	(B)
13.70[b]			11.13	12.24	16.16	13.95	14.57	n_O	(B)
16.2			12.35	13.02	17.82	14.78	15.87	σ	(A)

[a] IP_a = 11.0 eV. − [b] IP_a = 12.7 eV.

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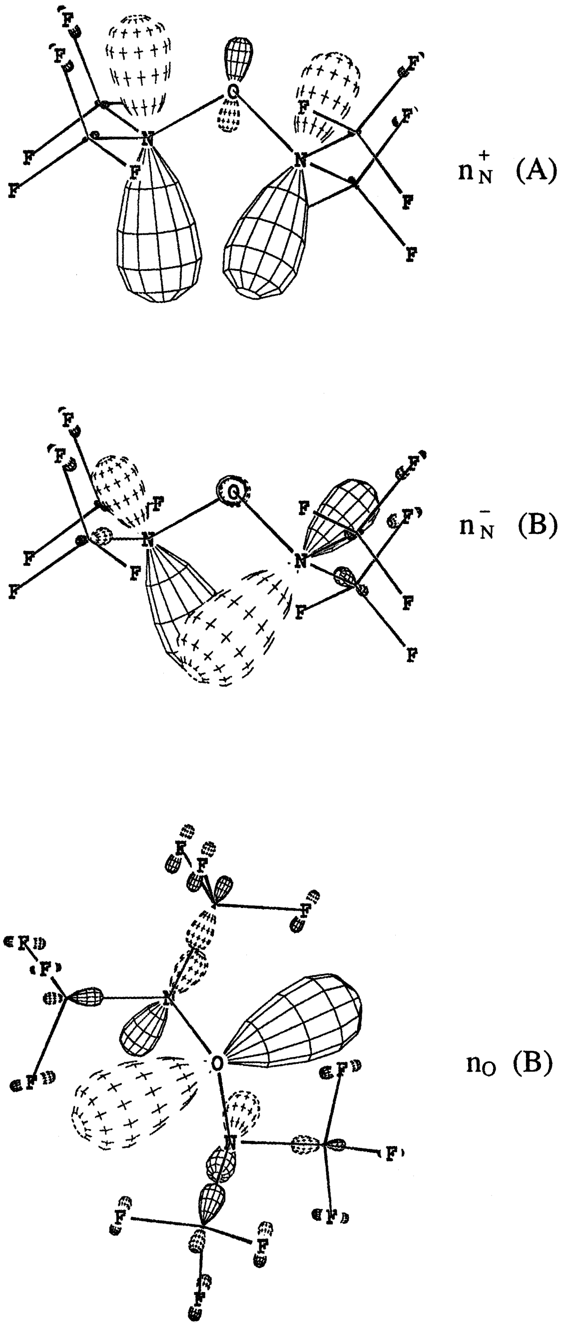
Figure 2. Plots of the three highest occupied MOs of $(CF_3)_2N-O-N(CF_3)_2$ (**1**) (PM3 results)



calculation of orbital energies ε_i which can be used to assign ionization potentials (IP_i) making use of the Koopmans theorem, $IP_i = -\varepsilon_i^{SCF}$.[4] These methods are, however, often of limited value for molecules like **1** with vicinal electron lone-pairs since their interaction is not correctly reproduced which often leads to wrong conformations. Good results have been obtained for a variety of molecules with the Becke3LYP (B3LYP) method,[5] a hybrid Hartree-Fock/density functional theory (HF/DFT) method.[6][7] This method also leads to excellent values for the first adiabatic ionization potential, $IP_{1,a}$, as the energy difference of the molecule and the radical cation. By performing single-point energy calculations for the radical cation on the molecule's geometry, i.e. without allowing for relaxation during ionization, the first vertical IP, $IP_{1,v}$, is accessible. Total energies from these calculations are given in Table 2; orbital energies and calculated IP values are listed in Table 1.

All theoretical methods lead to a C_2 structure as the most stable conformer of **1** that is twisted from the C_{2v} structure by about 30° as measured from the C−N···N−C dihedral angles. For the untwisted C_{2v} structure higher energy values of 1.0−5.8 kcal mol^{-1} were obtained. These results indicate that the molecule has a double minimum (W shaped) energy potential for its deformation, both C_2 minima are equally populated, and transition between the conformers through the C_{2v} conformation is rapid. This makes it difficult to distinguish experimentally between C_2 and C_{2v} symmetry. In Table 3 the structure parameters of **1** as obtained from electron diffraction,[1] from HF and from B3LYP calculations using the basis set 6−31+G* are compared. The agreement between experimental and theoretical data is generally not quite satisfactory. Deviations are smaller for the B3LYP than for the HF results and for C_2 than for C_{2v} symmetry. The latter observation may be considered as an additional indication for a twisted conformation of **1**.

The orbital energies given in Table 1 refer to the more stable C_2 conformer and correspond to the structure of minimum energy found by the respective method. All calculations lead to the same interpretation of the spectrum: The first two ionizations, which are nearly degenerate, are assigned to the two n_N MOs, and the third ionization is assigned to the n_O^p MO. The strong bands centred at about 16.0 and 17.5 eV are mainly composed of n_F ionizations. When only the first three MOs are considered, the energies calculated for ε by the AM1 method show the best agreement with the IP values, but there is only a minor difference to the PM3 results, while − as expected − the orbital energies of the ab initio methods cannot be used equally well. Deviations from the Koopmans theorem[4] of 0.3−0.8 eV are found for the AM1 results, the PM3 values are more uniformly wrong by 0.7−0.9 eV, and the deviations of the ab initio methods range from −1.4−(−1.5) eV (B3LYP/6−31+G*) to 1.8−2.5 eV (HF/6−31+G*). Although it has to be admitted that caution is necessary, the AM1 and the PM3 method can be praised for their performance in the interpretation of the PE spectrum of **1**. In comparing the quality of the computational methods, not only the size of the deviations but also their uniformty has to be considered and according to this aspect the B3LYP/6−31+G* results rank first.

Leaving the limitations of the Koopmans theorem,[4] and calculating the first adiabatic and vertical IP from the energy difference of molecule and radical cation, the values obtained on the B3LYP/6−31+G* level of theory are in quite satisfactory agreement with the experimental ones (Table 1).

As is evident from Figure 2, there are coefficients on all atoms of the N−O−N chain in the three highest occupied

Table 2. Calculated total energy E [au] and enthalpy of formation ΔH_f [kcal mol^{-1}] of two conformers and the radical cation $M^{+\cdot}$ of $(CF_3)_2N{-}O{-}N(CF_3)_2$ (**1**)

	E B3LYP/6−31+G*	E HF/6−31+G*	ΔH_f AM1	ΔH_f PM3
sp,sp (C_2)	−1535.2127732	−1528.4542501	−521.46	−598.23
sp,sp (C_{2v})	−1535.2065303	−1528.4450707	−520.51	−595.74
$\Delta(C_{2v}-C_2)$ [a]	3.92	5.76	0.95	2.49
$M^{+\cdot}$[b]	−1534.7755083			
$M^{+\cdot}$[c]	−1534.8149655			

[a] kcal mol^{-1}. − [b] Single-point calculation on the molecule's structure. − [c] Optimized structure.

Table 3. Structure parameters [pm,°] of $(CF_3)_2N{-}O{-}N(CF_3)_2$ (**1**) from electron diffraction (ED), ab initio HF and B3LYP calculations

	ED[a] (C_{2v})	B3LYP[b] (C_{2v})	B3LYP[b] (C_2)	HF[b] (C_{2v})	HF[b] (C_2)
N−O	146.2(8)	143.8	142.4	139.2	138.1
N−C	143.5(4)	147.2	145.9, 146.1	145.2	144.0, 144.3
C−F	132.3(2)	132.9−134.6	133.2−135.0	130.0−131.4	130.3−131.7
N−O−N	105.2(2.6)	112.3	109.7	114.1	111.0
C−N−C	117.9(1.2)	114.9	117.2	115.0	117.3
O−N−C	109.3(8)	107.2	107.6, 109.2	107.6	108.0, 109.5
F−C−F	109.3(2)	108.1−108.5	108.0−109.2	108.2−108.6	108.2−109.2
C−N···N−C	0.0	0.0	30.8	0.0	32.8

[a] From ref.[1]. − [b] Basis set 6−31+G*.

MOs of **1** indicating mutual interaction of n_N and n_O orbitals. The nearly degenerate energy levels of the two n_N MOs are closely related to the sp,sp conformation of **1** in which both nitrogen electron lone-pairs are synperiplanar to the opposite N−O bonds;[1] $n_N{}^+$ and $n_N{}^-$ are the symmetric and antisymmetric linear combination of the two nitrogen lone-pair orbitals (n_1 and n_2), respectively, with reference to the relevant symmetry operation. The MOs depicted in Figure 2, which correspond to the C_2 structure obtained with the PM3 method (torsional angle 31.3°), should be considered as qualitative illustrations, since the shape of the MOs varies with the structure and the method used in the calculation.

The energy difference Δn_N of $n_N{}^+$ and $n_N{}^-$ is attributed to the interaction of n_1 and n_2 and is dependent on their mutual geometrical orientation.[8] In 1,3-diamines Δn_N values between 0 and more than 1 eV have been observed by PE spectroscopy.[9] The PE spectrum of 1,3-diazaadamantane[10] shows two well-separated n_N ionization bands at 7.75 ($n_N{}^-$) and 8.78 eV ($n_N{}^+$). The orientation of the lone-pairs in this compound corresponds to the ap,ap conformation of **1**,[1] in which the nitrogen electron lone-pairs are antiperiplanar to the vicinal N−O bonds, and the splitting is dominated by through-space interaction. On the other hand, 2-substituted 1,3-dimethylimidazolidines[11] have a single broad band, and the energies of the two n_N orbitals are split by only 0.0−0.3 eV indicating little interaction, which is consistent with envelope conformations of the five-membered ring and an axial-equatorial orientation of the two *N*-methyl groups.

For the sp,sp conformation of **1** one would expect good through-space interaction of the nitrogen lone-pair orbitals n_1 and n_2 leading to a sizeable Δn_N value and an energy sequence $n_N{}^- > n_N{}^+$. However, this interaction would have its maximum value in the undistorted C_{2v} conformation (see below), whereas the torsion in the C_2 form will reduce the overlap of n_1 and n_2 and thus result in a smaller Δn_N. The splitting is then obviously overcompensated by n_N/n_O interactions. The $n_O{}^p$ orbital is geometrically orthogonal to n_1 and n_2 in the C_{2v} form so that there will be some interaction only in twisted C_2 conformations. On the other hand, the $n_O{}^s$ orbital overlaps effectively with n_1 and n_2. However, only the linear combination $n_N{}^+$ has the same symmetry as $n_O{}^s$ so that this orbital is destabilized while $n_N{}^-$ remains unaffected. This vicinal n_N/n_O interaction is also conformation dependent having its maximum extent in the untwisted C_{2v} form. For this conformation the following MO energies are calculated with the B3LYP/6−31+G* method: −9.75 eV ($n_N{}^+$, A_1), −10.22 eV ($n_N{}^-$, B_2), −10.78 eV (n_O, B_1). In this case the two n_N MOs would no longer be nearly degenerate, and accordingly the first two *IP*s of the PE spectrum should be sufficiently split in order to be detected separately. The actual PE spectrum is thus an indication of the twisted C_2 form. Here the $n_N/n_O{}^s$ interaction is obviously approximately of the same magnitude as the 1,3-n_N/n_N interaction which explains the observed orbital degeneracy $n_N{}^+ \approx n_N{}^-$ of **1**.

That the conformational properties of **1** are mainly determined by the mutual interactions of the electron lone-pairs is also indicated by the large difference between adiabatic and vertical *IP* values of more than 1 eV for the first and the third *IP*. The ionizations reduce the electrostatic repulsion of the electron pairs and lead to a less twisted, i.e. more C_{2v} like, conformation of the radical cation than in the neutral molecule.

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Experimental Section

The PE spectrum of **1** was recorded with a Leybold-Heraeus UPG200 spectrometer equipped with an He(I) radiation source (21.21 eV). The spectrum was calibrated with the lines of xenon at 12.130 and 13.436 and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ± 0.03 eV for ionization energies, for broad and overlapping signals it was only ± 0.1 eV.

Semi-empirical AM1[2] and PM3[3] calculations were performed with the MOPAC[12] program package (version 6.1, IBM version of MOPAC 6.00), ab initio HF[13] and Becke3LYP[5] calculations with the program GAUSSIAN 94.[14] Geometries were fully optimized at the respective levels of theory. In the AM1 and PM3 calculations the keyword "PRECISE" was used to tighten the convergence criteria. MOs were plotted by using the program PERVAL.[15]

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