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Theoretical investigation on the conformational space of perfluorohydroxylamine, F₂NOF

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Abstract

The conformational space of perfluorohydroxylamine, F₂NOF, is studied using the CCSD/aug-cc-pVDZ level of theory. It is found that the lowest-energy form of F₂NOF exhibits an *anti* conformation. This finding agrees with other theoretical studies, which indicate that the *anti* form is the most stable conformation upon H₂NOH fluorination on oxygen and/or nitrogen takes place [L. Radom, W.J. Hehre, J.A. Pople, J. Am. Chem. Soc. 94 (1972) 2371]. On the other hand, the present result is in complete disagreement with recent theoretical studies, in which the *syn* form of F₂NOF is proposed to be the minimum-energy conformation [P. Antoniotti, F. Grandinetti, Chem. Phys. Lett. 366 (2002) 676]. An NBO analysis at the B3LYP/aug-cc-pVDZ level of theory reveals that the interaction between the nitrogen lone pair and the OF antibond on one hand, and interactions between one oxygen lone pair and the two NF antibonds on the other hand, are responsible for the deep minimum, in which the *anti* conformer lies. Only those stabilizing interactions originated in the abovementioned oxygen lone pair accounts for the very flat region, in which the *syn* form is located.
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1. Introduction

Recently, Antoniotti and Grandinetti [1] carried out a detailed theoretical investigation on the mechanism of the reaction between the ¹D state of the oxygen atom and NF₃. The authors used the coupled-cluster (CC) method at different levels of approximation together with *correlation consistent* basis sets. Geometry optimizations and harmonic vibrational frequency calculations at the CCD/cc-pVDZ level of theory were performed for all the species involved in the mechanism under study in

[1]. Further, the geometries were refined using the CCSD/cc-pVDZ method but no new frequencies were obtained. Single point calculations at the CCSD(T)/ aug-cc-pVDZ level were finally accomplished by the authors to improve on the quality of some thermodynamic magnitudes.

Relevant to the present work is the following reaction, labeled (1b) in [1]

$$\text{O–NF}_3 \rightarrow [\text{TS}] \rightarrow \text{F}_2\text{N–OF} \tag{1}$$
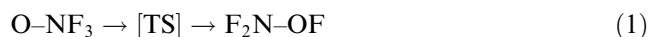
The authors claim that a *syn* conformation, in which the nitrogen lone pair is in a synperiplanar orientation with respect to the OF single bond, is a true minimum on the F₂NOF potential energy surface according to a first real frequency of 28.5 cm^{-1}. We note, however, that

the implementation of the CC method used by the authors provides numerical vibrational frequencies instead of analytical ones. It is in general accepted that numerical frequencies are subject to errors that can be as large as some tens of cm^{-1}. It is evident that the above frequency lies within that error.

Earlier works using semiempirical [2] and Hartree–Fock methods [3] suggest that the *anti* conformation, in which the nitrogen lone pair is in an antiperiplanar orientation with respect to the OF single bond, is the most stable form of F_2NOF instead of the *syn* one. Feller and Dixon perform a series of CCSD(T)/aug-cc-pV6Z calculations to determine the heat of formation of the parent molecule hydroxylamine, H_2NOH [4]. These authors report that the *syn* form of the molecule is more stable than an *anti* form by about 4.7 kcal/mol. Microwave spectroscopic studies on hydroxylamine also demonstrate that the *syn* conformation is the dominant one in the gas phase [5]. Interestingly, modest ab initio calculations seem to suggest that H_2NOH fluorination at oxygen and/or nitrogen leads to a reversal in the relative stability of the *syn* and *anti* forms [6]. This transposition could be in principle explained as an increase in the anomeric effect upon fluorination [7]. The anomeric effect can be defined in terms of the natural bond orbital (NBO) method as an interaction between the lone pair of an electronegative atom and a vicinal sigma antibond. Finally, we would like to mention that as part of our studies on the conformational behavior of species containing a single NO bond, the related molecule *N,N*-difluoro-*O*-trifluoromethylhydroxylamine, F_2NOCF_3, is investigated using both Ar-matrix IR spectroscopy and the B3LYP, B3PW91 and MP2 methods and triple-ζ plus polarization and diffuse functions basis sets [8]. It is found that a conformation, in which the CO bond is *syn* with respect to the nitrogen lone pair, is the most stable form of F_2NOCF_3. A gauche conformation, in which the CO bond forms a dihedral angle of 165.4° with the lone pair on nitrogen, was also found to be stable and located at 4.4 kcal/mol above in energy. These findings are rather surprising since the NBO analysis of different donor–acceptor interaction energies for several F_2NOCF_3 conformations suggests that the *anti* form would be the most stable form. Strong $n(N) \rightarrow \sigma^*(CO)$ and $n(O) \rightarrow \sigma^*(NF)$ interactions are the main responsible for the hypothetical stabilization of the *anti* form. It is argued in [8] that both steric and bond–bond repulsion interactions between the NF_2 and CF_3 groups contribute to the observed destabilization of the *anti* conformation. Thus, the study of a species without steric constraints, such as F_2NOF, would be of help to understand in more detail the conformational features of F_2NOCF_3.

In view of the lack of experimental information on F_2NOF and some discrepancies between theoretical methods concerning its minimum conformation, a deeper investigation at higher levels of theory on the F_2NOF molecule would be welcome. A CCSD/aug-cc-pVDZ study of the conformational space of perfluorohydroxylamine is presented in this work. Moreover, a natural bond orbital analysis is accomplished at the B3LYP/aug-cc-pVDZ level of theory to shed light into the relative stability of the different conformers.

2. Method and computational details

The CCSD method (see [9] for a good introduction to the CC theory) and the correlation consistent aug-cc-pVDZ basis set [10] as implemented in the Gaussian 98 package [11] are used to scan the potential energy surface of F_2NOF as a function of $\tau(FONF)$. All geometric parameters, except for the dihedral angle under study, are optimized without constraints for all the starting geometries chosen to scan the potential energy surface of F_2NOF.

For some relevant conformers, a vibrational frequency analysis is performed at the CCSD/aug-cc-pVDZ level of theory. It must be stressed that the vibrational frequencies to be reported in the present work are obtained through numerical differentiation of the total energy with respect to the nuclear coordinates.

For the conformers found at the CCSD/aug-cc-pVDZ level of theory, a NBO analysis [12] is performed using the B3LYP hybrid exchange-correlation functional [13a,b] of the density functional theory [14a,b] together with the aug-cc-pVDZ basis set as implemented in the Gaussian 98 package [15]. A grid having 99 radial shells and 590 angular points per shell is used for numerical integrations to reduce as much as possible the errors associated with the lack of analytical formulae.

3. Results and discussion

Fig. 1 shows the potential energy curve of perfluorohydroxylamine, F_2NOF, as a function of the $\tau(F1NOF3)$ dihedral angle obtained at the CCSD/aug-cc-pVDZ level of theory (atom labels are defined in that figure). Table 1 summarizes some of the geometric parameters of the two conformers shown in the figure.

It can be seen from the table that there exists an excellent agreement between the geometric parameters calculated for the *syn* conformation at the CCSD/aug-cc-pVDZ level of theory and those reported by Antoniotti and Grandinetti [1]. However, the CCSD/aug-cc-pVDZ vibrational analysis shows that this species is a first-order saddle point on the potential energy surface of F_2NOF with a vibrational frequency of 33.6 i cm^{-1}. This finding is in complete disagreement with the results reported in [1]. It should be noted, nevertheless, that the *syn* conformation lies on a very flat
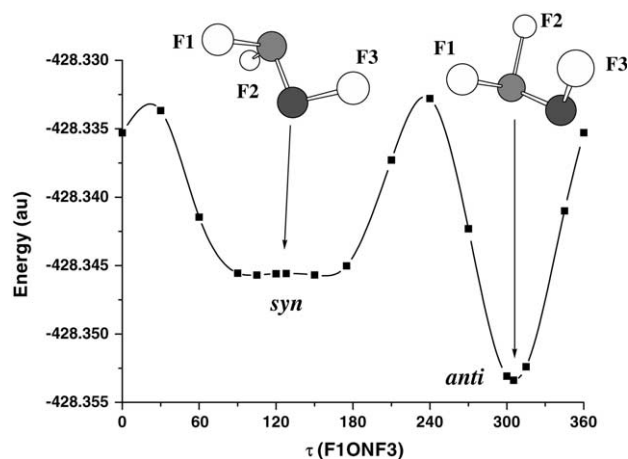
Fig. 1. Potential energy curve as a function of τ(F1NOF3) for the F$_2$NOF molecule calculated at the CCSD/aug-cc-pVDZ level of theory. See text and Table 1 for details. White, light grey, and dark grey represent fluorine, nitrogen, and oxygen, respectively.

Table 1
Selected geometric parameters for the *syn* and *anti* conformations of F$_2$NOF calculated at the CCSD/aug-cc-pVDZ (CCSD for short) and B3LYP/aug-cc-pVDZ (B3LYP for short) levels of theory

Parameter	CCSD		B3LYP	
	syn[a]	*anti*	*syn*	*anti*
r(NO)	1.394 (1.397)	1.330	1.383	1.259
r(NF1)	1.389 (1.382)	1.385	1.397	1.392
r(NF2)	1.389 (1.382)	1.385	1.397	1.393
r(OF3)	1.431 (1.435)	1.464	1.428	1.540
α(F1NO)	102.4 (102.5)	108.0	102.8	112.4
α(F1NF2)	101.0 (101.4)	101.7	100.9	102.3
α(NOF3)	102.1 (102.3)	109.4	103.1	111.9
τ(F1NOF3)	127.9	305.3	127.5	302.6

Bond lengths, r, are in Å. Bond angles, α, and dihedral angles, τ, are in degrees. See Fig. 1 for the meaning of labels.
[a] Values from [1] are given in parentheses.

region of the curve shown in Fig. 1. Thus, better levels of theory could well alter the present picture [16]. On the other hand, there exists an *anti* conformation, which is lower in energy than the *syn* one by 4.9 kcal/mol. The corresponding vibrational analysis shows that this conformation is a true minimum on the potential energy curve of F$_2$NOF. An examination to its geometric parameters in Table 1 indicates that the OF3 bond distance undergoes an enlargement of more than 0.03 Å at the CCSD/aug-cc-pVDZ level of theory, whereas the NO bond distance decreases by more than 0.06 Å. In line with these results, the F1NO and NOF3 bond angles strongly increase about 6–7°. A F1NOF3 dihedral angle of about 305° indicates that the OF3 bond is almost *anti* with respect to the lone pair on the nitrogen atom. These findings agree well with the suggestion made in [6] concerning the reversal in the relative stability of *syn* and *anti* conformations on hydroxylamine upon fluorination. These facts clearly indicate that the

thermodynamics involved in reaction 1, and hence the free energy profile shown in Fig. 2 of [1], deserve a revision. Seeking for completeness, the harmonic vibrational frequencies of the *anti* conformer obtained at the CCSD/aug-cc-pVDZ level of theory are listed in Table 2 together with a supposed assignment in the hope that it could be a useful guidance in future experimental measurements. The assignment is based on inspection of displacement vectors associated with the calculated normal modes and on the comparison with related species such as H$_2$NOH [17a,b].

To get a deeper understanding on the relative stability of the *syn* and *anti* forms of F$_2$NOF, a NBO analysis at the B3LYP/aug-cc-pVDZ level of theory is performed for all conformers included in Fig. 1 [15]. This model is chosen because the calculated potential energy curve as a function of τ(F1NOF3) is strikingly similar to that of the CCSD method as can be seen from Fig. 2. An important difference arises between the CCSD and B3LYP results, however. The *syn* conformation is a minimum on the potential energy curve of F$_2$NOF at the B3LYP level with the lowest vibrational frequency amounting to 33.3 cm^{-1}. We believe, nevertheless, that this fact does not affect the overall picture provided by the NBO analysis on the features of the different conformations.

For completeness, Table 1 also lists the relevant geometric parameters of the two conformations under study obtained at the B3LYP/aug-cc-pVDZ level of theory. It can be seen from the table that the geometry of the *syn* form is well reproduced by the hybrid density functional theory with some minor departures from the CCSD geometry. The *anti* conformer, on the other hand, presents important deviations from the CCSD geometry, specially for the NO and OF3 bonds and the F1NO and NOF3 bond angles. Unfortunately, experimental geometric data for molecules of the type R$_2$NOF are not available. It should be noted, however, that
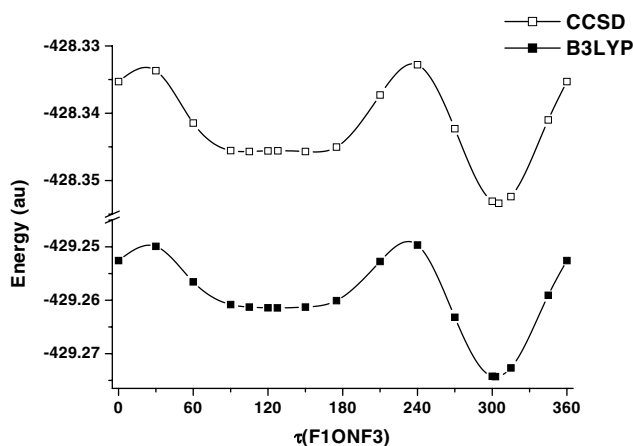

Fig. 2. Potential energy curves as function of τ(F1NOF3) for the F$_2$NOF molecule calculated at the CCSD/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels of theory.

Table 2
Harmonic vibrational frequencies (in cm^{-1}) and assignment for the *anti* conformer of F_2NOF obtained at the CCSD/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels of theory

Mode	CCSD/aug-cc-pVDZ	B3LYP/aug-cc-pVDZ[a]	Assignment
ν_1	1061	1166 (34)	NF symmetric stretching (A′)
ν_2	896	865 (27)	NO stretching (A′)
ν_3	815	756 (6)	FNF deformation (A′)
ν_4	726	573 (0.3)	OF stretching (A′)
ν_5	553	567 (62)	NOF bending (A′)
ν_6	523	490 (27)	NF_2 wagging (A′)
ν_7	962	903 (100)	NF antisymmetric stretching (A″)
ν_8	281	220 (10)	NF_2 rocking (A″)
ν_9	200	197 (0.1)	NF_2 twisting (A″)

The assignment is based on the C_s point group.
[a] Calculated band intensities are given in parentheses (100 ≡ 213.6 km/mol).

Minkwitz et al. [18] perform a theoretical study on the $(CF_3)_2NOF$ molecule by using both Hartree–Fock and B3LYP methods together with a 6-311G* basis set. Those authors find that the calculated OF bond distance is 1.379 Å for the HF method and 1.577 Å for the B3LYP one. That important difference is in line with the discrepancy between the CCSD and B3LYP methods found in the present work. As far as we know, no further systematic studies have been performed on R_2NOF molecules to elucidate their geometric and conformational features. It is worth mentioning, nevertheless, that the same trend in the change of the geometric parameters between the *syn* and *anti* conformations is preserved when passing from the CCSD level of theory to the B3LYP one.

The harmonic vibrational frequencies of the *anti* form of F_2NOF obtained at the B3LYP/aug-cc-pVDZ level of theory are listed in Table 2. The calculated frequencies follow the same trend as the bond distances do, see Table 1. Thus, the calculated OF stretching mode is 726 and 573 cm^{-1} for the CCSD/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ levels of theory, respectively.

An inspection to the NBO occupancies allows us to explain in more detail the differences in the geometries of the *syn* and *anti* forms shown in Table 1. The relevant NBO occupancies are listed in Table 3. It can be argued from this table that the important shortening observed in the NO bond distance in the *anti* form with respect to the *syn* conformation is mainly due to a considerable

Table 3
Occupancies of selected natural bond orbitals, in |e|, for the *syn* and *anti* forms of F_2NOF obtained at the B3LYP/aug-cc-pVDZ level of theory

NBO	*syn*	*anti*
n(N)	1.98048	1.77462
n_2(O)	1.91403	1.83146
σ*(F1N)	0.10385	0.14984
σ*(F2N)	0.09099	0.14280
σ*(NO)	0.06416	0.05616
σ*(OF3)	0.03895	0.27557

decrease in the occupancies of the nitrogen and π oxygen (in the canonical representation [19]) lone pairs, thus diminishing the strong lone pair–lone pair interaction. Moreover, a modest decrease in the occupancy of the NO antibond also favors the strengthening of the bond in the *anti* form. The lengthening of the OF3 bond in the *anti* form, on the other hand, could be explained by a huge increase of almost 0.25 e in the occupancy of the σ*(OF3) antibond.

A close examination to the second-order perturbation theory analysis of the Fock matrix in the NBO basis allows us to establish that the main contributions to the energy lowering are due to stabilizing interactions between the lone pairs on N and O and various antibonds of the F_2NOF molecule. Fig. 3 shows the overall interactions exhibited by the natural lone pairs of atoms F1, F2, F3, N, and O. It is clear from the figure that only those interactions due to the lone pairs on N and O follow the same trends the potential energy curves shown in Fig. 2 do. The contribution due to the lone pairs of
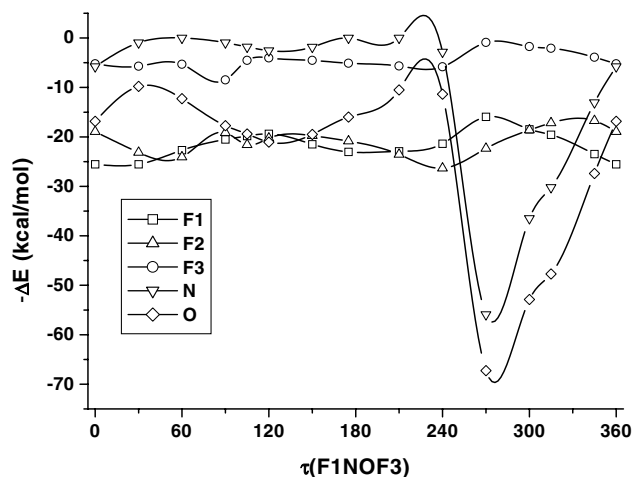
Fig. 3. Energy lowering (with the opposite sign) due to stabilization interactions between the lone pairs of every atom and several antibonds of the F_2NOF molecule as a function of τ(F1NOF3) calculated at the B3LYP/aug-cc-pVDZ level of theory.

the fluorine atoms, as expected, are of little importance to explain the relative stability of the *syn* and *anti* forms.

A detailed picture of the stabilizing interactions associated with the lone pairs of N and O is sketched in Figs. 4 and 5. It can be seen from Fig. 4 that only one interaction, namely n(N) → σ*(OF3), accounts for the overall stabilizing process due to the nitrogen lone pair. It should be noted, however, that there is only a minor contribution from that interaction to the stabilization of the *syn* conformation. On the other hand, Fig. 5 reveals that the stabilizing process associated with interactions between $n_2(O)$, the π oxygen lone pair in canonical notation [19], and the two σ*(FN) antibonds dominates the over-all interaction pattern. Contrary to the results mentioned above for the nitrogen lone pair, the canonical π oxygen lone pair exhibits important contributions to the stabilization of both conformers. It can be said in summary that the shallow region between 90° and 170° of the potential energy curve as function of the τ(FNOF) dihedral angle originates mainly from a stabilization interaction between an oxygen lone pair and NF antibonds, whereas the region about 300° presents contributions from stabilization interactions between the nitrogen lone pair and an OF antibond and between an oxygen lone pair and NF antibonds as mentioned above.

Fig. 4. Energy lowering (with the opposite sign) due to stabilization interactions between the lone pair of the nitrogen atom and several antibonds of the F_2NOF molecule as a function of τ(F1NOF3) calculated at the B3LYP/aug-cc-pVDZ level of theory. Note that the two NF antibonds, σ*(F1N) and σ*(F2N), are considered as a whole.
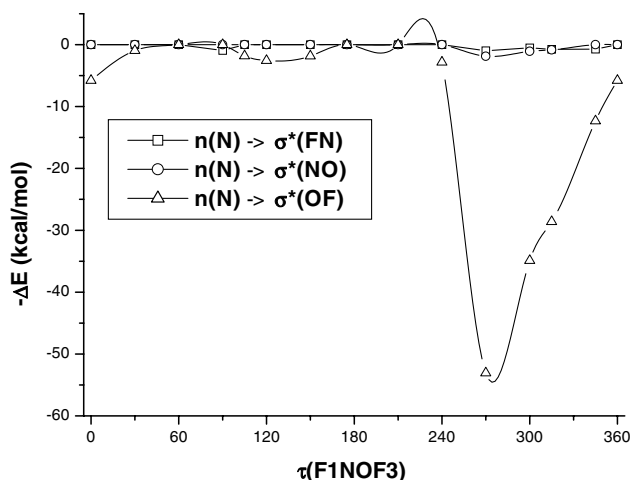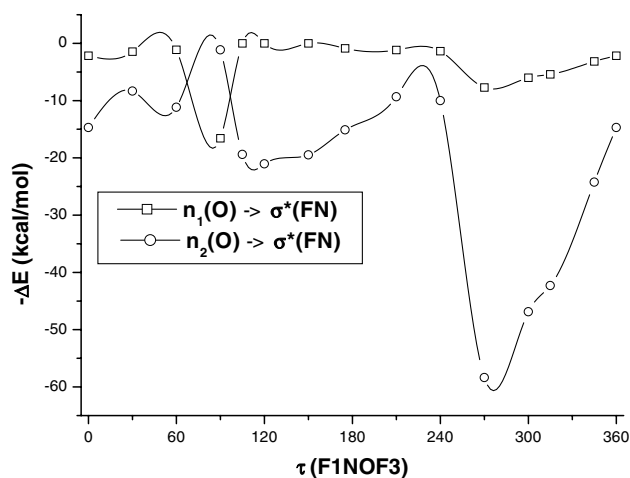

Fig. 5. Energy lowering (with the opposite sign) due to stabilization interactions between the lone pairs of the oxygen atom and several antibonds of the F_2NOF molecule as a function of τ(F1NOF3) calculated at the B3LYP/aug-cc-pVDZ level of theory. Note that the two NF antibonds, σ*(F1N) and σ*(F2N), are considered as a whole.

4. Conclusions

The conformational space of perfluorohydroxylamine, F_2NOF, as a function of τ(FNOF) was studied using the CCSD/aug-cc-pVDZ level of theory.

The most important finding reported in the present work is that the lowest-energy isomer of F_2NOF exhibits an *anti* conformation. This result agrees well with earlier theoretical studies, which indicate that the *anti* form becomes the most stable one upon H_2NOH fluorination on oxygen and/or nitrogen takes place [6]. On the other hand, this is in complete disagreement with results recently reported by Antoniotti and Grandinetti [1], who propose that in the minimum-energy conformer the OF bond is in a *syn* position with respect to the nitrogen lone pair. This conformation became a first-order saddle point on the potential energy surface of F_2NOF according to the present calculations at the CCSD/aug-cc-pVDZ level.

The relative stability of the *syn* and *anti* conformations was further investigated using a natural bond orbital analysis at the B3LYP/aug-cc-pVDZ level of theory. The natural bond orbital occupancies allowed to explain the considerable shortening found in the NO bond length in the *anti* form with respect to the *syn* one in terms of a decrease in the interaction between nitrogen and oxygen lone pairs. This is a consequence of an important diminishing in the occupancies of the corresponding natural lone pairs. A very modest decrease in the occupancy of the NO antibond also contributes to the NO bond shortening observed in the *anti* form. On the other hand, a very important increase in the occupancy of the OF antibond is mainly responsible for the enlargement exhibited by the OF bond length in the *anti* conformer with respect to the *syn* conformation.

The natural bond orbital analysis revealed that the interaction between the nitrogen lone pair and the OF antibond on one hand, and the interactions between one oxygen lone pair and the two NF antibonds on the other hand, follow the same trends as the potential energy curve as function of a τ(FNOF) dihedral angle. All those stabilizing interactions are responsible for the

deep minimum associated with the *anti* conformer. On the other hand, only those stabilizing interactions originating from the oxygen lone pair accounts for the very flat region, in which the *syn* conformation lies.

Acknowledgements

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