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FLUORINE AND HYDROGEN NITRATE: ROTATIONAL BARRIERS AND RESONANCE STRUCTURES*

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SUMMARY

While the magnitudes of the rotational barriers for $HONO_2$ and $FONO_2$ have been known for over 20 years, the conformation of $FONO_2$ has been established as planar only recently. The larger rotational barrier for $FONO_2$ (42 kJ/mole vs. 32 for $HONO_2$) seems counter-intuitive in light of the easily rationalized planarity of the $HONO_2$ and the controversial planarity of $FONO_2$. To provide insight into this phenomenon, the rotational barriers in $HONO_2$ and $FONO_2$ have been investigated using ab initio molecular orbital calculations including correlation. The calculated barriers agree well with the experimentally determined values. An explanation is offered for the relative and absolute magnitudes of the barriers.

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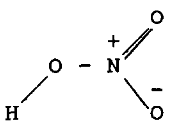
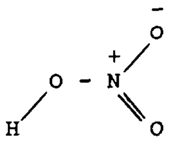
BACKGROUND

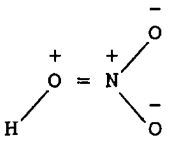
$HONO_2$ [1] has been well-established as planar. The rationalization for this conformation's preference is the stabilization derived from the $\delta+/\delta-$ attraction between the H and one terminal O (1a below). While resonance structure 1c is expected only to have a minor effect, it does support planarity. Also, the destabilizing effect of two formal positive charges adjacent to one another in 1c is mitigated by the stabilizing effect of $H^{\delta+}$ - $O^{\delta-}$ attraction.



1a

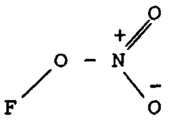


1b

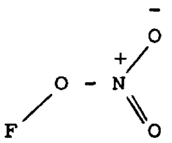


1c

Structural determination of fluorine nitrate has proven a formidable task for experimentalists [2] and theorists [3] alike. While $FONO_2$ is now unequivocally known to be planar, it is nonetheless hardly obvious why it should be. Indeed, simple resonance structure reasoning suggests the opposite. In particular, consider the three primary resonance structures for $FONO_2$, 2a-c, analogous to those for $HONO_2$.



2a



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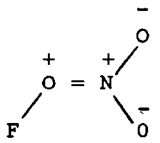
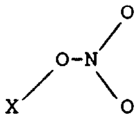


2c

Arguments against planarity have cited the destabilizing influence of $\delta-/\delta-$ repulsion between F and a terminal O (2a) and the minimal contribution of 2c because the positive oxygen is adjacent to both the positive nitrogen and an electron-withdrawing fluorine. Earlier calculations have shown [3] the planarity to be the result of very weak π-type bonding, both in the plane and perpendicular to the plane of the molecule.

The above reasoning would seem to suggest that the planarity of $HONO_2$ is more stabilized than the planarity of $FONO_2$.

One would then predict that the rotational barrier, the energy difference of the planar and perpendicular structures, 3 and 4, should be greater for $HONO_2$ than for $FONO_2$.



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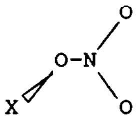

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Experimental studies show this conclusion to be false -- $E_{rot}(FONO_2)$ = 42 ± 4 kJ/mol[2c] and $E_{rot}(HONO_2)$ = 32 ± 0.4 kJ/mo. [4]. It is also surprising that the rotational barriers are so high. This paper presents ab initio calculations of the rotational barriers of $FONO_2$ and $HONO_2$ to examine why that of $FONO_2$ is larger than that of $HONO_2$.

Computational Method

All calculations were performed on the DEC VAX 11/780 using the GAUSSIAN 82 series of programs [5]. The planar and perpendicular forms of $FONO_2$ and $HONO_2$ (perpendicular means FON or HON plane perpendicular to NO_2 plane) were fully optimized using the 4-31G basis [6] and the 6-31G** basis [7]. The 6-31G** basis was used for $HONO_2$ because it provides p functions on H as well as the d functions on heavy atoms provided by 6-31G*. It has been shown that the 4-31G basis gives reliable geometries, i.e. bond lengths and angles close to the experimental values, for molecules containing N, O, and F [8]. The results for both bases are collected in Table I.

A single point calculation was done at the MP2/6-31G** level [9] using the 4-31G optimized geometries. (This calculation is noted as MP2/6-31G**//4-31G.) The barrier to rotation is then calculated as the difference in total energy between the optimized planar and perpendicular conformations. These results are collected in Table II.

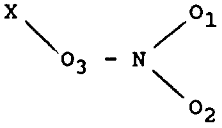
Mulliken populations [10] for the two molecules in each conformation are found in Table III and valence molecular orbital energies are shown in Tables IV and V.

TABLE I

Geometries for $HONO_2$ and $FONO_2$[a,b]

Molecule	Conformation	Basis	XO_3	O_3N	NO_1	NO_2	$<O_1NO_2$	$<O_1NO_3$	$<XO_3N$
$HONO_2$	planar	4-31G opt	0.9606	1.373	1.194	1.219	128.95	114.87	107.65
		6-31G** opt	0.9511	1.332	1.173	1.188	129.10	114.88	105.42
		expt[c]	0.964	1.406	1.211	1.199	130.3	115.9	102.2
	perp.	4-31G opt	0.9627	1.406	1.2026	1.2029	128.75	115.63	108.68
		6-31G** opt	0.9507	1.3617	1.1774	1.1774	129.00	115.50	106.50
$FONO_2$	planar	4-31G opt	1.418	1.459	1.187	1.194	132.50	109.50	107.40
		6-31G* opt	1.359	1.386	1.165	1.17	132.5	109.5	108.4
		expt[d]	1.42	1.40	1.29	1.29	125	-	105.0
	perp.	4-31G opt	1.434	1.466	1.193	1.193	131.90	114.05	102.23
		6-31G* opt	1.3644	1.4061	1.1695	1.1695	131.66	114.17	102.71

[a] The atoms are numbered as shown:



(X = H, F)

[b] Bond lengths in angstroms, angles in degrees.

[c] Cox, A. P.; Riveros, J. M. J. Chem. Phys. (1965) 42, 3106.

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RESULTS

Geometry. As shown in Table I, the 4-31G optimized geometrical parameters of the planar conformations for both molecules are in excellent agreement with the experimental values except for the O_3-N bond length (O_3 is the oxygen bonded to the F or H). The discrepancy for $FONO_2$ is larger than that for $HONO_2$, but we have argued in another paper [3] that the correct O_3-N bond length in $FONO_2$ is probably between the 4-31G value of 1.46 Å and the 1937 experimental value of 1.40 Å. A calculation of CH_3ONO_2 yielded a similar discrepancy, i.e. the O_3-N bond length in CH_3ONO_2 is 1.402 Å experimentally as compared to the 6-31G optimized value of 1.360 [11].

The geometries of the two conformations are very similar to each other at each calculational level. The largest difference between planar and perpendicular conformations is in the O_3-N bond length in $HONO_2$ suggestive of some loss of double bond character. The multiple bond that would be partially lost on rotation is shown in resonance structure 1c [12].

The 6-31G** optimized bond lengths are consistently shorter than those at the 4-31G level. The largest differences between the 4-31G and the 6-31G** calculated lengths are the F-O bond in $FONO_2$ and the O_3-N bond in both molecules. These results are consistent with numerous other studies comparing the 4-31G and 6-31G** bases for F, O, N molecules [13].

Rotation Barrier. The best calculational results (MP2/6-31G**) for the rotational barriers are within the uncertainty of the experimental values for both $HONO_2$ and $FONO_2$. Calculations that do not include correlation give poorer quality results and erroneously reverse the relative magnitudes of the barriers. For $FONO_2$, the rotational barrier increases consistently as the calculation improves and includes correlation: The planar conformation is stabilized more than the perpendicular conformation. The barrier for $HONO_2$ improves from the 4-31G calculation to the MP2 calculation, but the increase is much less than that for $FONO_2$.

The anomalously large value obtained for the $HONO_2$ barrier at the 6-31G** level suggests that polarization functions are more important for the representation of the planar conformation than for the perpendicular. Correlation appears to play a greater role in describing the perpendicular conformation.

TABLE II

Total Energies[a] and Rotational Barriers[b] for $HONO_2$ and $FONO_2$

Basis	Molecule	Conformation	Total E	Barrier
HF/4-31G//4-31G	$HONO_2$	planar perp.	-278.992112 -278.979908	32.04
	$FONO_2$	planar perp.	-377.578549 -377.570469	21.21
HF/6-31G**//6-31G**	$HONO_2$	planar perp.	-279.450746 -279.435912	38.94
	$FONO_2$	planar perp.	-378.148022 -378.133995	36.82[c]
MP2/6-31G**//4-31G	$HONO_2$	planar perp.	-280.172479 -280.159613	33.25
	$FONO_2$	planar perp.	-379.056977 -379.041304	41.15
EXPT	$HONO_2$			32±0.4[d]
	$FONO_2$			42±4[e]

[a] Hartrees (1 hartree = 627.5 kcal/mole = 2625 kJ/mole)

[b] kcal/moles

[c] A recent paper confirms this result: V. Morris, G. A. Walker, P. Jones, Y. Cao, S. C. Bhatia, J. H. Hall, Jr., J. Phys. Chem., 93 (1989) 7071.

[d] Ref. 2c

[e] Ref. 4

Mulliken Charges. Although Mulliken population analysis is often of only limited utility, comparisons can be made and trends can be seen that are supported by other data. The Mulliken charges, shown in Table III, are approximately the same for the two conformations of $HONO_2$. Likewise the two conformations of $FONO_2$ have similar Mulliken charges. The net charge on O_3 is of particular interest. If resonance structures 1c and 2c play a significant role in stabilizing the planar conformations of the two molecules, the charge on O_3 should be different in the two conformations, less negative or more positive in the planar conformation. The difference for the $HONO_2$ conformations is negligible and that for the $FONO_2$ conformations is only slightly larger. This result suggests only a minor contribution from resonance structure 2c.

The 1, 4 overlaps are consistent with previous expectations. The formal negative charges on both F and O in $FONO_2$ result in a net antibonding interaction in the planar conformation that is, however extremely small. The 1, 4 interaction between H and O in the planar conformation of $HONO_2$ is larger and favorable, consistent with a weak hydrogen-bond type interaction. $FONO_2$ and $HONO_2$ have similar 1, 4 overlaps for the perpendicular conformations.

Isodesmic Reaction. The ΔH for the following isodesmic reaction can be computed using the MP2/6-31G** energies for $FONO_2$ and $HONO_2$, as well as for H_2O and HOF [14]:

$$FONO_2 + H_2O \rightarrow HONO_2 + HOF$$

The ΔH is 1.86 kJ/mole. The nearly zero ΔH suggests that the bonds on both sides of the equation are equivalent, i.e. the OF bond in $FONO_2$ is similar to that in HOF in strength and the O-NO_2 bonds in $FONO_2$ and $HONO_2$ are similar in strength. Standard heats of formation for gas phase species also give a nearly zero ΔH and support the conclusion [15].

TABLE III

Mulliken Population Charges for $HONO_2$ and $FONO_2$ in the planar and perpendicular conformations at the 6-31G*(*) level[a]

Molecule	Conformation	N	O_1	O_2	O_3	X^b	1,4-overlap[c]
$HONO_2$	planar	+.891	-.437	-.417	-.431	+.395	+.011
	perpendicular	+.867	-.410	-.410	-.440	+.393	+.003
$FONO_2$	planar	+.966	-.400	-.407	-.030	-.129	-.001
	perpendicular	+.895	-.368	-.368	-.022	-.137	+.003

[a] Atoms numbered as in Table I

[b] X = H in $HONO_2$, F in $FONO_2$

[c] 1,4-overlap = overlap between X and O

Molecular orbital analysis. Molecular orbital correlations can be constructed for $HONO_2$ and $FONO_2$ as the XO bond rotates from the planar to the perpendicular conformation. While most orbitals increase in energy upon rotation to the perpendicular form, not all do (see Tables IV and V). Also, with the exception of two orbitals in each case, #12 and #13 for $HONO_2$ and #15 and #17 for $FONO_2$, the change in energy is fairly small. While the total energy is not the sum of the individual orbital energies, changes in total energy are often reflected in changes in orbital energies. The key to understanding the rotational barriers then appears to lie in understanding the changes in the two orbitals that undergo the largest change in energy. These molecular orbitals are shown in Figures 1 and 2.

TABLE IV

Energies (in hartrees) of the 6-31G** valence molecular orbitals for $HONO_2$ in the planar and perpendicular conformations

Orbital #[a]	Planar Conformation	Perpendicular Conformation	Energy (Perpendicular -Planar)
16	-0.49301 (3a")	-0.48821 (5a")	+ .005
15	-0.52043 (9a')	-0.50954 (4a")	+ .011
14	-0.55204 (8a')	-0.54575 (7a')	+ .006
13	-0.58501 (2a")	-0.61632 (3a")	- .031
12	-0.69892 (7a')	-0.66242 (6a')	+ .037
11	-0.79126 (6a')	-0.78059 (2a")	+ .011
10	-0.81435 (1a")	-0.80820 (5a')	+ .006
9	-0.83285 (5a')	-0.83943 (4a')	- .007
8	-0.96928 (4a')	-0.96088 (3a')	+ .008
7	-1.46740 (3a')	-1.45881 (2a')	+ .009
6	-1.48482 (2a')	-1.47770 (1a")	+ .007
5	-1.72415 (1a')	-1.71531 (1a')	+ .009

[a] Upon rotation, the plane of symmetry changes and hence the orbital symmetry designations. However, there is no crossing in the correlation between the two conformations. Thus we refer to the orbitals by their number rather than their symmetry designation.

TABLE V

Energies (in hartrees) of the 6-31G* valence molecular orbitals for the $FONO_2$ in the planar and perpendicular conformations

Orbital #[a]	Planar Conformation	Perpendicular Conformation	Energy (Perpendicular -Planar)
20	-0.52106 (4a")	-0.51552 (6a")	+ .006
19	-0.55514 (11a')	-0.54135 (5a")	+ .014
18	-0.57184 (10a')	-0.56185 (9a')	+ .010
17	-0.59277 (3a")	-0.61749 (4a")	- .025
16	-0.69204 (9a')	-0.70589 (8a')	- .014
15	-0.76079 (8a')	-0.73849 (7a')	+ .022
14	-0.76915 (2a")	-0.77982 (3a")	- .011
13	-0.82057 (7a')	-0.82865 (2a")	- .008
12	-0.86306 (1a")	-0.84803 (6a')	+ .015
11	-0.86792 (6a')	-0.86032 (5a')	+ .008
10	-0.97265 (5a')	-0.96918 (4a')	+ .003
9	-1.39805 (4a')	-1.38877 (3a')	+ .009
8	-1.52304 (3a')	-1.51801 (1a")	+ .005
7	-1.70177 (2a')	-1.69969 (2a')	+ .002
6	-1.78827 (1a')	-1.78196 (1a')	+ .006

[a] Upon rotation, the plane of symmetry changes and hence the orbital symmetry designations. However, there is no crossing in the correlation between the two conformations. Thus we refer to the orbitals by their number rather than their symmetry designation.

For $HONO_2$, the conformational change from planar to perpendicular causes the non-bonding π orbital #13 (Figure 1a) to become σ N-O bonding orbital (Figure 1b). The change from non-bonding to bonding results in lower energy. The bonding (N-O and O-H) orbital #12 (Figure 1c) in the planar conformation retains O-H bonding upon rotation (Figure 1d), but loses N-O bonding and therefore rises in energy.

For $FONO_2$, orbital #17 in the planar conformation shows π antibonding interactions O_3-F and O_3-N (Figure 2a). Upon rotation to the perpendicular form (Figure 2b), the O-F antibonding interaction is maintained, but the O_3-N interaction is lost. Also lost is the N-O_2 bonding. The net result is lower energy. For orbital #15, the planar conformation (Figure 2c) exhibits weak N-O_3 and N-O_2 σ bonding as well as O-F antibonding inter-

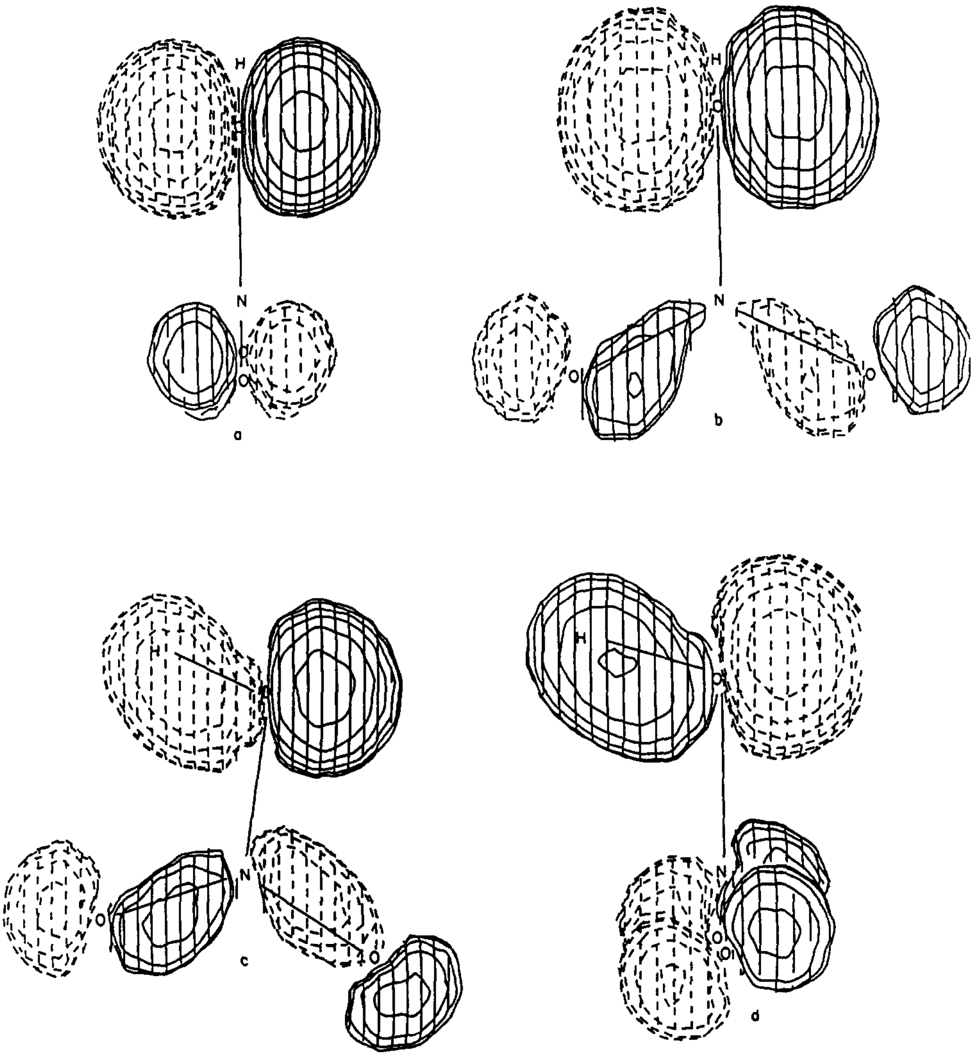

Fig. 1. Jorgensen plots of the molecular orbitals for $HONO_2$ using the 6-31G** basis. a. #13 in the planar conformation; b. #13 in the perpendicular conformation; c. #12 in the planar conformation; and d. #12 in the perpendicular conformation. Produced by Lynn Read at Princeton University and drawn by Kristy Askam at Long Island University, Southampton Campus.

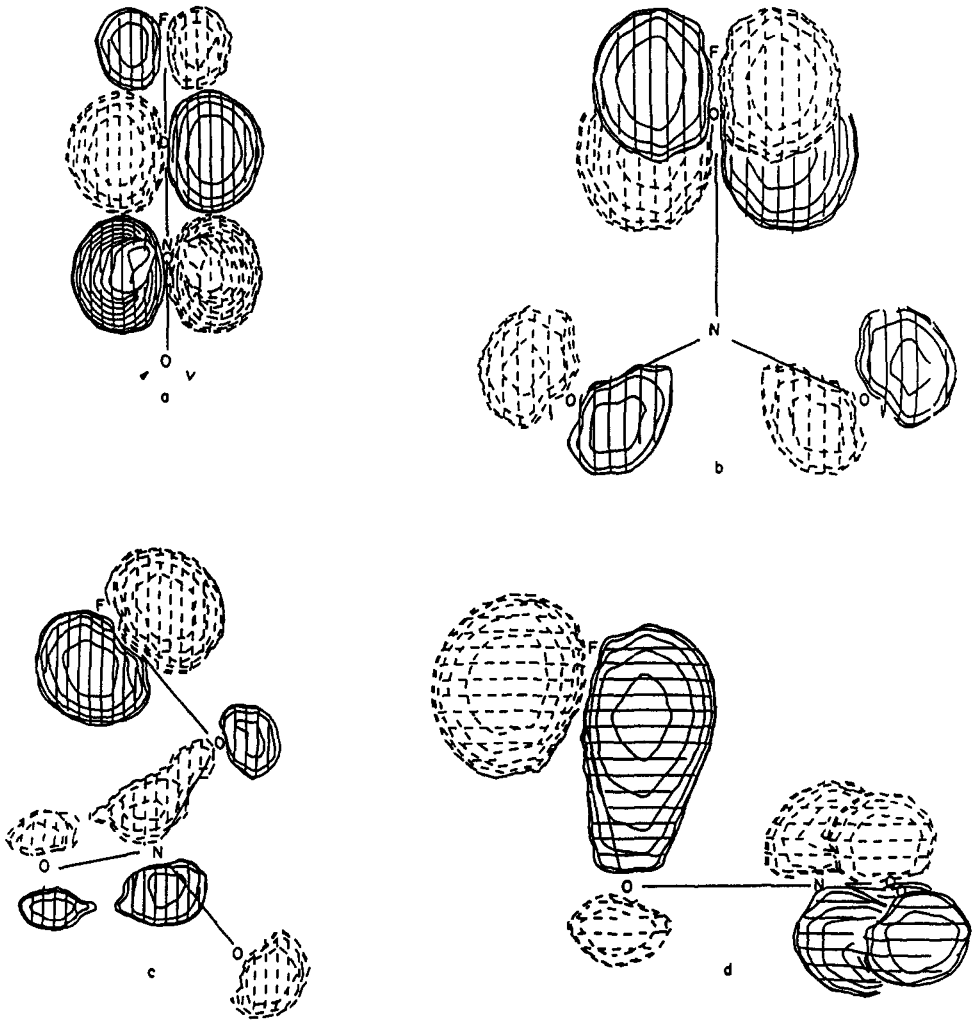

Fig. 2. Jorgensen plots of the molecular orbitals for $FONO_2$ using the 6-31G* basis. a. #17 in the planar conformation; b. #17 in the perpendicular conformation; c. #15 in the planar conformation; and d. #15 in the perpendicular conformation. Produced by Lynn Read at Princeton University and drawn by Kristy Askam at Long Island University, Southampton Campus.

actions. The perpendicular conformation (Figure 2d) exhibits weak O_1-N-O_2 π bonding, O-F σ bonding, and N-O_3 antibonding characteristics. The conversion from σ to π interactions results in a net increase in energy.

DISCUSSION

For both molecules, one orbital increases in energy upon rotation and one decreases in energy. For $HONO_2$, both changes are significant, exchanging bonding interactions for non-bonding and vice-versa. For $FONO_2$, the energy lowering for orbital #17 is also significant as bonding and antibonding interactions are interchanged. However, the change for orbital #15 is smaller, exchanging σ for π bonding. These changes also would give a smaller barrier for $FONO_2$ because the energy lowering is greater in magnitude than the energy raising.

However, the molecular orbital discussion is based on the 6-31G** calculations which do in fact give, erroneously, a larger rotational barrier for $HONO_2$ than for $FONO_2$.

The total energy change for the planar form of $FONO_2$ from the 6-31G* calculation to the correlation calculation is larger than that change for the perpendicular form. If the total change is reflected in the change for these individual orbitals, planar #17 decreases more in energy than perpendicular #17, making the gap between them less and the rotational barrier higher (since #17 decreases in energy upon rotation). For orbital #15, when the planar form decreases more than the perpendicular, the gap increases and the rotational barrier increases (since #15 increases in energy upon rotation).

For $HONO_2$, the situation is reversed because the perpendicular form decreases more in energy with correlation than the planar. As orbitals #13 and #12 decrease more in energy in the perpendicular conformation, the gap for #13 increases, and the gap for #12 decreases, both changes decreasing the barrier.

The larger rotational barrier for $FONO_2$ compared to $HONO_2$ appears to result from the F contributions to the key molecular orbitals that control the magnitude of the barrier. In orbital #17, the F orbitals are antibonding with respect to the O_3 contributions in both conformations whereas the H in orbital

#13 does not contribute at all in either conformation, i.e., is non-bonding. In orbital #15, the F contribution changes from antibonding to minimally bonding, whereas the H contribution in orbital #12 remains bonding in both conformations.

In summary, we find that ab initio quantum chemical calculations with explicit correlation corrections are needed to reproduce both the relative and absolute magnitudes of the observed rotational barriers of $HONO_2$ and $FONO_2$. However, it is seen that no single effect nor single orbital seems to dominate the explanation that $FONO_2$ has a higher rotational barrier than $HONO_2$.

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