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Hydrogen Bonding Between FNO and H_2O: Structure and Energetics

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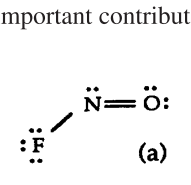
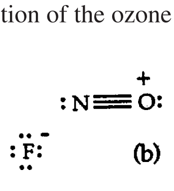
Nitrosyl fluoride, of some interest in atmospheric chemistry, has three atoms which could potentially serve as proton acceptors in the formation of hydrogen bonds. The optimized structure of FNO and H_2O was determined at the MP4/6-31G** level of calculation. In the resulting structure, the hydrogen bonds at the fluorine with an energy of 5.15 kcal/mol, contrary to the prediction that less electronegative atoms make better proton acceptors/electron donors but consistent with results of proton affinity studies and with the contribution of a resonance structure with no bond between the N and F and a negative charge on the fluorine atom. The resulting structure also shows a significant increase in the length of the NF bond from 1.51 to 1.61 Å.

Introduction

Hydrogen bonding is a very important phenomenon responsible for, among other things, the unique properties of water and the intricate structure of biological molecules critical to maintaining life. A previous study on hydrogen bonding of molecules with more than one nitrogen, fluorine, or oxygen atom[1] suggests that the less electronegative atom (N rather than O; N or O rather than F) is the site that attracts the hydrogen bond rather than the more electronegative atom: the more electronegative atom would seem to have a greater negative charge, which could attract the positive charge on the hydrogen atom; however, the less electronegative atom is better able to share electrons. In fact, the more electronegative atom does not always have the more negative formal charge. In HOF for example, the more electronegative F draws charge from the O, but the O draws charge from the H, where there is a much greater difference in electronegativity. The O actually has the greatest formal negative charge in the molecule. For all the molecules studied, the hydrogen bonds with the greatest strength per hydrogen bond are those with the less electronegative atom as the proton acceptor, suggesting that solid state structures use hydrogen bonds to the less electronegative atom.

Since FNO is an atmospheric degradation product of hydrofluorocarbons and hydrochlorofluorocarbons, the chemical bonding in nitrosyl fluoride has been a matter of considerable interest for decades,[2] and the FNO molecule's role in the chemistry of the earth's atmosphere has been a subject of some discussion.[3−6] Because the N−X bond is known to be weak and thought to be the result of a large contribution from resonance structure b shown below, it is easily photolyzed, yielding the radical F that is an important contributor to the depletion of the ozone layer.[7]


(a)


(b)

Computational studies done on FNO have shown that the NF bond is predicted to be too short at the Hartree−Fock level by more than 0.1 Å, a common problem with NF bonds in general. With electron correlation corrections, the NF distance is within 0.01 Å of the experimental value of 1.512 Å.[8] A protonation study of the FNO molecule suggests that protonation at the nitrogen or the oxygen generates a stable $F(NO)H^+$ molecular ion. However, protonation of the fluorine effectively rends the fluorine bond, resulting in the formation of a very stable but loosely bound complex of HF and NO^+. The preferred site of protonation, indicated by lowest energy of the complex, is the fluorine atom.[9]

The study of hydrogen bonding with molecules with more than one proton acceptor site concludes that the more stable complex would be hydrogen bonding to the less electronegative atom, N, whereas the protonation study indicates that the more stable complex formed would be with hydrogen bond formation at the fluorine atom. It is not uncommon for protonation results to differ from hydrogen bond results;[10] however, a large contribution to the FNO structure from resonance structure b would also reduce the likelihood of a nitrogen-bonded hydrogen bond, since there is a formal positive charge on that portion of the structure and a formal negative charge on the fluorine.

We intend to investigate computationally the formation of a hydrogen bond between FNO and a proton donor and have chosen H_2O as the source of the hydrogen for the hydrogen bond given the interest in the interaction in atmospheric studies.[6]

Computational Method

The geometries of FNO, H_2O, and the FNO-H_2O complex were fully optimized using Gaussian O3[11] at the MP4/6-31G** level after initially exploring optimized MP2/6-31G** structures of the complex to determine the optimal proton acceptor in FNO. (The MP2/6-31G** optimized structure turned out to be a saddle point on the MP4 energy surface, which therefore required a full optimization at the MP4 level to obtain a minimum for determining frequencies.) Separate optimizations were attempted to look for local energy minima with the hydrogen bond to the N, O, and F. All structures attempted straight-forwardly optimized to the same geometry with the water hydrogen bonded to the fluorine atom of FNO. Since the geometry found is clearly the global minimum, only one optimized structure with the water hydrogen bonded to the FNO fluorine was studied further.

The frequencies and zero point energies were determined at the MP4/6-31G** level.

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TABLE 1: MP4 Optimized Geometries, Energies, and Frequencies for FNO, H_2O, and the $FNO\cdots H_2O$ Complex

molecule	geometric parameter	MP4 results[a]	MP4 energy with ZPE[b]	frequencies[c]
FNO	r_{NF}	1.542	−299.168 391	486.36
	r_{NO}	1.166		772.68
	$<_{FNO}$	110.54		1776.58
H_2O	r_{HO}	0.9615	−76.209 414	1692.48
	$<_{HOH}$	103.88		3881.54
				4008.73
$FNO\cdots H_2O$	r_{O1N}	1.157	−305.386 027	45.51
$O1{-}NF\cdots H1{-}O2{-}H2$	r_{NF}	1.616		108.94
	r_{FH1}	1.969		159.16
	r_{O2H1}	0.965		192.80
	r_{O2H2}	0.961		280.09
	$<_{O1NF}$	110.28		436.98
	$<_{FNH1}$	53.06		550.36
	$<_{NH1O2}$	99.74		731.36
	$<_{H1O2H2}$	104.29		1708.89
	$<_{O2H1NO1}$	−70.97		1835.79
	$<_{H1NFO1}$	87.37		3855.10
	$<_{H2O2H1N}$	−118.30		3986.05

[a] Angles in degrees, bond lengths in Angstroms. [b] Hartees. [c] Wavenumbers.

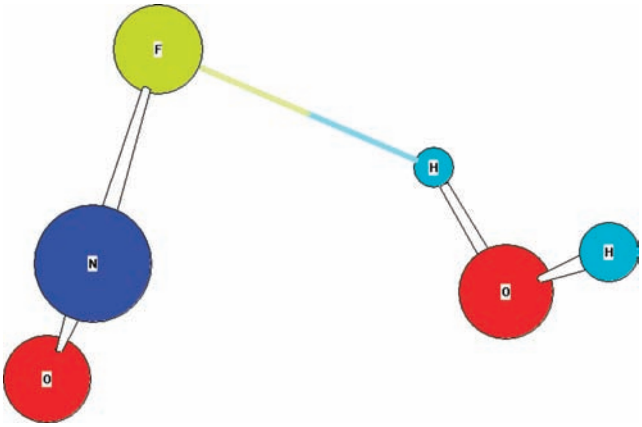

Figure 1. MP4 optimized geometry of the $FNO\cdots H_2O$ complex.

Results

The optimized geometries, energies, and frequencies for FNO, H_2O, and the hydrogen-bonded $FNO\cdots H{-}OH$ complex are given in Table 1. The $FNO\cdots H{-}OH$ complex is shown in Figure 1. The preferred proton acceptor is the fluorine atom. The calculated frequencies, all being positive, support the fact that the structure is a minimum on the energy surface.

Discussion

The hydrogen bond energy was calculated to be 5.15 kcal/mol, a typical hydrogen bond energy. It can be seen that the resonance structure b has a significant contribution in the structure of FNO in that the hydrogen choose to bond with the fluorine and not the less electronegative N. Further evidence can be seen from Table 1, in which the length of the original FN bond in FNO is 1.517 Å. However, when the hydrogen in water is bonded to it, the FN bond lengthened to 1.616 Å. This change is much greater than any change in NF, OF, or NO bond lengths upon dimer formation in the previous study.[3] (Typical changes are 0.01 Å.) This comparison is consistent with the protonation studies that suggest the lengthening of the NF bond (1.517−1.592 Å) and a shortening of the NO bond (1.160−1.148 Å) would eventually break the NF bond and form H_2OF^- and NO^+. The NF bond length in the complex is also consistent with the bond length calculated for the plausible trigonal bipyramidal structure of NF_5.[12]

Conclusion

Although hydrogen bonding does occur between FNO and H_2O, the data shows that the hydrogen bonds with the F, as indicated by the protonation studies, and not with the N, as suggested by the hydrogen bonding studies, and that the FN bond further lengthens and weakens.

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