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Hydrogen Bonding in Molecules with More Than One Proton Acceptor Site: HOF, HNO, H_2NF, and H_2NOH

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Ab initio molecular orbital calculations at the MP 2/6-31 + G** and MP 4/6-31 + G** levels were performed to determine the preferential site of hydrogen bond formation in small molecules where more than one such site exists. For HOF, HNO, H_2NF, and H_2NOH the better hydrogen bond, as measured by bond strength, occurred when the proton acceptance site was the less electronegative atom. Structures and energies for all configuations were determined.

Background

Hydrogen bonding is an important concept in chemistry: it explains numerous phenomena from protein structure to the unusual properties of water. It is also a small effect on the energy scale of intermolecular interactions, worth about 10−50 kJ/mol of neutral hydrogen bonds in most situations, and so is difficult to study experimentally and theoretically. As advances are being made in some areas, such as experimentally determined monomer structures and dimer energies, other areas need further work, such as dimer structures. In fact, the structure of the ammonia dimer, assumed to be the standard, linear, N···H−N, hydrogen bond, has been challenged by microwave spectroscopic analysis[1] and is being reinvestigated.[2]

A little developed area that may provide new insight into the nature of hydrogen bonding is the hydrogen bond between monomers with more than one potential site for proton acceptance/electron donation. Previous calculational studies predicted[3] that the proton affinity of the less electronegative atom in such a molecule, N in hydroxylamine and fluoramine and O in hydrogen hypofluoride, would be higher than the proton affinity of the more electronegative atom, the O in hydroxylamine and the F in fluoramine and hydrogen hypofluoride. Lack of a thorough model led to the misinterpretation of the vibrational spectra and structure of the hydrogen bonded HOF molecule.[4] It was initially assumed that the hydrogen bond in the dimer would be formed with the fluorine of one molecule serving as the electron donor; after all, fluorine is more electronegative and therefore more negative and more attractive as a site for hydrogen bond formation.

This interpretation was challenged:[5] the OF vibrational frequency does not shift when comparing solid and gas phase spectra. Oxygen is less electronegative than fluorine and therefore more capable of donating electrons. While fluorine is more electronegative than oxygen and draws charge from oxygen to become partially negatively charged, oxygen is much more electronegative than hydrogen and draws much more charge from hydrogen than fluorine draws from oxygen. The net result is that oxygen is more negatively charged than fluorine in HOF. This interpretation of the charge distribution is supported by calculations.[6] The final analysis of the solid-state structure of HOF[7] supports the formation of the hydrogen bond with oxygen as the electron donor.

An early study[8] of the two configurations for the HOF dimer used structures fully optimized at the HF/3-21G level using GAUSSIAN 82.[9] The dimer involving a hydrogen bond to the fluorine atom as the proton acceptor/electron donor formed a cyclic structure with two such bonds and a total binding energy of 56.53 kJ/mol. While the cyclic structure was clearly the global minimum, it is interesting to note that the *per bond* hydrogen bond energy is in fact greater for the oxygen proton acceptor model, as proposed above, than for the fluorine proton acceptor: 30.31 kJ/mol versus 56.53/2 = 28.26 kJ/mol. This suggests that solid state structures may differ significantly from dimer structures. Higher level calculations are clearly needed to verify the order of binding energies.

Difluoramine is another molecule with two potential sites for electron donation in the formation of a hydrogen bond: the nitrogen atom and the fluorine atom. The vibrational spectra of HNF_2 comparing the gas and solid phases[5] shows frequency shifts in modes involving the hydrogens, indicating the presence of hydrogen bonding. However, the NF_2 mode does not show any frequency shift, splitting, or line broadening, a result similar to the OF mode for HOF, which suggests that the hydrogen bond in HNF_2 is to the N and not the F. The structure of difluoramine has only recently been determined[10] and the dimer forms a cyclic structure with two hydrogen bonds: N1−H1···F2−N2−H2···N1.[11]

A systematic study of the dimers of molecules with two potential sites for hydrogen bond formation could further advance our understanding of the phenomenon. We have examined the monomers and dimers of HOF, HNO, H_2NF, and NH_2OH (HNF_2 was attempted, but the dimers fell apart upon optimization), all of which have experimentally determined monomer structures, using ab initio molecular orbital (MO) calculations to determine the minimum energy configurations. Since there are two possible sites on each molecule to serve as electron donors/proton acceptors, the determination of the better, i.e., lower energy, configuration should provide some new insight into the nature of the hydrogen bond. MO calculations are particularly well-suited to this study because configurational restraints can be imposed on the various systems to explore possible, but nonexistent, structures.

Computational Methodology

Each monomer and two dimer configurations, one for each proton acceptance site, were fully optimized at the MP2/6-

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TABLE 1: MP2/6-31+G Optimized Geometries and Harmonic Frequencies of HOF, HNO, H_2NOH, and Their Dimers (Bond Lengths in Angstroms, Angles in Degrees, Frequencies in cm^{-1})**

HOF

parameter	optimized	experimental	parameter	optimized	experimental
r_{HO}	0.9739	0.9657[a]	υ_1 (OF stretch)	952.92	916.84[a]
r_{OF}	1.4533	1.4350[a]	υ_2 (HOF bend)	1384.18	1396.22[a]
∠HOF	97.2798	97.54[a]	υ_3 (HO stretch)	3791.63	3763.95[a]

$(HOF)_2$

parameter	oxygen dimer	fluorine dimer	parameter	oxygen dimer	fluorine dimer
H1−O1	0.9787	0.9773	υ_1	32.58 (F1O1 O2F2 dihedral bend)	53.34 (OF sym stretch)
O1−F1	1.4560	1.4555	υ_2	49.88 (F1H2 stretch)	138.10 (H1F2 sym stretch)
H1−O1−F1	96.48	97.26	υ_3	80.20 (F1O1O2H2 bend)	144.87 (HOF bend out of ring)
H2−O2	0.9759	0.9773	υ_4	189.00 (O···H stretch)	155.50 (H anti sym bend out of ring)
O2−F2	1.4514	1.4555	υ_5	295.87 (H1···O2H2 sym bend)	168.71 (H sym bend out of ring)
H2−O2−F2	97.99	97.26	υ_6	494.95 (H1···O2H2 antisym bend)	407.77(OH antisym stretch)
H1−O2	2.008		υ_7	954.64 (O2F2 stretch)	957.78 (HOF bend in ring)
H1−F2		2.0635	υ_8	955.06 (O1F1 stretch)	960.42 (OF sym stretch)
H2−F1	2.760	2.0635	υ_9	1377.15 (H2O2F2 bend)	1410.55 (OH bend)
O1−H1−O2	150.79		υ_{10}	1477.31 (H1O1F1 bend)	1442.48 (OH bend)
O1−H1−F2		143.08	υ_{11}	3710.59 (O1H1 stretch)	3738.96 (OH stretch)
H1−F2−O2		100.85	υ_{12}	3774.06 (O2H2 stretch)	3754.56 (OH stretch)

HNO

parameter	optimized	experimental	parameter	optimized	experimental
r_{HN}	1.0502	1.063[b]	υ_1 (NO stretch)	1475.39	1501[c]
r_{NO}	1.2376	1.212[b]	υ_2 (HNO bend)	1576.57	1565[c]
∠HNO	107.29	108.6[b]	υ_3 (HN stretch)	3101.28	2684[c]

$(HNO)_2$

parameter	nitrogen dimer	oxygen dimer	parameter	nitrogen dimer	oxygen dimer
H1−N1	1.047	1.0464	υ_1	11.63 (N1O1 stretch)	80.24 (NO stretch)
N1−O1	1.2376	1.2402	υ_2	77.53	234.48 (O···H stretch)
H1−N1−O1	108.13	106.601	υ_3	104.81 (N1···H2 stretch)	164.45 (NH stretch)
H2−N2	1.047	1.0464	υ_4	177.89 (NH1 stretch)	174.89 (HNO bend)
N2−O2	1.2407	1.2402	υ_5	204.27 (N1H2 stretch)	192.39 (HNO bend)
H2−N2−O2	106.46	106.601	υ_6	296.67 (HNO bend)	236.52 (Hs bend out of plane)
H1−O2	2.8402	2.3691	υ_7	1474.71 (N2O2 stretch)	1479.08 (NO stretch)
H2−O1		2.3691	υ_8	1483.65 (HNO bend)	1480.35 (NO stretch)
N1−H2	2.3773		υ_9	1561.73 (H1NO1 bend)	1583.56 (NH stretch)
N1−H2−N2	129.38		υ_{10}	1596.17 (H2N2 stretch)	1594.87 (NH stretch)
			υ_{11}	3159.48 (N1H1 stretch)	3176.46 (NH stretch)
			υ_{12}	3172.44 (N2H2 stretch)	3183.85 (NH stretch)

H_2NF

parameter	optimized	experimental	parameter	optimized	experimental
r_{NF}	1.0196	1.0225[d]	υ_1 (NF stretch)	949.68	891[d]
r_{NF}	1.4436	1.4329[d]	υ_2 (NH_2 twist)	1287.29	1233[d]
∠HNF	100.80	101.08[d]	υ_3 (NH_2 scissor)	1341.95	1241[d]
∠FNF	105.88	106.27[d]	υ_4 (NH_2 bend)	1648.39	1564[d]
			υ_5 (NH_2 sym stretch)	3503.88	3234[d]
			υ_6 (NH2 antisym stretch)	3629.23	3346[d]

$(H_2NF)_2$

parameter	nitrogen dimer	fluorine dimer	parameter	nitrogen dimer	fluorine dimer
N1−F1	1.44134	1.45210	υ_1	42.34 (N1F1 stretch)	8.69 (NH bend)
N1−H11	1.01959	1.02049	υ_2	70.13 (HNF bend)	115.16 (HNF bend)
N1−H12	1.02009	1.01971	υ_3	111.89 (NH_2 twist)	128.42 (NH_2 twist)
H1−N1−H1	106.19	100.29	υ_4	126.00 (NH_2 twist)	152.01 (NH_2 twist)
H1−N1−F1	101.48	100.29	υ_5	208.21 (HNF bend)	158.54 (NH_2 twist)
N2−F2	1.45267	1.45209			
N2−H21	1.02234	1.02049			
N2−H22	1.01970	1.01971			
H21−N2−H22	106.20	106.20			
H21−N2−F2	99.73	100.29			
N1−H21	2.24952				
H11−F2	2.69761	2.16779			
N1−H21−N2	128.64				
N1−H11−F2	84.13				
N1−F1−H21		112.32			

TABLE 1. Continued

parameter	nitrogen dimer	oxygen dimer	parameter	nitrogen dimer	oxygen dimer
υ_6	327.36 (NH_2 twist)	193.74 (NH_2 twist)	υ_{13}	1647.75 (NH_2 antisym stretch)	1649.27 (NH_2 twist)
υ_7	935.81 (N2F2 stretch)	935.79 (NF sym stretch)	υ_{14}	1650.18 (NH_2 sym stretch)	1651.91 (NH_2 bend)
υ_8	959.86 (N1F1 stretch)	939.88 (NF antisym stretch)	υ_{15}	3482.71 (NH_2 antisym stretch)	3505.04 (NH_2 stretch)
υ_9	1301.34 (NH_2 bend)	1305.28 (N out-of-plane H stretch)	υ_{16}	3512.09 (NH_2 sym stretch)	3507.61 (NH_2 stretch)
υ_{10}	1312.17 (HNF bend)	1307.94 (NH_2 twist)	υ_{17}	3615.86 (NH_2 twist)	3627.69 (NH_2 stretch)
υ_{11}	1333.06 (NH_2 twist)	1355.19 (NH_2 twist)	υ_{18}	3631.29 (NH_2 twist)	3629.00 (NH_2 stretch)
υ_{12}	1366.48 (NH_2 twist)	1362.80 (NH_2 twist)			

H_2NOH

parameter	optimized	experimental	parameter	optimized	experimental
r_{NH}	1.0168	1.016[e]	υ_1 (HNOH dihedral bend)	450.56	430[e]
r_{NO}	1.4523	1.453[e]	υ_2 (NO stretch)	937.24	895[e]
r_{OH}	0.966	0.962[e]	υ_3 (NH_2 rock)	1168.16	1120[e]
∠HNH	106.23	107.1[e]	υ_4 (NH_2 twist)	1336.58	
∠HNO	103.34	103.2[e]	υ_5 (NOH bend)	1405.57	1357[e]
∠NOH	101.85	101.4[e]	υ_6 (NH_2 bend)	1696.29	1605[e]
∠HNOH	124.74		υ_7 (NH_2 sym stretch)	3535.01	3297[e]
			υ_8 (NH_2 antisym stretch)	3645.23	3350[e]
			υ_9 (OH stretch)	3874.10	3656

$(H_2NOH)_2$

parameter	nitrogen dimer	oxygen dimer	parameter	nitrogen dimer	oxygen dimer
N1−H1	1.01763	1.01783	υ_1	75.92 (NONO bend)	65.59 (NOON dihedral bend)
N1−O1	1.44802	1.44957	υ_2	203.44 (N•••H sym stretch)	170.16 (OH•••O stretch)
O1−H1	0.98120	0.97473	υ_3	230.44 (N•••H antisym stretch)	185.37 (NOH bend)
H1−N1−H1	106.02	105.68	υ_4	237.53 (NOH bend)	207.92 (NOH bend)
H1−N1−O1	104.14	103.90	υ_5	253.88 (NH_2 twist)	215.17 (NH_2 twist)
N1−01-H1	101.08	101.70	υ_6	338.78 (NH_2 twist)	343.90 (NH_2 twist)
N2−H21	1.01762	1.02077	υ_7	733.57 (N•••H sym stretch)	481.27 (OH•••O bend)
N2−H22		1.01711	υ_8	865.31 (NO antisym stretch)	710.22 (OH stretch)
N2−O2	1.44780	1.46107	υ_9	952.31 (NO antisym stretch)	927.10 (OH bend out of plane)
O2−H2	0.98120	0.9667	υ_{10}	959.21 (NO sym stretch)	949.01 (NO stretch)
H2−N2−H2	106.04	102.83	υ_{11}	1196.83 (NH_2 twist)	1197.43 (NH_2 sym stretch)
H2−N2−O2	104.16	102.20	υ_{12}	1224.83(NH_2 twist)	1209.43 (NH_2 antisym stretch)
N2−O2-H2	101.11		υ_{13}	1316.79 (NH_2 twist)	1325.93 (NH_2 twist)
H1−N2	1.93409		υ_{14}	1322.49 (NH_2 twist)	1373.07 (NOH bend)
H1−O2		1.90837	υ_{15}	1515.92 (NOH bend)	1406.62 (HNOH bend)
H2−N1	1.93598	2.23093	υ_{16}	1576.53 (NOH bend)	1512.25 (NOH bend)
O1−H1−N2	156.92		υ_{17}	1688.46 (NH_2 bend)	1692.27 (NH_2 bend)
H1−N2−O2	102.03	99.86	υ_{18}	1695.28 (NH_2 bend)	1714.28 (NH_2 bend)
O1−H1−O2		162.37	υ_{19}	3523.02 (NH_2 sym stretch)	3495.21 (N2H2 stretch)
H1−O2-N2		106.91	υ_{20}	3529.35 (NH_2 antisym stretch)	3525.70 (NH_2 twist)
N2−H22−N1		146.57	υ_{21}	3554.64 (NH sym stretch)	3622.44 (NH_2 stretch)
H22−N1−O1		102.83	υ_{22}	3595.25 (N•••H antisym stretch)	3629.02 (NH_2 bend)
			υ_{23}	3631.49 (NH_2 scissor)	3713.94 (OH stretch)
			υ_{24}	3631.74 (NH_2 scissor)	3869.33 (OH stretch)

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31+G** level with diffuse functions on non-hydrogen atoms[12] using the GAUSSIAN 94 programs[13] available on the Cornell Theory Center RS6000 computers. Intermolecular distances, binding energies for neutral complexes, and vibrational frequency shifts are well described with this bases set and Møller−Plesset perturbation theory.[14]

Differences in basis set superposition error (BSSE) are likely to be small enough so as not to effect the conclusions drawn.

Vibrational frequencies were computed for the MP2 optimized structure.

Since the difference between the binding energies of the two dimers could be a kilojoule per mole or less, and better calculations could even reverse the relative order of the two dimer configurations, a single point calculation of each monomer and both its dimers at the MP4/6-31+G** level using the optimized geometries of the MP2 calculation was executed.

Results and Discussion

The MP2/6-31+G** optimized structures and harmonic frequencies of the monomers and dimers of HOF, HNO, H_2NF, and H_2NOH are summarized in Table 1 and compared with available experimental data for the monomers. The dimers are shown in Figure 1. They are designated as fluorine, oxygen, or nitrogen dimers to indicate the initial proton acceptance site. There is good agreement between experimental and optimized structures of the monomers, particularly for H_2NOH. Bond lengths are within 0.001 Å and angles within 0.8°. The worst agreement is for the OF bond and the NO double bond, optimizations giving bonds too long by 0.018 and 0.026 Å, respectively.

The vibrational frequencies predicted for the monomers are in reasonable agreement with experimental values. Higher

TABLE 2: Energies of $(HOF)_2$, $(HNO)_2$, $(H_2NF)_2$, and $(H_2NOH)_2$ Dimers

	dimer	EUMP2[a]	UMP4[a]	ZPE[b,c]	H bond energy[b,d]	corrected for ZPE[b,c,e]
$(HOF)_2$	oxygen	−350.24408320950	−350.28670746	79.92	22.96	16.36
	fluorine	−350.24371658564	−350.28734716	79.75	26.64	20.21
$(HNO)_2$	nitrogen	−260.29405802238	−260.34257254	79.68	16.71	10.64
	oxygen	−260.29463316816	−260.34371024	80.57	19.70	12.74
$(H_2NF)_2$	nitrogen	−310.67182156368	−310.72278558	153.31	24.95	19.50
	fluorine	−310.67121482768	−310.72273819	152.72	24.82	19.97
$(H_2NOH)_2$	nitrogen	−262.75984692540	−262.81310327	226.41	52.93	42.43
	oxygen	−262.75367335109	−262.80751420	224.55	38.25	29.61

[a] hartrees. [b] kJ/mol. [c] Zero point energy. [d] −H = dimer energy − 2(monomer energy). [e] Hydrogen bond energy.

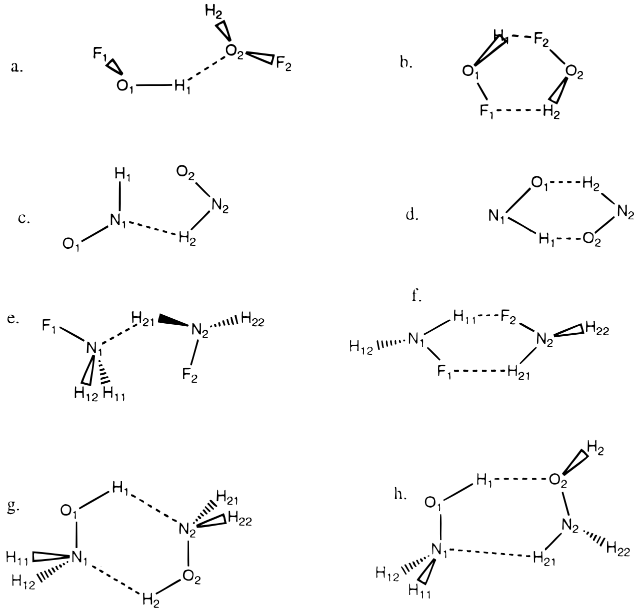

Figure 1. Structures for (a) HOF oxygen dimer, (b) HOF fluorine dimer, (c) HNO nitrogen dimer, (d) HNO oxygen dimer, (e) H_2NF nitrogen dimer, (f) H_2NF fluorine dimer, (g) H_2NOH nitrogen dimer, and (h) H_2NOH oxygen dimer. (Numbers on atoms are used for clarification for the parameters described in Table 1.)

frequencies show the greatest deviation, over 13% in the case of HNO. The best agreement occurs when calculations for HOF are compared to the experimental values of isotopically pure $H^{16}OF$, the greatest deviation being less than 4%.

With hydrogen atoms on each monomer and at least two proton acceptance sites, a feature common to all the dimer structures is a ring arrangement of five to six atoms. The optimal structure involves the formation of two hydrogen bonds and a symmetric ring in the cases of the HOF fluorine dimer, the HNO oxygen dimer, the H_2NF fluorine dimer and the H_2NOH nitrogen dimer. The H_2NOH oxygen dimer forms an asymmetric ring with two hydrogen bonds. The HOF oxygen dimer, the HNO nitrogen dimer, and the H_2NF nitrogen dimer each have a second hydrogen that approaches another heavy atom to form the ring structure, but at a distance equal to or greater than the sum of the van der Waals radii.[15] Additionally, the XHY angle is 90° or less in all three cases and therefore these molecules do not have a second hydrogen bond. Hydrogen bond energies, shown in Table 2, are computed as the difference in MP4 energy between two monomers and the dimer, which is then corrected for the difference in zero point energy as computed from the MP2 frequencies.

With the exception of HOF, the favored MP2 optimized dimer, i.e., the lower energy configuration, is also lower in energy at the MP4 level. (OF bonds have been notoriously difficult to adequately describe even at the MP2 level, for example, in F_2O_2.[16]) For the smaller molecules, HOF and HNO, the favored dimer involves the formation of the initial hydrogen bond to the more electronegative atom, F and O, respectively; for the larger molecules, H_2NF and H_2NOH, the favored dimer uses the less electronegative atom, N in both cases. (The H_2NF nitrogen dimer is slightly lower in energy at the MP4 level, but inclusion of zero-point energy corrections reverses this relation.) The preference for a given structure results directly from the opportunity to form a second hydrogen bond and, in the case of H_2NOH, to form a better hydrogen bond.

In all the molecules, the less electronegative atom is a central atom, while the more electronegative atom is at or near the terminus of the structure. For the smaller molecules, HOF and HNO, the formation of a second hydrogen bond and a stable ring structure occurs when the terminus atom, the more electronegative one, forms the initial hydrogen bond. For H_2NOH a second hydrogen bond can be formed with a six-membered ring even when the central, less electronegative atom is used initially. When the two different dimers of the same monomer are each able to form two hydrogen bonds, the favored structure involves the proton acceptance at the less electronegative atom, as in the nitrogen dimer of H_2NOH.

For all the molecules, the hydrogen bonds with the greatest strength are those with the less electronegative atom as the proton acceptor. For the HOF fluorine dimer, the hydrogen bond energy for two hydrogen bonds is 20.21 kJ/mol or an average of 10.11 kJ/mol of hydrogen bonds; for the oxygen dimer's single hydrogen bond, the energy is 16.36 kJ/mol. Likewise, the oxygen dimer of HNO involves 12.74/2 or 6.37 kJ/mol of hydrogen bonds, compared to the nitrogen dimer's 10.64 kJ per single hydrogen bond, the fluorine dimer of H_2NF, 19.97/2 or 9.99 kJ/mol of hydrogen bonds, versus the nitrogen dimer, 19.50 kJ/mol; and H_2NOH, with two hydrogen bonds for each dimer, 29.61 kJ of hydrogen bond energy for the oxygen dimer versus 42.43 kJ for the nitrogen dimer.

Conclusion

This study of preference for a proton acceptance site when more than one such atom is available suggests that solid state structures may use hydrogen bonds to the less electronegative atom. Dimer structures in the gas phase or matrix isolation studies, particularly of small molecules with 3−4 atoms, may involve hydrogen bonding to the more electronegative atom.

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