Use of Oxidation-State Differences and Molecular Orbitals to Interpret Bonding in the Series ONXYZ (X, Y, Z = H, F, Cl), $HNNX_3$, $HNNX_2Y$, and $HNNXY_2$ (X, Y = H, F) and OCX_3^-, OCX_2Y^-, and $OCXY_2^-$ (X, Y = H, F)

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Bonding in the series ONXYZ (X, Y, Z = H, F, Cl), $HNNX_3$, $HNNX_2Y$, $HNNXY_2$ (X, Y = H, F), and OCX_3^-, OCX_2Y^-, $OCXY_2^-$ (X, Y = H, F) shows evidence of a significant ionic contribution modifying the underlying covalent bonding. Increased ionic character can be correlated with oxidation-state differences between the bound atoms and is expressed in terms of shorter bond lengths. All members of the series, with the exception of ONH_3, $HNNH_3$, and OCH_3^-, possess a multiple O−N, N−N, or C−O bond modified by the ionic character of that bond. The O−N, N−N, and O−C single bonds in ONH_3, $HNNH_3$, and OCH_3^-, respectively, show some variation in length relative to "typical" single bonds of these types due to differences in ionic character. The two highest-occupied molecular orbitals in the ONXYZ or $OCXYZ^-$ (X, Y, Z = H, F) series which are π_{NO}* or π_{CO}* (when X = Y = Z = H) exhibit a distinct shift in their nodal plane as hydrogen is replaced by fluorine. The nodal plane moves from a location between the oxygen and the nitrogen or carbon to between the nitrogen or carbon and the fluorines impacting on the nature and length of the bonds joining these atoms. The pattern of N−F and C−F bond lengths in the series, ONH_3−ONF_3 and OCH_3^-−OCF_3^-, respectively, lends support to the idea of resonance structures of the form $ONXY^+$ F^- or OCXY F^- (where X, Y = H, F).

Introduction

The nature of bonding in species such as ONF_3[1−9] and OCF_3^-[7−12] has generated much interest but differing interpretations. These molecules can be represented by Lewis structures showing a single N−O or C−O bond. The problem is that determination of the bond lengths either experimentally or by computational modeling suggests that the NO (1.17Å) and CO (1.225Å) bonds in ONF_3 and OCF_3^-, respectively, are multiple bonds rather than the single bonds represented by their Lewis structures. This raises a question as to the nature of bonding at the central nitrogen or carbon because a Lewis structure involving such multiple bonds would imply that the nitrogen or carbon was hypervalent. Another feature of these molecules is that the N−F or C−F bonds are longer than would be anticipated for a single N−F (1.36 Å) or C−F (1.33−1.38 Å) bond. One explanation[7,8] for the structural features in ONF_3 and OCF_3^- focuses on the degree of ionic character of the bonds and asserts that the geometry can be best understood in terms of ligand packing around the central atom. It should be noted that in ONH_3 the N−O bond length of ~1.36 Å[2] is much more in accord with the single bond Lewis model though even in this case it is somewhat shorter than would be expected. Alternative resonance structures involving $ONF_2^+F^-$ or OCF_2F^- have been proposed[8] to explain the short O−N and O−C bonds and long N−F and C−F bonds without incorporating hypervalent arguments. Some studies have investigated the hypervalent model incorporating back bonding to the central atom.[6,10]

However there has not, to our knowledge, been a comprehensive study of bonding in these molecules, utilizing a series of closely related species, to compare and contrast the bonding in molecular orbital terms and to relate the changes in the N−O, C−O, N−F, and C−F bond lengths to changes in electron distribution and ionic character. The purpose of this investigation is to carry out such a study and to see whether it is possible to represent the correlation between ionic character and bond length using a simple model. Essentially all previous studies have focused on ONF_3[1,3−9] and OCF_3^-.[7−12] In this investigation the ligands attached to the −NO, −NNH, and −CO were varied incrementally. The intent was to relate the changes in the N−O, N−N, and C−O bond lengths to the changing ionic character of those bonds as impacted by the attached ligands. An easily understood model using oxidation states was used to approximately represent the changing ionic character of the bonds. An alternative approach to interpreting bonding in these molecules using changes in the molecular orbitals is also provided. Because resonance structures of the form $ONF_2^+F^-$ and OCF_2F^- have been proposed in an attempt to explain the bond lengths,[8] exploration of the properties of the series ONH_3−ONF_3 and OCH_3^-−OCF_3^- may provide evidence either supporting or contradicting that proposal. By replacing oxygen by the isoelectronic group HN and investigating the series $HNNH_3$−$HNNF_3$ with respect to rotation about the N−N bond, information about the barrier to rotation and nature of the N−N bond could be obtained.

Calculation and Results

All calculations were carried out using the Windows version of Gaussian 03.[13] The calculations were initially performed at the QCISD level[14] using a cc-pVDZ basis set,[15] and all structures were optimized. Because of the presence of several strongly electronegative atoms and concerns as to the appropriateness of the QCISD method relative to the CCSD method additional

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TABLE 1: Geometrical Parameters for ONX_3 (X = H, F, Cl), Oxidation States, and Mulliken Charges[a]

parameters	ONH_3	ONF_3	$ONCl_3$
R_{NO}	1.3595 [1.3871]	1.1688 [1.1687]	1.1826
R_{NX}	1.0409 [1.0341]	1.4222 [1.4481]	1.9269
ONX	114.143 [111.932]	117.228 [117.512]	115.127
XNOX	120.000 [120.000]	120.000 [120.000]	120.0000
Energy	−131.331931 [−131.397055]	−428.295567 [−428.445282]	−1508.413142

	N	O	H	X
ONH_3	−1 (+0.250) [+0.317]	−2 (−0.643) [−0.883]	+1 (+0.131) [+0.189]	
ONF_3	+5 (+0.795) [+1.882]	−2 (−0.246) [−0.620]		−1 (−0.183) [−0.421]
$ONCl_3$	+2 (−0.046)	−2 (−0.201)		0 (+0.083)

[a] Bond lengths are in Å, angles are in degrees, and energy is in Hartrees. Results obtained using QCISD/cc-pVDZ method and basis set or (in square brackets) CCSD(T)/aug-cc-pVDZ method and basis set.

TABLE 2: Geometrical Parameters for ONH_2X (X = F, Cl) and $ONHX_2$ (X = F, Cl), Oxidation States, and Mulliken Charges[a]

parameters	ONH_2F	ONH_2Cl	$ONHF_2$	$ONHCl_2$
R_{NO}	1.2265 [1.2345]	1.2296	1.1866 [1.1858]	1.2083
R_{NH}	1.0348 [1.0319]	1.0318	1.0371 [1.0364]	1.0338
R_{NX}	1.6360 [1.6997]	2.1700	1.4811 [1.5203]	119.298
ONH	118.490 [118.529]	119.096	122.489 [123.882]	119.298
ONX	117.021 [116.107]	119.055	115.689 [115.526]	116.298
XNOH	108.621 [105.334]	106.126	122.534 [122.960]	119.073
energy	−230.334896 [−230.431844]	−590.383805	−329.322250 [−329.446313]	−1049.40289 32

	N	O	H	F
ONH_2F	+1 (+0.485) [+0.660]	−2 (−0.401) [−0.612]	+1 (+0.189) [+0.263]	−1 (−0.462) [−0.575]
ONH_2Cl	0 (+0.302)	−2 (−0.313)	+1 (+0.218)	0 (−0.425)
$ONHF_2$	+3 (+0.669) [+1.219]	−2 (−0.318) [−0.620]	+1 (+0.215) [+0.311]	−1 (0.283) [−0.456]
$ONHCl_2$	+1 (+0.124)	−2 (−0.294)	+1 (+0.244)	0 (−0.037)

[a] Bond Lengths are in Å, angles are in degrees, and energy is in Hartrees. Results are obtained using the QCISD/cc-pVDZ method and basis set or (in square brackets) the CCSD(T)/aug-cc-pVDZ method and basis set.

TABLE 3: Geometrical Parameters for ONF_2Cl, $ONFCl_2$, and ONFClH, Oxidation States, and Mulliken Charges[a]

parameters	ONF_2Cl	$ONFCl_2$	ONFClH
R_{NO}	1.1734	1.1779	1.1959
R_{NH}			1.0357
R_{NF}	1.4445	1.4651	1.4892
R_{NCl}	1.8747	1.9028	1.9639
ONH			121.059
ONF	115.368	114.293	115.060
ONCl	118.323	116.197	117.255
FNOH			119.935
FNOF	115.908		
FNOCl	122.046	117.197	117.366
ClNOCl		125.606	
energy	−788.333554	−1148.372793	−689.360992

	N	O	H	X
ONF_2Cl	+4 (+0.481)	−2 (−0.240)		−1 (−0.202) (F) 0 (+0.164)(Cl)
$ONFCl_2$	+3 (+0.204)	−2 (−0.221)		−1 (−0.219) (F) 0 (+0.118) (Cl)
ONFClH	+2 (+0.394)	−2 (−0.301)	+1 (+0.231)	−1 (−0.277) (F) 0 (−0.048) (Cl)

[a] Bond lengths are in Å, angles are in degrees, and energy is in Hartrees.

calculations were carried out on the series ONX_3, ONX_2Y and the series OCX_3^-, OCX_2Y^- (where X, Y = H, F) at the CCSD(T)[14] level using an aug-cc-pVDZ[15] basis set. Tables 1−3 provide the optimized structures, energies, oxidation states, and Mulliken charges for the series ONX_3, ONX_2Y, and $ONXY_2$ (where X, Y = H, Cl, F), respectively. Table 4 provides similar information for the series $HNNH_3$, $HNNH_2F$, $HNNHF_2$, and $HNNF_3$, which are isoelectronic with the corresponding ON series of compounds. Table 5 lists the variation in selected parameters of the HNN series of molecules as a function of internal rotation about the N−N bond. Table 6 lists the optimized molecular parameters, energies, oxidation states, and Mulliken charges for the series OCH_3^- through OCF_3^-. Figures 1 and 2 present plots of the oxidation-state differences vs bond length for the series XNH_3 through XNF_3 where X = O, HN (Figure 1), and OCH_3^- through OCF_3^- (Figure 2), respectively. The solid lines represent a simple second-order polynomial fit to the data. Figures 3 and 4 represent the highest-occupied molecular orbitals (HOMO) and second highest-occupied molecular orbitals (HOMO-1) in the series ONH_3−ONF_3 and OCH_3^-−OCF_3^-, respectively.

Discussion

In covalently bound molecules, Lewis structure models in concert with the concept of formal charge provide an effective method for determining the general molecular structure, the nature of the bonds, and a rough estimate of the electron density at the atoms in the molecule. Because formal charge assumes sharing of electrons is completely equal between all atoms, it fails to take into account the differing electronegativities of the atoms and the polar nature of the bonds. In cases where these differences become substantial and the bonding takes on a significant ionic character, the formal charge description can be quite misleading. For example the formal charges on the oxygen and nitrogen in the series ONH_3−ONF_3 remain unchanged at −1 and +1 throughout the series, and in the series OCH_3^-−OCF_3^-, the charges on the oxygen and carbon are constant at −1 and 0, respectively. Formal charge provides no way of differentiating between the members of these series. An alternative concept, oxidation state, which assumes purely ionic bonding and is thus also an approximate model, does however allow a better prospect for representing ionic character changes as the ligands are varied. In this model the bonding electrons

TABLE 4: Geometrical Parameters of Minimum-Energy Conformers of $HNNH_3$, $HNNH_2F$, $HNNHF_2$, and $HNNF_3$, Oxidation States, and Mulliken Charges[a]

parameters[b]	$HNNH_3$	$HNNH_2F$	$HNNHF_2$	$HNNF_3$
R_{NN}	1.4709	1.3164	1.2409	1.2326
R_{NH} (a)	1.0378	1.0182	1.0302	1.0270
R_{NH} (b)	1.0247		1.0249	
R_{NH} (c)	1.0386	1.0387	1.0249	
R_{NF} (a)		1.5605		1.3551
R_{NF} (b)			1.5253	1.4857
HNN (a)	100.12	111.793	107.558	106.62
HNN (b)	105.40		117.737	
HNN (c)	117.26	116.609		
FNN (a)		120.035		114.31
FNN (b)			118.727	119.71
HNNH	180.0		180.0	
HNNF		0.0		180.0
energy	−111.480 009	−210.449 140	−309.473 604	−408.432 136

	N (a)	N (b)	H (a)	H (b)	H (c)	F (a)	F (b)
$HNNH_3$	−2 (−0.557)	−2 (+0.080)	+1 (+0.057)	+1 (+0.155)	+1 (+0.132)		
$HNNH_2F$	−2 (−0.506)	0 (+0.369)	+1 (+0.144)		+1 (+0.185)	−1 (−0.378)	
$HNNHF_2$	−2 (−0.217)	+2 (+0.469)	+1 (+0.157)	+1 (+0.229)			−1 (−0.319)
$HNNF_3$	−2 (−0.141)	+4 (+0.582)	+1 (+0.166)			−1 (−0.122)	−1 (−0.242)

[a] Bond lengths are in Å, angles are in degrees, and energy is in Hartrees. [b] R_{NH} (a) −NH group, R_{NH} (b) N−H bond trans or cis to N−H bond in −NH group. R_{NH} (c) remaining N−H bonds, R_{NF} (a) N−F bond trans or cis to N−H bond in −NH group. R_{NF} (b) remaining N−F bonds.

TABLE 5: Variation in Molecular Parameters during Internal Rotation about the N−N Bond[a]

HNNF*	energy	R_{NN}	R_{NF}*	R_{NF}'	R_{NF}''
		$HNNF_3$			
0°	18.29	1.2308	1.3997	1.4580	1.4625
45°	1.08	1.2325	1.4510	1.3572	1.5220
90°	6.21	1.2341	1.5384	1.3738	1.4156
135°	15.58	1.2319	1.4109	1.5057	1.4047
180°	0.00	1.2324	1.3552	1.4849	1.4871
		$HNNHF_2$			
0°	43.81	1.2477	1.0287	1.5026	1.5076
45°	33.14	1.2507	1.0298	1.3767	1.6854
90°	67.58	1.2491	1.0358	1.4641	1.5745
135°	30.12	1.2463	1.0271	1.6373	1.4338
180°	0.00	1.2409	1.0248	1.5236	1.5269

HNNF	energy	R_{NN}	R_{NF}	R_{NH}'	R_{NH}''
		$HNNH_2F$			
0°	0.00	1.3171	1.5593	1.0387	1.0387
180°	18.54	1.3564	1.4381	1.0465	1.0464
		$HNNH_3$			
0°	10.47	1.4899	1.0297	1.0315	1.0319
45°	2.03	1.4744	1.0353	1.0249	1.0400
90°	4.24	1.4785	1.0392	1.0262	1.0334
135°	8.95	1.4869	1.0282	1.0354	1.0308
180°	0.00	1.4710	1.0247	1.0386	1.0385

[a] Energy is in kJ mol^{-1}, bond lengths are in angstroms, and angles are in degrees. R_{NH} and R_{NF} refer to bonds associated with the $-NX_3$, $-NX_2Y$, $-NXY_2$, and $-NY_3$ (X = H, Y = F).

are assigned to atoms based solely on electronegativity differences with the atom of higher electronegativity (F > O > N = Cl > C > H) receiving all of the bonding electrons. By use of this model, the oxidation state of the nitrogen changes from −1 to +5 in the series ONH_3−ONF_3 while that of the oxygen remains at −2. In the series OCH_3^-−OCF_3^-, the oxidation state of the carbon changes from −2 to +4 while in the series HNN^*H_3−HNN^*F_3 the oxidation state of the N* changes from −2 to +4. In all these species the oxidation state of the fluorine is constant at −1 so the differences in oxidation state for bonded atoms can be used as a rough measure of the changing ionic character of the O−N, O−C, N−F, and C−F bonds. Corresponding to these changes in oxidation state the O−N bond length shortens in the series ONH_3 (1.3871 Å) through ONF_3 (1.1687 Å) as does the O−C bond length in the series OCH_3^- (1.3624 Å) through OCF_3^- (1.2310 Å) and the N−N bond length in the series $HNNH_3$ (1.4709 Å) through $HNNF_3$ (1.2326 Å). As can be seen in Figures 1 and 2, plots of these bond lengths vs the difference in oxidation state for the connected atoms fits rather well to a simple second-order polynomial. It should be noted that the results obtained for the ONH_3−ONF_3 series and the OCH_3^-−OCF_3^- series using the QCISD/cc-pVDZ method and basis set or the CCSD(T)/aug-cc-pVDZ method and basis set show a consistent difference in that the O−N and O−C bond lengths are noticeably longer for ONH_3 and OCH_3^- using the latter approach. However the O−N and O−C bond lengths converge rapidly for both methods/basis sets as fluorines replace the hydrogens. Both methods/basis sets show a similar trend, i.e., decreasing bond length with increasing oxidation state difference. All members of the series studied with the exception of ONH_3, OCH_3^- and $HNNH_3$ have O−N, O−C, and N−N bond lengths, respectively, which are essentially double bonds whose lengths are somewhat modified by changing ionic character. The bond lengths in ONH_3 (1.3871 Å), OCH_3^- (1.3624 Å), and $HNNH_3$ (1.4709 Å) are more typical of single bonds. Again it should be noted that the O−N and O−C bond lengths in ONH_3 and OCH_3^- are noticeably longer and more in line with the expectation (derived from their molecular orbital occupancy) that they would be single bonds when determined using the CCSD(T)/aug-cc-pVDZ method and basis set than when determined using the QCISD/cc-pVDZ method and basis set. The former approach indicates a generally higher ionic character as evidenced by the Mulliken populations than does the latter approach. However even when using diffuse functions the O−C bond length in OCH_3^- is shorter than what would be expected for a typical O−C single bond (1.42−1.44 Å), and this can be attributed to the partial ionic character of the bond. In all cases, the N−F and C−F bonds decrease in length as the oxidation state difference increases.

Investigation of the molecular orbitals and how they change through a series of related molecules also provides a way to understand the structure and nature of bonding in these molecules. For this part of the investigation, the two series ONH_3, ONH_2F, $ONHF_2$, and ONF_3 and OCH_3^-, OCH_2F^-, $OCHF_2^-$, and OCF_3^- were investigated. In ONH_3 and OCH_3^-,

TABLE 6: Geometrical Parameters for OCH_3^-, OCH_2F^-, $OCHF_2^-$, and OCF_3^-, Oxidation States, and Mulliken Charges[a]

parameters	OCH_3^-	OCH_2F^-	$OCHF_2^-$	OCF_3^-
R_{CO}	1.3100 [1.3624]	1.2632 [1.2715]	1.2374 [1.2426]	1.2253 [1.2310]
R_{CH}	1.1707 [1.1437]	1.1499 [1.1239]	1.1326 [1.1161]	
R_{CF}		1.5570 [1.6936]	1.4731 [1.5116]	1.4252 [1.4445]
HCO	118.093 [115.224]	118.691 [118.901]	121.237 [122.507]	
FCO		115.072 [113.886]	115.487 [115.060]	117.158 [117.304]
HCHO	120.000 [120.000]			
HCFO		114.771 [109.244]	122.439 [123.169]	
FCFO				120.000 [120.000]
energy	−114.759829 [−114.822243]	−213.839438 [−213.948915]	−312.923316 [−313.057148]	−411.999324 [−412.152644]

	H	C	O	F
OCH_3^-	+1 (−0.181) [−0.209]	−2 (+0.315) [+0.750]	−2 (−0.772) [−1.122]	
OCH_2F^-	+1 (−0.136) [−0.164]	0 (+0.512) [+1.011]	−2 (−0.668) [−0.909]	−1 (−0.572) [−0.775]
$OCHF_2^-$	+1 (−0.109) [−0.203]	+2 (+0.689) [+1.484]	−2 (−0.609) [−0.874]	−1 (−0.485) [−0.703]
OCF_3^-		+4 (+0.831) [+1.899]	−2 (−0.575) [−0.836]	−1 (−0.419) [−0.688]

[a] Bond Lengths are in Å, angles are in degrees and energy in Hartrees. Results are obtained using the QCISD/cc-pVDZ method and basis set or (in square brackets0 the CCSD(T)/aug-cc-pVDZ method and basis set.

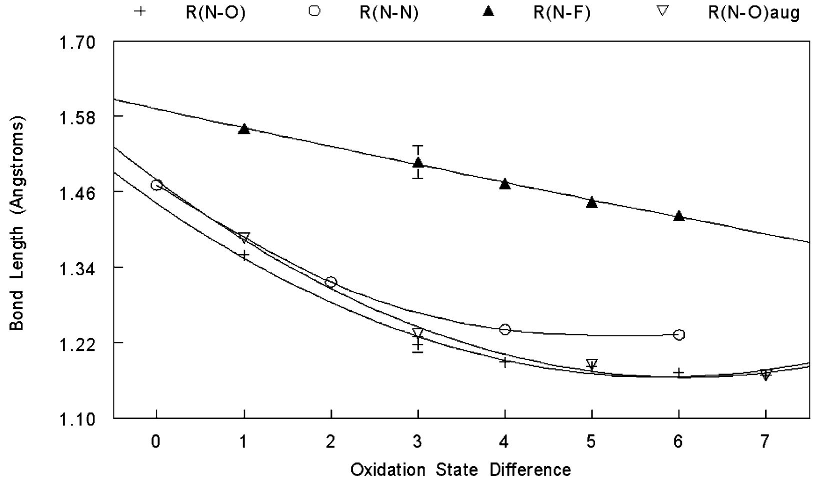

Figure 1. Plot of oxidation-state differences vs bond length for the N−O, N−N, and N−F bonds in the series ONXYZ (X, Y, Z = H, Cl, F) and HNNXYZ (X, Y, Z = H, F). R(N−O), R(N−N), and R(N−F) refer to results obtained using the QCISD/cc-pVDZ approach. R(N−O)aug refers to results obtained using the CCSD(T)/aug-cc-pVDZ approach.

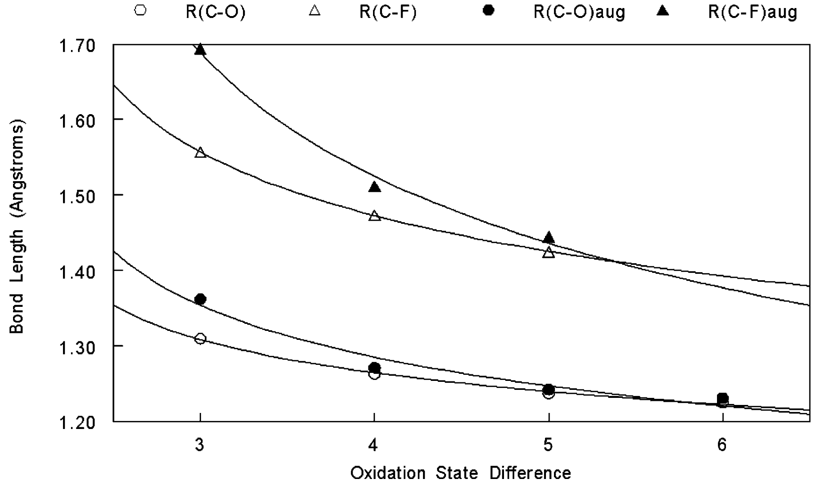

Figure 2. Plot of oxidation-state differences vs bond length for the C−O and C−F bonds in the series $OCXYZ^-$ (X, Y, Z = H, F). R(C−O) and R(C−F) refer to results obtained using the QCISD/cc-pVDZ approach. R(C−O)aug and R(C−F)aug refer to results obtained using the CCSD(T)/aug-cc-pVDZ approach.

the five HOMOs can be represented as

$$\pi_{XO}^{2}\,\pi_{XO}^{2}\,\sigma_{XO}^{2}\,\pi_{XO}^{*2}\,\pi_{XO}^{*2} \qquad (X = N, C)$$

This MO configuration would imply that the O−N and O−C bonds should be single bonds as is evidenced by their bond lengths though again with the qualification that the O−C bond length in OCH_3^- is somewhat shortened due to its partial ionic character. All of the molecular species studied have at least two π_{XO} (X = N, C) bonding orbitals and two doubly occupied π^* orbitals, which are clearly π_{XO}^* (X = N, C) in ONH_3 and OCH_3^- but change significantly as fluorines replace the

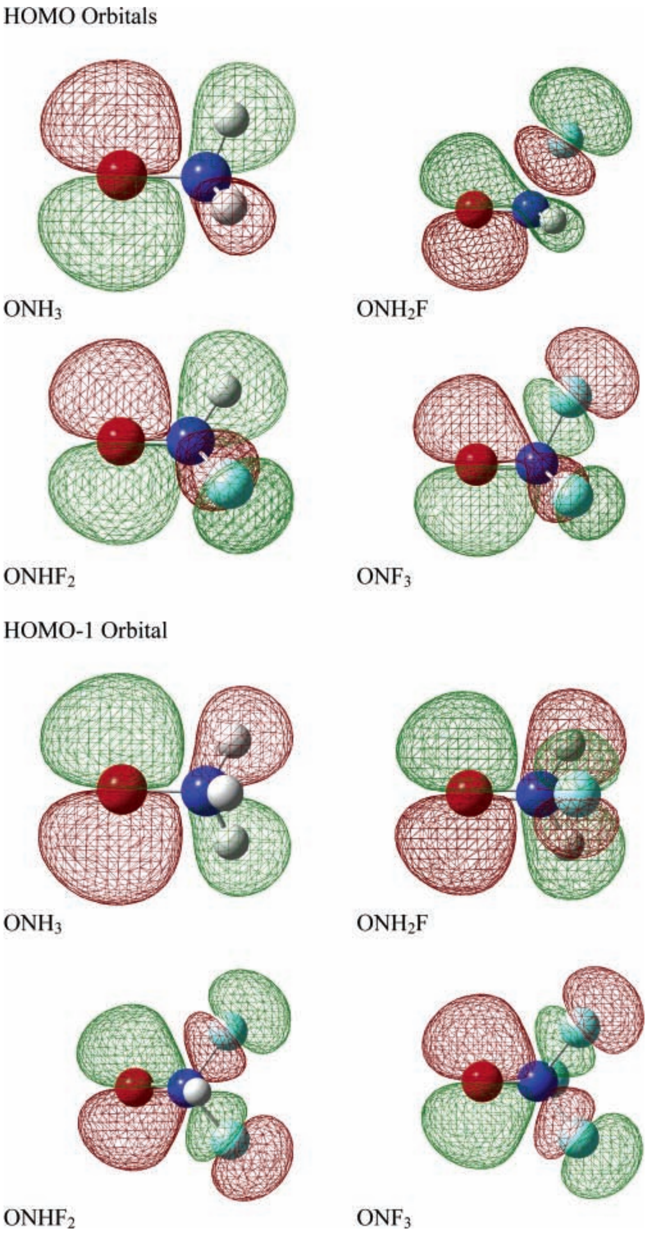

Figure 3. HOMO and HOMO-1 in the series ONH_3−ONF_3.

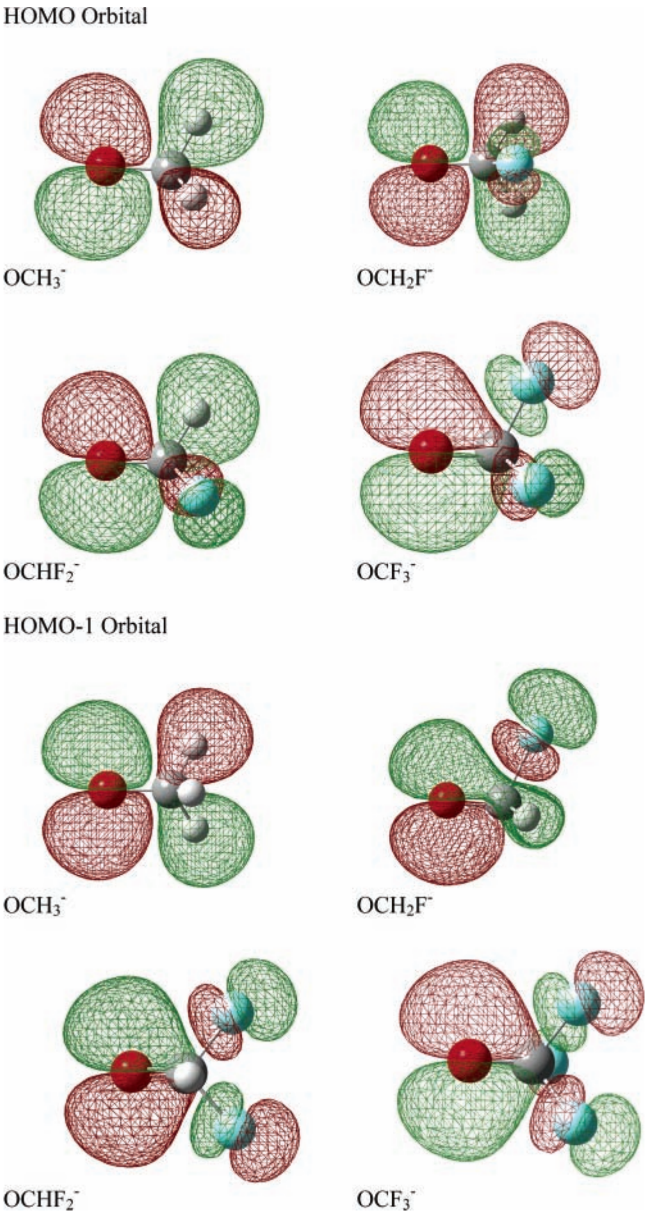

Figure 4. HOMO and HOMO-1 in the series OCH_3^- − OCF_3^-.

hydrogens. Introduction of fluorines to replace the hydrogens as ligands has two consequences. First linear combinations of the π_{XO} orbitals with the fluorine p orbitals results in an increase in the number of occupied orbitals with π_{XO} character contributing to a stronger X−O bond. For example, while there are only two occupied orbitals with π_{NO} character in ONH_3, there are four orbitals with π_{NO} character in ONH_2F. Second there is a marked effect on the two highest-occupied orbitals in the molecules in each series Figures 3 and 4). As already indicated, these are both π_{XO}* in ONH_3 and OCH_3^- with the nodal plane lying between the central atom and the oxygen though clearly closer to the central atom. However as hydrogens are replaced by fluorines, the nodal plane is displaced toward the electron-attracting fluorine side of the molecule, the lobe which initially was localized on the oxygen extends to encompass the central atom and the nodal plane now lies between the central atom and the fluorines. This means that these orbitals now contribute a bonding component to the X−O bond, further strengthening and shortening it, while contributing an antibonding component to the X−F bonds, helping to explain their longer than expected length. This is most clearly apparent in the OCH_3^-−OCF_3^- series. Incidentally a similar change in the position of the nodal plane is observed in the HOMO orbital in the series $HNNH_3$−$HNNF_3$.

Parts a−d of Table 5 illustrate how selected molecular parameters in the series $HNNH_3$−$HNNF_3$ change under internal rotation about the N−N bond. Conjugation between the fluorine p orbitals and the π_{NN} orbitals results in a relatively flat energy surface as a function of dihedral angle in $HNNF_3$ but a significantly higher internal rotation barrier in $HNNHF_2$, as would be expected. Only in the case of $HNNH_2F$ does it become impossible to carry out internal rotation about the N−N bond as would be anticipated for a π_{NN} bond. In this latter case, the molecule dissociates to HNNH + HF. As expected in $HNNH_3$ where the N−N bond is not a multiple bond internal rotation is relatively unrestricted. What is interesting to note in this series is the wide variation in N−F bond lengths. Where the N−F bond(s) are coplanar or close to coplanar with the N−N bond the N−F bond lengths are quite short (1.35−1.43 Å), but where they are significantly out of the plane containing the N−N bond the N−F bonds are unusually long (≥1.5 Å). Obviously the shorter coplanar N−F bonds are the result of conjugation between the N−N π electrons and those of the fluorine p orbitals. Note that in the series ONH_2F−ONF_3 the N−F bond length decreases from 1.6997 to 1.4481 Å and that, similarly, in the series ONH_2Cl−$ONCl_3$ the N−Cl bond length decreases from 2.170 to 1.927 Å and finally in the series OCH_2F^-−OCF_3^- the C−F bond length decreases from 1.6936 to 1.4445 Å. This is more marked when using the CCSD(T)/aug-cc-pVDZ approach because of the distinctly longer N−F or C−F bond lengths obtained for ONH_2F and OCH_2F^- compared with those obtained using the QCISD/cc-pVDZ approach. If we consider that these species could be represented as $ONXY^+F^-$ (where X, Y = H, F), $ONXY^+Cl^-$ (where X, Y = H, Cl), or $OCXYF^-$ (where X, Y = H, F) then the partial positive charge on the nitrogen or carbon will increase as X and Y change from being both hydrogen to both fluorine (or chlorine) and as a result the ionic N^+F^-, N^+Cl^-, and CF^- bonds should become progressively shorter. The remaining N−F, N−Cl, or C−F bonds will be conjugated with the π_{NO} or π_{CO} and be quite short. In ONH_2F, ONH_2Cl, and OCH_2F^-, there will be only one ionic resonance structure, whereas in $ONHF_2$, $ONHCl_2$, and $OCHF_2^-$, there will be two, and in ONF_3, $ONCl_3$, and OCF_3^-, there will be three. The pattern of N−F, N−Cl, and C−F bond lengths in these species certainly seems to fit well with the idea of the proposed ionic resonance structures.

Oxidation state differences between the bound atoms, O−N, N−N, O−C, N−F, N−Cl, and C−F provide a simple but reasonable means of representing ionic character changes for these bonds as a function of changing ligands and appear to correlate well with the corresponding bond lengths in a series. The molecular orbital picture shows that all of these molecules possess at least two π bonding orbitals. Addition of fluorines whose p orbitals conjugate with the π orbitals increases the amount of π bonding character. However of more significance is the observation that as hydrogens are replaced by fluorines the two highest-occupied orbitals, which are clearly π_{NO}* or π_{CO}* in ONH_3 or OCH_3^-, respectively, experience a shift in the nodal plane from lying between the oxygen and the nitrogen or carbon to where it lies between the nitrogen or carbon and the fluorines (Figures 3 and 4). The electron distribution in these orbitals now takes on bonding character between the oxygen and nitrogen or carbon, helping to explain the shortening of these bonds and antibonding character between the nitrogen or carbon and the fluorines explaining their somewhat longer bond lengths. The pattern of energy changes in the series $HNNH_3$−$HNNF_3$ does support the existence of a true π N−N bond. Finally the pattern of N−F, N−Cl, and C−F bond length changes lends support to the idea of ionic resonance structures for these systems.

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