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Bonding and Geometry of OCF_3^-, ONF_3, and Related Molecules in Terms of the Ligand Close Packing Model

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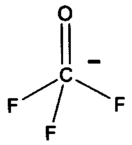
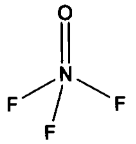
The nature of the bonding in OCF_3^- and the isoelectronic molecule ONF_3 has been the subject of much discussion for many years, because these species appear to have unusual bond lengths and angles. We have reinvestigated the nature of the bonding in these and some related molecules by analyzing their calculated electron density distributions. The results show that the bonding in the series OBF_3^{2-}, OCF_3^-, ONF_3 ranges from predominately ionic in OBF_3^{2-} to predominately covalent in ONF_3 and that the interligand distances are consistent with the close packing of the ligands around the central atom. The AO bonds (A = B, C, N) are double bonds ranging in nature from a very ionic B=O bond to a predominately covalent N=O double bond, but all three are strong and short so that, in accordance with the ligand close packing (LCP) model, the AF bonds are correspondingly long. Also consistent with this model the bonds in a three-coordinated AOF_2 molecule are shorter than those in the corresponding AOF_3 molecule. Protonation of the doubly bonded oxygen, which converts the A=O bond to a single A−OH bond in each case, considerably lengthens the A−O bond, and the bond angles accordingly adopt values much closer to the tetrahedral angle. The difficulties of trying to describe the bonding in these molecules in terms of Lewis structures are discussed.

Introduction

The nature of the bonding in ONF_3 and the isoelectronic anion OCF_3^- has been the subject of much discussion over many years since their structures were first determined.[1,2] The CF and NF bonds have been considered to be unusually long (139.7 and 143.1 pm), the CO and NO bonds unexpectedly short (122.7 and 115.8 pm), and the ONF and OCF bond angles unexpectedly larger than tetrahedral (118.1° and 116.6°). In OCF_3^- the CO bond is almost as short as the CO bond in formaldehyde (120.9 pm),[3] and in ONF_3 the NO bond is almost as short as in NOF (114 pm) [4] and in NO_2^+ (115.4 pm).[5] In contrast the CF bonds are considerably longer than in CF_4 (131.9 pm),[6] and the NF bonds are considerably longer than in NF_3 (136.5 pm)[7] and in NF_4^+ (130 pm).[8] The lengths of the CO and NO bonds are consistent with their being described as double bonds so that both carbon and nitrogen appear to be forming five covalent bonds as in **I** and **II**, contrarily to the octet rule. The geometry of OCF_3^- has therefore usually been rationalized in terms of octet rule resonance structures such as **III** and **IV**. However, it is usually assumed that the octet rule structure **III** is not consistent with the short CO bond, so it is postulated that structure **IV**, which is apparently more consistent with the short CO bond and the long CF bonds, is the most important resonance structure. Structure **IV** can be derived from **III** by back-donation of an oxygen lone pair of electrons into the CO bond accompanied by the transformation of a fluorine bonding pair to a fluorine lone pair, a process that is frequently called negative hyperconjugation. In molecular orbital terms, back-bonding or negative hyperconjugation has been described as electron donation from the oxygen lone pair orbitals to the σ^* orbitals of the C−F bonds, thus giving the CO bond some double-bond or π character and weakening the CF bonds.[9] The bonding in the ONF_3 molecule can be described by similar resonance structures **V** except that the “no-bond” in **IV** is replaced by an ionic bond in **V** which cannot be assumed to necessarily be longer than a covalent bond, so that the long NF bonds are not satisfactorily accounted for.



I



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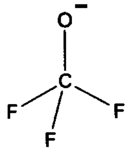

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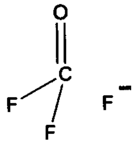
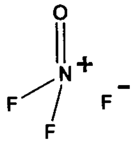


IV



V

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It is important to realize that resonance structures such as **IV** and **V** give a *description* of the bonding in valence bond terms but do not provide an *explanation* for the bond lengths, because the resonance structures were postulated to be consistent with the bond lengths. Similarly, back-donation into the CF or NF σ^* orbitals in the molecular orbital model is postulated to be consistent with the bond lengths, but in the absence of other evidence for this effect it cannot be regarded as an explanation of the bond lengths.

Very recently Zhang and Seppelt[10] have determined the crystal structures of three related ions, namely, $CF_3CF_2O^-$, $(CF_3)_2CFO^-$, and $OCFCF_2O^-$, and calculated the structures of the free ions by ab initio methods. They describe the bonding in these ions in the conventional manner, that is, in terms of the importance of resonance structures such as **III** or negative hyperconjugation. However, prior to the work of Zhang and Seppelt,[10] Wiberg[11] had given a different interpretation of the bond lengths in OCF_3^-. He based this interpretation largely on his finding from ab initio calculations that the CO bond in CF_3O^- (121.4 pm) is considerably shorter than that in its parent alcohol, CF_3OH (132.8 pm), and that this property is not unique to CF_3O^- as it is also observed for CH_3O^-, $CH_3CH_2O^-$, $(CH_3)_3CO^-$, and CFH_2O^- relative to their alcohols. The same effect has also been found previously for two analogous molecules of boron, F_2BO^- and F_2BOH, in which the calculated BO bond length increases from 120.7 to 134.4 pm on protonation of the oxygen.[12] Moreover, while the CO bond lengths *decrease* from the alcohol to the anion, in every case the CF (BF) and/or CH bonds *increase* in length. Wiberg concluded that the differences in the CO bond length between the alcohol and the alkoxide cannot be due to back-bonding (negative hyperconjugation) because this difference is much less affected by the nature of the substituents, H, CH_3, or F, than would be expected on the basis of the expected very different energies of CH, CCH_3, and CF σ^* orbitals. Wiberg also calculated atomic charges using the AIM method.[13] He found the charges on all the atoms to increase on going from the alcohol to the anion, and he attributed the decrease in the length of the CO bond to the increased attraction due to the increased charges on carbon and oxygen. However, he did not comment on his finding that as the CO bond decreases in length the CF and CH bond lengths increase at the same time despite the increased charges on C, F, and H.

In this paper we describe an alternative explanation for the structural features of CF_3O^-, ONF_3, and other related molecules. While we agree with Wiberg that the atomic charges are an important factor determining the bond lengths in these molecules, we show that they also depend in an important way on the packing of the ligands around the central atom in accordance with the ligand close packing (LCP) model.[12,14,15] According to this model bond lengths and bond angles are mainly determined by ligand−ligand interactions, that is by the packing of the ligands around the central atom, leading to almost constant interligand distances in a variety of molecules. Ligand close packing is particularly important for the elements of period 2 such as Be, B, C, and N because of their small size, and for ligands that are more electronegative than the central atom, such as F and O. Such ligands have an appreciable negative charge and are therefore considerably larger than the positively charged central atom, so they are attracted to it, forming a close-packed arrangement around it. We have shown[12,14,15] that each ligand can be assigned an intermolecular ligand radius that determines its contact distance with other ligands. This ligand radius is almost constant for a given central atom but varies with the difference in the electronegativities of the ligand and the central atom because this determines the charge on the ligand and therefore its size. The ligand radii relevant to this paper are given in Table 1.

Table 1. Intramolecular Ligand Radii

central atom	ligand radius (pm) F	O	C
B	113	119	137
C	108	114	125
N	106	112	120

Calculations

The calculations for OBF_3^{2-}, $HOBF_3^-$, OCF_3^-, $HOCF_3$, ONF_2^+, ONF_3, and $HONF_3^+$ were performed using the Gaussian 94 program.[16] They were based on Becke's three-parameter exchange functional (B3)[17] as slightly modified by Stephens et al.,[18] used in conjunction with the Lee, Yang, and Parr (LYP)[19] correlation-gradient-corrected functional, and using the 6-311+G(2d,p) basis set.[20] Topological analysis of the charge density was performed using the AIMPAC[21] and MORPHY[22] software packages. For OCF_3^-, calculations were also carried out at the MP2 level. Atomic charges for the molecules $CF_3CF_2O^-$, $(CF_3)_2CFO$, and $FCOCF_2O^-$ were calculated from a B3LYP wave function obtained from Zhang and Seppelt's calculated atomic parameters using the 6-31+G(d,p) basis set.[10]

Results and Discussion

OCF_3^- and Other OAF_n Molecules. Table 2 gives our ab initio calculated molecular parameters for OCF_3^- together with previously reported values. There is good agreement between the B3LYP values and the MP2 values and with the experimental values except that the calculated C−F bond length is appreciably greater than the experimental value, presumably because both the MP2 and B3LYP calculations make inadequate correction for electron correlation, which is known to be particularly important in fluorides. The apparent agreement between the Hartree−Fock calculated CF bond length[11] and the experimental value presumably arises from a fortuitous cancellation of errors. The results of the B3LYP calculations for

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Table 2. Bond Lengths (pm) and Bond Angles (deg) for OCF_3^-

bond length and bond angle	this work B3LYP 6-311+G(2d)	this work MP2 6-311+G(2d)	Seppelt B3LYP 6-31+G(d,p)	Wiberg HF 6-311++G*	expt
C−F (pm)	143.9	143.1	144.3	138.4	139.2
C−O (pm)	121.3	121.6	122.2	121.4	122.7
F−C−O (deg)	117.3	117.2	117.2	116.5	116.5
F−C−F (deg)	100.6	100.7	100.8		102.0

Table 3. Bond Lengths, Bond Angles, and Interligand Distances for Some OAF_n Molecules

	AO (pm)		AF (pm)		OAF (deg)		FAF (deg)			
	calc	expt	calc	expt	calc	expt	calc	expt	F···F (pm)	O···F (pm)
OBF	120.6		128.4		180	180				
OBF_2^-	120.7		140.5		126.8		106.4		225(226)*	234 (232)
OBF_3^{2-}	133.3		152.4		117.7		100.8		235 (226)	244 (232)
$HOBF_2$	135.4	134.4	132.5	132.3	121.7	122.8	116.6	118.6	227 (226)	234 (232)
$HOBF_3^-$ [b]	145.3		140.7		108.1		109.3		231 (226)	233 (232)
			142.9		111.3		106.8		229 (226)	238 (232)
$MOBF_3$[c]		145.0		135.0		112.0		109.9	224 (226)	232 (232)
				138.8		110.1		108.8	224 (226)	233 (232)
				140.8		108.7		108.7	225 (226)	232 (233)
OCF_2	117.1	117.0	132.0	131.7	125.2	126.2	107.6	109.5	215 (216)	222 (223)
OCF_3^-	121.3	122.7	143.9	139.2	117.3	116.5	100.6	102.0	216 (216)	223 (223)
$HOCF_3$	134.6		132.8		108.6		108.5		217 (216)	217 (223)
			135.0		112.4		106.4		216 (216)	224 (223)
ONF_2^+	112.9		131.2		125.8		108.4		213 (212)	217 (218)
ONF_3	117.5	115.8	144.4	143.1	117.5	118.1	100.4	100.8	220 (212)	223 (218)
$HONF_3^+$	131.3		132.1		108.1		107.8		216 (212)	213 (218)
			135.1		113.6		105.6		215 (212)	223 (218)

[a] Values in parentheses are sums of the ligand radii. [b] $HOAF_3$ molecules have C_s symmetry. The upper number in each entry is for the unique F atom trans to the OH group, and the lower number is for the other two equivalent F atoms. [c] $MOBF_3 = [ReO(OBF_3)(1\text{-methylimidazole})_4]BF_4^-$.

Table 4. Atomic Charges and Electron Densities at the Bond Critical Point

	q(A)	$-q$(O)	$-q$(F)	q(OH)	q(H)	ρ_b(AO)	ρ_b(AF)
OBF	2.26	1.45	0.81			0.316	0.234
OBF_2^-	2.33	1.59	0.87			0.276	0.180
OBF_3^{2-}	2.36	1.67	0.90			0.241	0.118
$HOBF_2$	2.41	1.38	0.82	−0.77	0.61	0.221	0.209
$HOBF_3^-$	2.41	1.32	0.86[a]	−0.82	0.50	0.176	0.164
			0.86				0.155
OCF_2	2.30	1.09	0.60			0.467	0.297
OCF_3^-	2.16	1.26	0.63			0.449	0.247
$HOCF_3$	2.30	1.04	0.62	−0.45	0.59	0.353	0.300
			0.62				0.286
ONF_2^+	1.14	0.01	0.06			0.628	0.382
ONF_3	1.09	0.30	0.26			0.595	0.273
$HONF_3^+$	1.16	0.48	0.10	+0.20	0.68	0.405	0.382
			0.12				0.354

[a] See footnote *b* to Table 3.

OBF_3^{2-}, $HOBF_3^-$, OCF_3^-, $HOCF_3$, ONF_2^+, ONF_3, and $HONF_3^+$, together with the results of our earlier calculations[14] on OBF, OBF_2^-, and OCF_2, are given in Table 3 together with the available experimental bond lengths, bond angles, and interligand distances. The interligand distances were calculated from the experimental data where this is available, otherwise from the calculated data, and are compared with the sum of the ligand radii from Table 1. Our calculated molecular dimensions for ONF_3 agree well with recent MP3/6-31G calculations of Levy and Hargittai,[23] who found $r(NO) = 116.7$ pm, $r(NF) = 141.5$, $\angle FNF = 100.6°$, and $\angle FNO = 118.3°$. Table 4 gives the atomic charges and the electron densities at the bond critical point obtained from the analysis of the electron density distribution for each of the molecules we studied. There is no available experimental data for the free OBF_3^{2-} or $HOBF_3^-$ ions, but the OBF_3 group is found as a ligand in the rhenium complex $[ReO(OBF_3)(1\text{-methylimidazole})_4]^+BF_4^-$.[24] The observed bond lengths and angles in this molecule are in good agreement with the calculated values for $HOBF_3$ except that the observed BF bond lengths are somewhat smaller than the calculated values. However, the observed F···F and O···F distances are in excellent agreement with the predicted values, while the calculated values are a littler larger than predicted, consistent with the longer calculated values for the BF bond lengths. It is commonly found that the ab initio calculations for predominately ionic fluorides at the level we have used give longer bond lengths than are observed experimentally.

We see that in each case the AO bonds are shorter than the A−F bonds, consistent with their formulation as double bonds, although the atomic charges show that the AO bonds, like the AF bonds, are not pure covalent bonds but vary from the very ionic BO bonds to the much less ionic NO bonds. In each case both the AO and the AF bonds increase in length from the 2-coordinate OBF to the 3-coordinate OBF_2^- and from all of the 3-coordinate AOF_2 molecules to the 4-coordinate AOF_3 molecules, consistent with the LCP model. The ratio of the average length of the bonds in OCF_3^- to the average length of the bonds in OCF_2 is 1.05, close to the ratio of 1.06 expected from the close packing of spherical ligands around the central atom. Moreover, as can be seen in Table 3, in most cases the F···F and O···F contact distances are very nearly the same in the AOF_2 molecules and the AOF_3 molecules, and in most cases they are close to the values predicted from the ligand radii in Table 1, which were obtained from a study of a large range of fluorides, oxides, and hydroxides.[12,14,15] The interligand distances in OBF_3^{2-} are, however, rather longer than expected. This, together with the very long bonds, the BF bonds being 21 pm

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Table 5. Atomic Charges, Bond Lengths, Bond Angles, and Interligand Distances in the OCF_n Groups of OCF_3^-, $CF_3CF_2O^-$, $OCFCF_2O$, and $(CF_3)_2CFO^-$

	OCF_3^-	$CF_3CF_2O^-$	$OCF\mathbf{CF_2O}^-$	$(CF_3)_2CFO^-$	$\mathbf{OCF}CF_2O^-$
q(O)	−1.48	−1.3	−1.29	−1.25	−1.02
q(F)	−0.63	−0.64	−0.63	−0.62	−0.63
q(C)	2.77	1.81	1.80	1.40	1.58
C−F (pm)					
calc	144.3	147.6	148.2	152.1	138.1
expt	139.7	140.2, 144.7	141.4, 147.8	141.6	135.2
C−O (pm)					
calc	122.2	122.9	122.6	125.6	117.2
expt	122.7	123.0	122.0	134.3	119.3
∠OCF					
calc	117.2	116.2	116.0	115.0	138.3
expt	116.5, 115.8		115.9	115.1	120.8
∠FCF					
calc	100.8	99.9	100.0		
expt	101.7, 102.7		99.4		
O···F expt	223 (222)		225 (222)	233 (222)	219 (222)
F···F expt	216 (216)		221 (216)		

longer than in BF_4^-, suggest that this ion is on the verge of stability as a consequence of the strong repulsions between the ligands resulting from their large charges.

It is interesting to look at the bond length changes on substituting an F ligand in an AF_4 molecule by an O ligand to give an AOF_3 molecule. The CF bond in CF_4 (131.9 pm)[6] increases by 7.3 pm to 139.2 pm in CF_3O^-, and the NF bond in NF_4^+ (130 pm)[8] increases by 13.1pm to 143.1 pm in ONF_3. Similar increases are observed in the calculated bond lengths.[11] The BF bond increases from 138.6 pm in BF_4^- [25] to 152.4 pm in OBF_3^{2-} and from 131.4 pm in BF_3[12] to 140.5 pm in OBF_2^-, and the CF bond increases from 123.5 pm in CF_3^+ [12] to 131.7 pm in OCF_2.[3] All of these bond length changes are consistent with the LCP model.

Protonation of the oxygen in these molecules considerably increases the A−O bond length, and the A−F bond length decreases correspondingly to keep all of the ligands close packed, giving comparable A−OH and A−F bond lengths and angles much closer to 120° or 109.5°. For example, the calculated bond lengths in $HOCF_3$ have the very similar values $r(CO) = 132.8$ pm and $r(F) = 130.1$ and 131.7 pm, and the OCF and FCF angles have the values 108.8°, 111.9°, and 110.3° compared to the very different values $r(CO) = 121.4$ and $r(F) = 138.4$ and angles of 116.6° and 101.6° in OCF_3^-. Similar changes in the bond lengths and angles were also found by Wiberg[11] for OCF_3^- and other alkoxides and their parent alcohols such as CH_3O^- and CH_3OH. Similarly the bond lengths and angles in F_2BOH and $HONF_3^+$ (Table 3) are very similar compared to the very different bond lengths and angles in F_2BO^- and ONF_3. There are two O···F distances in the $HOAF_3$ molecules which have C_s symmetry because the electron density around an OH group is not cylindrically symmetrical as we have discussed elsewhere.[12,15] So the oxygen has different contact distances in different directions, in this case to the unique F atom trans to the H, and to the other two equivalent F atoms.

Wiberg[11] pointed out that on protonation of the oxygen in OCF_3^- and other alkoxide ions the charge on the oxygen atom is reduced. He suggested that in OCF_3^- this is because the protonated oxygen is more weakly attracted by the positive carbon atom and the bond lengthens correspondingly. We see that the charge on oxygen is similarly reduced on protonation of both OBF_2^- and OBF_3^{2-}, although not in ONF_3, in which the charges are very small. However, in each case protonation converts a formal double bond into a formal single bond with a corresponding considerable reduction in the value of ρ_b, and the bond lengthens accordingly.

$CF_3CF_2O^-$, $(CF_3)_2CFO^-$, and $FCOCF_2O^-$. The calculated and experimental data for the OCF_n groups in these molecules are compared in Table 5. As a fluorine in OCF_3^- is replaced by a CF_3 or COF group, the charge on carbon decreases substantially, the charge on oxygen decreases slightly, and that on fluorine remains constant. As the charge on carbon decreases, the calculated CF and CO bond lengths increase as the “ionic” contribution to the bonding decreases, and the OCF and FCF angles decrease accordingly. The experimental bond lengths and angles generally follow the same trends except as discussed below. Zhang and Seppelt[10] attribute the increased CF bond length in CF_3CF_2 O^- to increased negative hyperconjugation, but this would be expected to decrease the CO bond length, whereas it actually increases slightly.

Replacing a second fluorine in CF_3O^- by a CF_3 group to give $(CF_3)_2CFO^-$ further increases the calculated CF and CO bond lengths from those in $CF_3CF_2O^-$ in accordance with the further decrease in the charge on carbon. The experimental value for the CO bond length in the OCF group is unexpectedly large and the experimental value for the CF bond length is unexpectedly small compared to the calculated values. Zhang and Seppelt[10] speculate that the charge on oxygen in $(CF_3)_2CFO$ is larger than in $CF_3CF_2O^-$, causing it to form stronger hydrogen bonds to the piperidinium cation than the $CF_3CF_2O^-$ ion. However, the calculated charge on oxygen in the free ion is actually slightly smaller than in $CF_3CF_2O^-$. Nevertheless, the oxygen in $(CF_3)_2CFO^-$ does have one considerably shorter contact (231pm) with a hydrogen atom of the piperidinium ion, suggesting that it is indeed more strongly hydrogen bonded. Presumably it is the crystal packing which is responsible for this short O···H contact which leads to a lengthening of the CO bond and probably to an increased charge on the oxygen in the crystal.

The most unexpected feature of the X-ray structure of $OFCCF_2O^-$ is that one of the CF bonds in the CF_2O group is particularly long (147.8) pm compared to the other CF bond (141.4 pm) and makes unusually small angles with the adjacent O, F, and C atoms. Zhang and Seppelt attributed these differences to a short hydrogen-bonded contact of 237 pm which this fluorine makes with a hydrogen of the $N(CH_3)_4^+$ cation. The lengthening of this bond allows the angles that this fluorine makes with the other ligands to decrease, thus keeping the interligand distances essentially constant. Zhang and Seppelt

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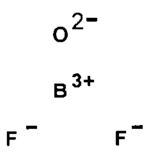
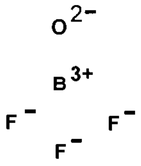
(25) Yakeo, H. T.; Curl, R. F. *J. Chem. Phys.* **1972**, *56*, 4313.

point out that this ion appears to be made up from a nearly planar OFCCFO molecule with a fluorine attached by a long bond to one of the carbon atoms. Consistent with this explanation, the CO and CF bond lengths in the nearly planar portion of the distorted COF_2 group approach those in the COF group. The bonds in this group, in which the carbon is only 3-coordinated, are considerably shorter than in any of the X_2FCO groups in which the carbon atom is 4-coordinated and are comparable to the bond lengths in COF_2 (CO, 117.0 ppm; CF, 131.7 ppm)[3] and oxalyl fluoride, OFCCFO (CO, 118.0 ppm; CF, 132.9 pm).[26]

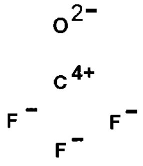
Lewis Structures, the Octet Rule, and the Nature of AO Bonds. The difficulty of writing acceptable Lewis resonance structures for molecules such as OCF_3^- arises because the bond lines in such structures do not have a clear meaning. Frequently they are taken to indicate essentially pure covalent bonds such as the C−C and C−H bonds, and structures **I** and **II** are then regarded as unsatisfactory because they appear to violate the octet rule. However, the atomic charges show that the bonding in the oxofluorides of boron is predominately ionic. To a first approximation OBF_n molecules are best described as consisting of a B^{3+} ion around which O^{2-} ions and F^- ions are close packed as, for example, in OBF_2^- (**VI**) and OBF_3^{2-} (**VII**) rather than as covalent molecules.



VI



VII



VIII

Because the atomic charges are smaller in OCF_3^-, the fully ionic formulation **VIII** is not satisfactory, and neither is the fully covalent formulation **I**. The best we can do it is to describe it as a resonance hybrid of **I** and **VIII** with roughly equal weights, or alternatively we can use **I**, recognizing that a bond line does not imply a fully covalent bond. To describe ONF_3 in the same way we would have to give a much greater weight to the covalent structure **II** than to the fully ionic structure.

It is important to recognize that an AO double bond can vary from a predominately ionic bond as in OBF_3^{2-} to a predominately covalent bond as in ONF_3. Two pairs of electrons are involved in the bond whether it is predominately ionic or predominately covalent, that is, whether the bonding electrons are largely located on the oxygen atom or are extensively shared with the A atom. A double bond is always shorter and stronger than a corresponding single AF or AOH bond in which only one pair of electrons is involved. It is frequently incorrectly assumed that describing an AO bond that is roughly 50% ionic and 50% covalent by the Lewis structure $A^+{-}O^-$ implies that it will be longer than a double bond and approximately equal in length to a single bond, as is often assumed in the case of structure **III** for OCF_3^-. However, this structure should be considered to denote a double bond that is 50% ionic and 50% covalent, and there is no reason to suppose that it will be longer than a purely covalent double bond. Nevertheless, it is unsatisfactory because it gives an unrealistic picture of the charge distribution.

Lack of recognition of the limitations of Lewis structures has led in the past to much unnecessary and often polemical discussion about the nature of the bonding in certain molecules. Lewis proposed the octet rule on the basis that he could account for the formulas of a large number of molecules if a valence shell contained no more than four shared pairs of electrons thus giving the atom a noble gas configuration. In other words, no more than four bond lines can be drawn to any atom. The octet rule is often justified on the grounds that only four orbitals—the 2s and three 2p orbitals—are available for bonding by most of the main group elements, as the d orbitals of the elements of period 3 and beyond have too high an energy to effectively participate in bonding. However, despite its long and useful history, the octet rule is not particularly relevant in the discussion of bonding in molecules that are not purely or very nearly purely covalent, which means the majority of inorganic molecules. The coordination number of an atom in many molecules, particularly when the ligands are more electronegtive than the central atom, as is very often the case, is primarily determined by the relative sizes of the central atom and the ligands. Thus period 2 elements have a maximum coordination number of four, but period 3 and 4 elements have a maximum coordination number of six, while period 5 and 6 elements may have higher coordination numbers. Thus while almost all molecules of the period 2 elements appear to obey the octet rule because no atom ever has more than four ligands, many molecules of the elements of period 3 and beyond, such as PCl_5 and SF_6, are exceptions to the octet rule. Exceptions to the octet rule among period 2 elements are possible when double bonds are present as in OCF_3^- and ONF_3 because, although they have a coordination number of four, the Lewis structure has five bonds. Provided that the bonding is sufficiently ionic, no more than one s and three p orbitals are required to describe the bonding. Clearly, in the limiting case of a fully ionic molecule, there is no contribution to the bonding from the valence shell s and p orbitals. The reason that NF_5 is not known is not that it is an exception to the octet rule but that nitrogen cannot have a coordination number greater than four. The bonding could be described using only s and p orbitals, just as for ONF_3.

The preceding discussion shows us that we do not need to use the concept of negative hyperconjugation in describing the bonding in these molecules. It was introduced simply as means of deriving one unsatisfactory Lewis structure from another unsatisfactory Lewis structure, both of which unsuccessfully attempt to describe the polarity of the bonds. Negative hyperconjugation cannot be regarded as a physical phenomenon any more than can the concept of resonance. In the molecular orbital model the description of hyperconjugation as the donation of nonbonding electrons into antibonding σ^* orbitals is simply an unnecessarily complicated way of describing the polarity of the bonds.

We have not fully resolved the question of how best to give a simple description of the bonding in molecules such as OBF_3^{2-}, OCF_3^-, and ONF_3, but it would seem that structures such as **I** and **II** are the best that we can do provided that we emphasize the ionic character of the bonds. If, instead, we wish to use resonance structures, the best description would be in terms of two resonance structures such as **I** and **VIII** with the contribution of the ionic structure **VIII** decreasing considerably with increasing electronegativity of the central atom from B, to C, to N.

Bond Lengths and the Electron Density at the Bond Critical Point. Figure 1 shows that there is a very clear correlation between the electron density at the bond critical point ρ_b and the bond length for BO, CO, NO, BF, CF, and NF bonds, as we have previously demonstrated for BeO, BO, and CO

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(27) Cruickshank, D. W. J.; Jones, D. W.;Walker, G. *J. Chem. Soc.* **1964**, 1303.

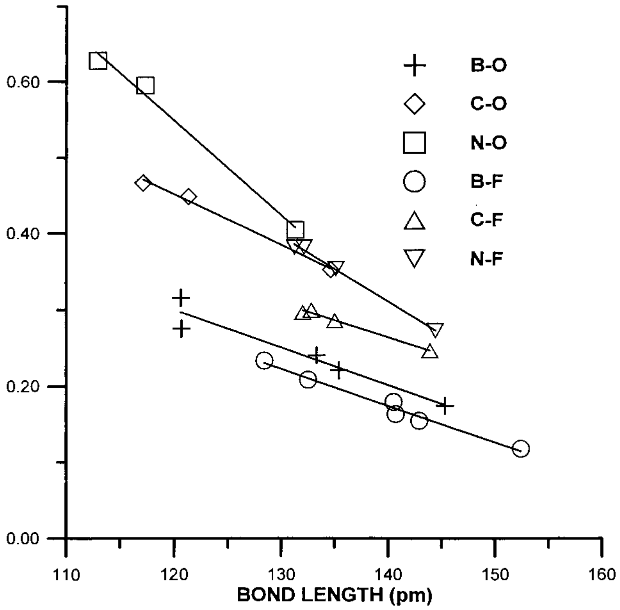

Figure 1. Correlation of bond length with the electron density at the bond critical point (ρ_b) for the bonds in the molecules discussed in this paper.

bonds.[12] Both A−OX single and A═O double bonds fit on the same curve and can have a range of ρ_b values and corresponding lengths, and while the two bond types each cover a somewhat different range, no sharp distinction can be made between a single bond and a double bond. These variations in the lengths of formally single and double bonds emphasize the difficulty of drawing any useful conclusions from the comparison of the length of a particular bond with some arbitrarily chosen standard bond length. Moreover, since a number of factors including polarity and ligand close packing affect bond lengths, in addition to multiple-bond character, it is not meaningful to interpret the apparent shortening of a bond just in terms of double-bond character, as is often done.

We can see from Figure 1 that the length of an AX bond is related in an approximately linear manner to the electron density at the bond critical point, ρ_b. For a given ligand X, ρ_b for a given A−X bond increases in the order A = Be, B, C, N.

Conclusions

We have shown the following in this paper.

(1) There is nothing particularly unusual about the bonding in OCF_3^- and in ONF_3.

(2) The A−F and A═O bond lengths in these and other related oxofluorides of boron, carbon, and nitrogen can all be understood in terms of the packing of the ligands around the central atom, that is, in terms of the ligand close packing (LCP) model.

(3) The bonds in the oxofluorides of boron, carbon, and nitrogen all have ionic character which decreases considerably from boron to nitrogen.

(4) BO, CO, and NO bonds, where the oxygen is a terminal atom, can all be regarded as double bonds independent of their ionic character, consistent with their short lengths. The longer BF, CF, and NF bonds and B−OH, C−OH, and N−OH bonds can be regarded as single bonds, also independent of their ionic character.

(5) Both the ionic character and the covalent character of AO, AF, and AOH bonds contribute to their length and strength, double bonds having both a larger ionic and a larger covalent character than single bonds.

(6) Negative hyperconjugation is not needed to explain bond lengths in OCF_3^-, ONF_3, and related molecules.

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