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Bond Lengths and Bond Angles in Oxo, Hydroxo, and Alkoxo Molecules of Be, B, and C: A Close-Packed Nearly Ionic Model

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We have surveyed the experimental data for oxo, hydroxo, and alkoxo molecules of Be, B, and C and have shown that the intramolecular interligand distances for a given central atom are remarkably constant and independent of coordination number and of the presence of other ligands. Atomic charges obtained from the analysis of the calculated electron densities for a large selection of molecules of this type have shown that these molecules are predominately ionic. On the basis of these results we suggest that the bond lengths and geometries of these molecules can be best understood in terms of a model in which anion-like ligands are close-packed around a cation-like central atom. Values of the interligand radius of each ligand obtained from the intramolecular interligand contact distances are smaller than the crystal ionic radii and decrease as expected with decreasing ligand charge. This model provides a simple quantitative explanation of the decrease in the bond lengths in these molecules with decrease in the coordination number from four to three and of the changes in bond length caused by the presence of other ligands with different ligand radii. With decreasing bond length the electron density at the bond critical point increases correspondingly for Be−O, B−O, and C−O bonds. The nontetrahedral angles found in all $A(OX)_4$ molecule are explained on the basis of a noncylindrically symmetrical charge distribution around oxygen.

Introduction

For many years, following the early suggestion of Pauling,[1] variations in the lengths of X−F and X−O bonds have commonly been interpreted in terms of multiple bond character resulting from back-bonding, after “correction” of the observed lengths for polarity on the basis of the Schomaker−Stevenson equation.[2] In a recent paper[3] on the lengths of bonds to fluorine we showed that there is no justification for the purely empirical Schomaker−Stevenson equation and that there is little convincing evidence for the supposed double-bond character in molecules such as BF_3 or SiF_4. In that paper we proposed that for coordination numbers $n \geq 3$ the observed bond lengths could be best understood in terms of the close packing of anion-like fluorine ligands around a central atom. This model was based on two sets of observations:

1. The experimental and calculated F- - -F distances in a variety of AF_n molecules ($n \geq 3$) have a very nearly constant value for a given central atom A despite the considerable variation in A−F bond lengths. For example, the B−F bond has a length of 130.7, 139.6, and 142.4 pm in BF_3, BF_4^-, and $CH_3BF_3^-$, respectively, yet the F- - -F distance remains constant at 226 pm, which is also the F- - -F distance in many other BF_3X^- and BF_2X molecules. Moreover, the ratio of the B−F bond lengths in BF_4^- and BF_3 is equal to the value of 1.06 predicted for close packing of anion-like F atoms around the central cation-like boron.

2. Atomic charges obtained by the analysis of calculated charge density distributions[3] indicate that the fluorides of Li, Be, B, C, Na, Mg, Al, Si, and P are predominately ionic in character. The charge on fluorine decreases from −0.92 in LiF to − 0.61 in CF_4 and from −0.92 in NaF to −0.76 in PF_3. It has long been recognized that the bonds in these fluorides have some ionic character, but, apart from LiF, NaF, and MgF_2, the ionic character as estimated, for example by Pauling,[1] is considerably less than is indicated by our calculated atomic charges. Nevertheless, even though the partial ionic character of the molecular fluorides of Be, B, C, Si, and P has been recognized, when they are in the molecular form their structures are almost always written with bond lines which are usually taken to indicate predominately covalent bonds. Moreover, their bond lengths are commonly compared with the sum of covalent radii. The radius of the anion-like fluorine ligand obtained from the F- - -F distances is somewhat smaller than the crystal radius of 133 pm, but it is essentially constant for a given central atom, and decreases with decreasing negative charge on the fluorine in the following series: F^- (132 pm), BeF_n (128 pm), BF_n (113 pm), CF_n (108 pm). This type of nonbonding radius has previously been called a 1,3 radius[4,5] but we call it a *ligand intramolecular nonbonding radius* or simply a *ligand radius*. Previously it has been assigned only a single value for a given ligand independent of the central atom. For example, a value of 108 pm has been given for fluorine,[4,5] which is the value that we assign to fluorine bonded to carbon.[3]

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In this paper we report density functional theory calculations of the geometry and atomic charges of some oxo and hydroxo molecules of beryllium, boron, and carbon and an analysis of both the experimental and calculated lengths of BeO, BO, and CO bonds. It is convenient to distinguish three types of oxygen ligand: a terminal oxygen AO_t, a bridging oxygen AO_bX or AO_bA, and a hydroxyl oxygen AOH. Although a hydroxyl oxygen is in principle a type of bridging oxygen, it is convenient to consider OH as a separate ligand because the proton is largely buried in the oxygen charge cloud. In the fully ionic limit the radii of O^{2-} and OH^- are very similar. Shannon[6] obtained the values 135, 136, and 138 pm for 2-, 3-, and 4-coordinated O^{2-} and 132, 134, and 135 pm for 2-, 3-, and 4-coordinated OH^- from the analysis of the interionic distances in a large number of ionic solids. So we have made the reasonable assumption that the values of 135 and 132 pm for the O^{2-} and OH^- ions, respectively, should also apply to both the 1- and 2-coordinated ions in fully ionic molecules. We show that, as for the molecular fluorides,[3] the bond lengths in 3- and 4-coordinated oxo and hydroxo molecules of Be, B, and C are largely determined by the packing of anion-like O, OH, or OX ligands around the central atom. From the O- - -O contact distances we derive values for the intramolecular nonbonding ligand radius of both terminal and bridging oxygen ligands. We will see that these ligand radii are smaller than the values given above for the free ions but are consistent with the less than fully ionic ligand charges, and that they account for the observed bond lengths on the basis of the ligand close-packing model.

Calculations

The B3LYP calculations were performed using the Gaussian 94 program.[7] They were based on Becke's three-parameter exchange functional (B3)[8] as slightly modified by Stephens et al.,[9] used in conjunction with the Lee, Yang, and Parr (LYP)[10] correlation-gradient-corrected functional. Topological analysis of the of both the total charge density and its Laplacian[11] were performed using the AIMPAC[12] and MORPHY[13] software packages. The calculated geometries agree well with the experimental data where this is available.

Results and Discussion

We first consider oxoboron molecules as there are more experimental and calculated data available for these molecules than for the corresponding beryllium and carbon molecules.

Oxoboron Molecules. The lengths of BO bonds in both 3- and 4-coordinated molecules have been well-established experimentally. Allen and co-workers[14] have given a mean value of 147(2) for the BO bond length in 24 salts containing the BO_4 group and 137(2) pm for 35 molecules of the type X_2B-OX. Earlier, Pauling[15] had given the same average values of 147(1) and 137(1) pm for tetrahedral BO_4 groups, and triangular BO_3 groups respectively, as had Hursthouse.[16] Wells[17] has commented on the considerable variations of bond lengths within these groups, particularly in complex borates, and he gives the ranges 128−143 pm (mean 136.5 pm) for BO_3 groups and 143−155 pm (mean 147.5 pm) for BO_4 groups.

Experimental bond lengths, bond angles, and O- - -O contact distances for 41 molecules are given in Table 1, and O- - -O distances for 10 complex polyborates containing both BO_3 and BO_4 groups are given in Table 2. We see that BO_4 groups have an average BO bond length of 148(2) pm and BO_3 groups an average bond length of 138(2) pm, in agreement with the average values given earlier by Pauling[15] and by Hursthouse.[16] Thus it appears that the BO bond length is largely determined by the coordination number of boron. Indeed these average bond length values give a tetrahedral to trigonal bond length ratio (d_4/d_3) of 1.07, close to the expected ratio of 1.061 for 4- and 3-coordinate close packing. The O- - -O distance in all the BO_3 and BO_4 groups is almost constant with an average value of 239 ± 2 pm even though the BO bond lengths cover a wide range from 132 to 150 pm. In many cases the OBO bond angles deviate considerably from the ideal angles of 120.0 and 109.5° for regular trigonal planar BO_3 and tetrahedral BO_4 groups, respectively, and cover a range of 106−125° although the average bond angles are almost always equal to 109.5 or 120°. There is a clear correlation between bond lengths and bond angles such that the longer bonds subtend the smaller angles as expected for a constant O- - -O distance. All these observations are consistent with a model in which three or four oxygen atoms are close-packed around a central boron atom, with the oxygen atoms having a ligand radius close to 119(2) pm. This is smaller than the values of 132 and 135 pm expected for fully ionic OH^- and O^{2-} ions, respectively, but, as we shall see, is consistent with the somewhat smaller charges on the ligand atoms. It is not possible to clearly distinguish between the expected slightly different ligand radii for O^{2-} and OH^- so the value of 119 pm should be considered as an average value for the two ligand radii, which would in any case be expected to differ by only about 3 pm.

The calculated charges, bond lengths and bond angles for BO^+, BO, BO_2^-, $B(OH)_2^+$, BO_3^{3-}, $B(OH)_3$, $(HO)_2BOH_2^+$, $B(OH)_4^-$, $B_3O_6^{3-}$, and $(HOBO)_3$ are given in Table 3. The charges of the O and OH ligands, which range from −1.72 to −1.44 and from −0.81 to −0.71, respectively, are much closer to the fully ionic limits of −2 and −1, respectively, than to the zero charges expected for fully covalent bonds and are consistent with the O ligand radius of 119 pm compared to 132−135 pm expected for O^{2-} and OH^-. So these molecules appear to be predominately ionic in character, and it seems more appropriate to describe the bonding in terms of an ionic model rather than the conventional covalent model.

That the covalent model is unsatisfactory can be seen in several ways. For example, the sum of the covalent radii for

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Table 1. Experimental Bond Lengths, Bond Angles, and O- - -O Nonbonding Distances for Some Compounds with BO_n Groups

	bond length (pm)		∠OBO (deg)		O- - -O (pm)	av O- - -O (pm)		ref
BO_3 Groups								
Li_3BO_3	1	136.9(4)	1−2	120.4(3)	238.4(10)	238(1)	O_t- - -O_t	*a*
	2	137.8(4)	1−3	120.4(3)	238.8(11)			
	3	138.3(4)	2−3	119.2(3)	238.1(11)			
$BaNaBO_3$	1	137.2(7)	1−2	119.5(8)	237.0(24)	239(2)		*b*
	2	137.2(7)	1−3	120.2(4)	240.3(17)			
	3	140.1(7)	2−3	120.2(4)	240.3(17)			
$BaBe_2(BO_3)_2$	1	137.2(3)	1−2	119.9(2)	237.5(7)	238(1)	O_t- - -O_t	*c*
	2	137.3(2)	1−3	120.2(2)	237.8(6)			
	3		2−3	120.2(2)	238.0(6)			
$Be_2(BO_3)(OH)$	1	136.2	1−2	118.9	236.5(2)*	237		*d*
	2	137.2	1−3	119.1	236.6(2)*			
	3	136.7	2−3	120.6	237.1(2)			
$K_2Zr(BO_3)_2$		137.8(1)		119.99(1)	238.7(1)	239	O_t- - -O_t	*e*
Ag_3BO_3		137.8(5)		120	238.7(7)	239(1)	O_t- - -O_t	*f*
$FeBO_3$		137.9(2)		120	238.8(4)	239	O_t- - -O_t	*g*
$Na_2[HOBO_2]$	1	135.1(3)	1−2	125.5(3)	240.5(8)	241(1)	O_t- - -O_t	*h*
	2	135.4(3)	1−3	118.9(2)	240.3(8)	236(1)	O_t- - -OH	
	3	143.9(3)	2−3	115.6(2)	236.4(8)			
B_2O_5 Groups								
$Mg_2B_2O_5{\cdot}H_2O$	1	135.1(10)	1−2	125.1(5)	240.3(23)	240(2)	O_t- - -O_t	*i*
	2	135.7(10)	1−3	119.5(5)	238.8(23)	248.8(23)	O_t- - -O_b	
	3	141.3(10)	2−3	115.4(5)	234.2(23)			
	3	139.6(10)	3−4	116.7(5)	238.9(23)			
	4	140.3(10)	3−5	121.7(5)	238.5(23)			
	5	133.7(10)	4−5	121.3(5)	239.0(23)			
$[[Cs(NbO)(B_2O_5)]_n$	1	135.3(4)	1−2	120.2(3)	235(1)	235(1)	O_t- - -O_t	*j*
	2	135.3(4)	1−3	122.4(3)	241(1)	241(1)	O5- - -O_b	
	3	139.2(4)	2−3	124.7(2)	243(1)	243(1)	O_b- - -O_b	
$Mg_2[B_2O_4(OH)]OH$	1	135.1(10)	1−2	125.1(7)	240.3(7)*	240(1)	O5- - -O5	*k*
	2	135.7(10)	1−3	119.5(6)	238.8&7)*	239(1)	O_t- - -O_b	
	3	141.3(10)	2−3	115.4(8)	234.1(7)*	234(1)	O_b- - -O_b	
	3	139.6(10)	3−4	116.7(5)	238.2(7)*	238(1)	O_b- - -OH	
	4	140.3(10)	3−5	121.7(5)	238.7(7)*	239(1)	O_b- - -O_t	
	5	133.7(10)	4−5	121.3(5)	238.9(7)*	239(1)	O_t- - -OH	
$[OBO]_3$ Rings								
$Na_3B_3O_6$	1	128.0(16)	1−2	122.8	238(1)*	238(1)	O_t- - -O_b	*1*
	2	143.3(9)	2−2	114.5	241(1)*	241(1)	O_b- - -O_b	
$K_3B_3O_6$	1	133.0	1−2	121.3(4)	238.1(5)	238(1)	O5- - -O_b	*m*
	2	139.8	202	117.3(8)	238.9(9)	239(1)	O_b- - -O_b	
$[HO{-}BO]_3$	1	135.5(8)	1−2	120.0(18)	236(2)	236(2)	O_b- - -O_tH	*n*
	2	137.3(7)	2−2	120.1(5)	238(2)	238(2)	O_b- - -O_b	
$Mg[B_3O_3(OH)_5]0{\cdot}5H_2O$	1	146.9(5)	1−2	107.9(1)	237.4(8)	237(1)	HO- - -OH	*o*
	2	146.7(3)	1−3	109.4(1)	243.3(9)	242(1)	HO- - -O_b	
A	3	152.2(4)	1−4	111.3(3)	241.7(7)	243(1)	O_b- - -O_b	
	4	145.8(2)	2−3	109.1(1)	243.5(7)			
			2−4	110.3(1)	240.0(6)			
			3−4	108.8(1)	242.3(6)			
	4	144.9(4)	4−5	111.4(1)	241.6(6)	239(1)	HO- - -OH	
	5	147.5(2)	4−6	111.5(1)	241.5(1)	244(1)	HO- - -O_b	
	6	147.0(4)	4−8	108.9(1)	240.0(9)	241(1)	O_b- - -O_b	
	8	150.1(5)	5−6	106.3(1)	235.7(7)			
			5−8	110.2(1)	244.0(8)			
			6−8	108.6(1)	241.3(9)			
	3	136.4(3)	3−6	124.0(1)	241.1(7)	235(4)	HO- - -O_b	
	6	136.7(3)	3−7	121.2(1)	238.8(8)	241(1)	O_b- - -O_b	
	7	137.7(5)	6−7	114.7(1)	231.0(8)			
$KB_3O_3(OH)_4{\cdot}H_2O$	2	146.2(3)	2−3	110.1(2)	238.9(8)	239(1)	HO- - -OH	*p*
	3	145.3(2)	2−6	109.3(2)	239.6(7)	239(1)	HO- - -O_b	
B	6	147.5(2)	2−7	108.7(2)	239.8(7)	244(1)	O_b- - -O_b	
	7	148.9(2)	3−6	108.1(2)	237.0(7)			
			3−7	110.2(2)	241.3(7)			
			6−7	110.5(2)	243.5(6)			
	1	135.3(3)	1−5	118.6(2)	232.2(7)	234(2)	HO- - -O_b	
	5	134.7(3)	1−7	121.5(2)	239.6(7)	240(1)	O_b- - -O_b	
	7	139.3(3)	5−7	119.2(2)	236.3(7)			
	4	135.2(3)	4−5	121.2(2)	239.1(7)	236(2)	HO- - -O_b	
	5	139.2(3)	4−6	118.1(2)	232.2(8)	239(1)	O_b- - -O_b	
	6	135.6(3)	5−6	120.7(1)	238.8(7)			

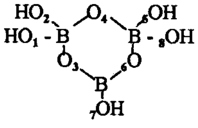
Table 1. Continued

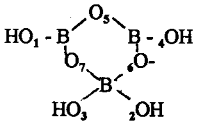
	bond length (pm)		∠OBO (deg)		O- - -O (pm)	av O- - -O (pm)		ref
$Na[B_3O_3(OH)_4]$	2	144.3(4)	2−3	114.4(2)	244.1(3)*	244	HO- - -OH	*q*
	3	146.0(3)	2−6	106.9(2)	236.9(3)*	239(2)	HO- - -O_b	
B	6	150.6(3)	2−7	111.7(2)	243.4(4)*	246	O_b- - -O_b	
	7	149.9(3)	3−6	107.1(2)	238.5(2)*			
			3−7	107.0(2)	237.9(3)*			
			6−7	109.6(2)	245.5(2)*			
	1	136.5(3)	1−5	113.4(2)	231.0(2)*	236(5)	HO- - -O_b	
	5	139.8(3)	1−7	125.3(3)	240.4(2)*	239	O_b- - -O_b	
	7	134.2(3)	5−7	121.2(2)	238.7(2)*			
	4	135.9(3)	4−5	119.4(2)	237.6(2)*	236(1)	HO- - -O_b	
	5	139.3(3)	4−6	120.7(3)	235.0(2)*	237	O_b- - -O_b	
	6	134.5(3)	5−6	119.8(3)	236.9(2)*			
				$B(OX)_3$ Groups				
$B(OH)_3$		136.1(4)		120	235.7(7)	236(1)	HO- - -OH	*r*
$B(OCH_3)_3$		136.8(2)		120	236.9(4)	237	XO- - -OX	*s*
$B(OTeF_5)_3$		135.8(6)		120	235.2(11)	235(1)	XO- - -OX	*t*
$B(OSnPh_3)_3$	1	137.6(6)	1−2	118.4(4)	235.1(15)	237(2)	XO- - -OX	*u*
	2	136.1(6)	1−3	120.3(4)	237.9(15)			
	3	136.7(6)	2−3	121.3(4)	237.8(15)			
				$B(OX)_4$ Groups				
$LiB(OH)_4$		147(1)		109.5	240(2)	240(2)	HO- - -OH	*v*
$NaB(OH)_4{\cdot}2H_2O$	1	147.8(5)	1−2	110. 4(4)	242.8(5)	237(2)	HO- - -OH	*w*
	2	147.9(7)	1−3	105.2(4)	234.9(5)	245(1)	HO- - -OH	
	3	147.7(6)	1−4	113.2(4)	246.3(4)			
	4	147.4(5)	2−3	112.1(4)	245.2(6)			
			2−4	107.6(4)	238.2(5)			
			3−4	108.3(4)	239.2(5)			
$Ca[B(OH)_4]_2{\cdot}2H_2O$	1	150(3)	1−2	103.8(2)	235(5)	236(1)	HO- - -OH	*x*
	2	148(3)	1−3	106.8(4)	237(5)	245(1)	HO- - -HO	
	3	145(3)	1−4	111.8(4)	246(5)			
	4	146(3)	2−3	114.5(4)	246(5)			
			2−4	111.1(5)	243(5)			
			3−4	108.7(4)	236(5)			
$Ca[B(OH)_4]_2$	1	147.5(3)	1−2	110.8	243.7(2)*	237(1)	HO- - -OH	*y*
	2	148.6(3)	1−3	111.8	244.2(2)*	244(1)	HO- - -OH	
	3	147.4(3)	1−4	110.8	243.0(2)*			
	4	147.8(3)	2−3	106.6	237.4(2)*			
			2−4	105.5	236.0(2)*			
			3−4	110.8	243.0(2)*			
	5	146.8(3)	5−6	108.2	240.5(2)*	241(1)	HO- - -OH	
	6	150.1(3)	5−7	110.5	241.6(2)*	243(1)	HO- - -OH	
	7	147.2(2)	5−8	111.3	244.1(2)*			
	8	148.9(3)	6−7	108.2	240.8(2)*			
			6−8	108.3	242.4(2)*			
			7−8	110.1	242.7(2)*			
$Ba[B(OH)_4]_2{\cdot}2H_2O$		148.3(10)		109.5	242(2)	242(2)		*z*
		147.4(13)		109.5	241(2)			
$Na_2[B(OH)_4]Cl$		148.1(2)		2 × 105.1(1)	235.1(5)	235(1)	HO- - -OH	*aa*
				4 × 111.7(1)	245.1(5)	245(1)	HO- - -OH	
$B(OMe)_4^-$	1	147.5(4)	1−2	112.9(2)	243.9(8)	226(1)	XO- - -OX	*ab*
	2	145.1(3)	1−3	112.9(2)	243.9(8)	244(1)	XO- - -OX	
	3	145.1(3)	1−4	102.0(3)	227.6(12)			
	4	145.4(5)	2−3	114.1(2)	243.5(8)			
			2−4	114.1(2)	243.8(9)			
			3−4	101.4(3)	224.8(9)			
$B(OTeF_5)_4^-$		147(1)		109.5	240(1)	240(1)	XO- - -OX	*ac*
$KB(OXO_2Cl)_4$	1	146.9(11)	1−2	107.1(8)	235.9(35)	236(1)	XO- - -OX	*ad*
	2	146.4(17)	1−3	113.3(8)	245.4(30)	245(1)	XO- - -OX	
	3	146.9(11)	1−4	107.3(8)	235.7(24)			
	4	145.8(13)	2−3	108.2(8)	237.6(26)			
			2−4	114.2(8)	245.1(26)			
			3−4	106.9(8)	235.1(30)			
	1	146.9(10)	1−2	107.4(8)	236.3(35)	236(1)	XO- - -OX	
	2	146.3(17)	1−3	113.8(8)	246.0(29)	246(1)	XO- - -OX	
	3	146.7(12)	1−4	106.9(8)	235.9(30)			
	4	146.8(13)	2−3	108.6(8)	237.9(26)			
			2−4	113.7(8)	245.4(28)			
			3−4	106.5(8)	235.2(32)			

Table 1. Continued

	bond length (pm)		∠OBO (deg)		O- - -O (pm)	av O- - -O (pm)		ref
$KB[O-C(O)CH_3]_4$	1	147.8(9)	1−2	101.3(1)	227.1(16)	229(1)	XO- - -OX	*ae*
	2	145.9(9)	1−3	112.6(3)	245.3(20)	245(1)	XO- - -XO	
	3	147.1(9)	1−4	110.6(3)	243.3(19)			
	4	148.1(9)	2−3	115.8(3)	248.2(19)			
			2−4	112.7(3)	244.7(19)			
			3−4	102.3(3)	229.9(18)			
			Other					
$(MeO)_2B-B(OMe)_2$		136.9(3)		119.9(4)	237.0(10)	237(1)	XO- - -OX	*af*
$(MeO)_2B-Me$		137.5(4)		120.9(5)	239.2(13)	239(1)	XO- - -OX	*ag*
$[HBO]_3$		137.6(2)		120.0(6)	238.3(11)	238(1)	O_b- - -O_b	*ah*
$[EtBO]_3$	1	138.0(1)	1−2	118.4(1)	237.7(3)	238	O_b- - -O_b	*ai*
	2	138.7(1)						
$[PhBO]_3$		138.6(1)		118.0(4)	237.6(7)	238(1)	O_b- - -O_b	*aj*
C		136.8(10)		114.2(8)	229.7(27)	230(3)	O_b- - -O_b	*ak*
D	1	136.9(7)	1−2	123.8(5)	240.2(17)	240(2)	O_b- - -O_b	*al*
	2	135.4(6)	1−3	119.2(5)	235.8(17)	336(2)	O_b- - -OH	
	3	136.5(7)	2−3	117.0(5)	231.8(18)	232(2)	O_b- - -OH	
E	1	134.7(5)	1−2	123.8(3)	238.9(12)	239(1)	O_b- - -O_b	*am*
	2	136.1(5)	1−3	119.2(3)	233.7(13)	234(1)	O_b- - -OX	
	3	136.3(5)	2−3	117.1(3)	232.4(12)	232(1)	O_b- - -OX	
$BrC_6H_4B(OH)_2$		136		122	238	238	HO- - -OH	*an*
F	$_1$B 2	152(1)	2−3	109.1(8)	247(3)	247(3)	O_b- - -O_b	*ao*
	3	151(1)	1−2	122.4(10)	238(3)	238(3)	O_b- - -O_b	
	$_2$B 1	140(1)	1−3	121.4(9)	238(3)			
	2	131(1)						
	$_3$B 1	138(1)						
	3	135(1)						

*Directly observed value.


$[B_3O_3(OH)_5]^{2-}$
A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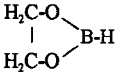
B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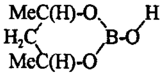
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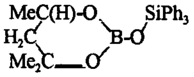
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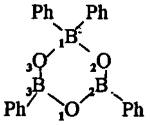
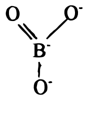
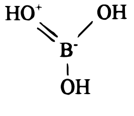

F

[a] Stewner, F. *Acta Crystallogr.* **1971**, *27B,* 904. [b] Tu, J.-M.; Keszler, D. A. *Acta Crystallogr.* **1995**, *C51,* 67. [c] Schaffen, K. I.; Keszler, D. A. *Inorg. Chem.* **1994**, *33,* 1201. [d] Zachariasen, W. H.; Plettinger, H. A.; Marezio, M. *Acta Crystallogr.* **1963**, *16,* 1144. [e] Akella, A.; Keszler, D. A. *Inorg. Chem.* **1994**, *33,* 1554. [f] Jansen, M. J.; Bratchel, G. *Z. Anorg. Allg. Chem.* **1982**, *489,* 42. [g] Diehl, R. *Solid State Commun.* **1975**, *17,* 743. [h] Menchetti, S.; Sabelli, C. *Acta Crystallogr. B38,* 1282. [i] Kudoh, Y.; Takéuci, Y. *Cryst. Struct. Commun.* **1973**, *2,* 595. [j] Becker, P.; Bohat?, L.; Fröhlich, R. *Acta Crystallogr.* **1995**, *C51,* 1721. [k] Takéuchi, Y.; Kudoh, Y. *Am. Mineral.* **1975**, *60,* 273. [l] Marezio, M.; Plettinger, H. A.; Zacharaisen, W. H. *Acta Crystallogr.* **1963**, *16,* 594. [m] Schneider, W.; Carpenter, G. B. *Acta Crystallogr.* **1970**, *B26,* 1189. [n] Peters, C.; Milberg, M. E. *Acta Crystallogr.* **1964**, *17,* 229. [o] Corraza, E. *Acta Crystallogr.* **1976**, *B32,* 1329. [p] Salentine, C. G. *Inorg. Chem.* **1987**, *26,* 128. [q] Dal Negro, A.; Pozas, J. M. M.; Ungaretti, L. *Am. Mineral.* **1975**, *60,* 879. [r] Zachariasen, W. H. *Acta Crystallogr.* **1954**, *7,* 305. [s] Gundersen, G. *J. Mol. Struct.* **1976**, *33,* 79. [s] Gundersen, G. *J. Mol. Struct.* **1976**, *33,* 79. [t] Sawyer, J. F.; Schrobilgen, G. J. *Acta Crystallogr.* **1982**, *B38,* 1561. [u] Ferguson, G.; Spalding, T. R.; O'Dowd, A. T. *Acta Crystallogr.* **1995**, *C51,* 67. [v] Höhne, E. *Z. Anorg. Allg. Chem.* **1966**, *342,* 1888. [w] Block, S.; Perloff, A. *Acta Crystallogr.* **1963**, *16,* 1233. [x] Sedlacek, P.; Dornberger-Schiff, K. *Acta Crystallogr.* **1971**, *B27,* 1532. [y] Siminov, M. A.; Kazanskaya, E. V.; Egorov-Tismenko, Yu. K.; Zhelezin, E. P.; Belov, N. V. *Dokl. Acad. Nauk SSSR.* **1976**, *230,* 91. [z] Kutschabsky, L. *Acta Crystallogr.* **1969**, *B25,* 1811. [aa] Effenberger, H. *Acta Crystallogr.* **1982**, *B38,* 82. [ab] Alcock, N. W.; Hagger, R. M.; Harrison, W. D.; Wallbridge, M. G. H. *Acta Crystallogr.* **1982**, *B38,* 676. [ac] Noirot, M. D.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1987**, *26,* 2216. [ad] Mairesse, G.; Drache, M. *Acta Crystallogr.* **1978**, *B34,* 1771.[ae] Dal Negro, A.; Rossi, G.; Perotti, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1232. [af] Braine, P. T.; Downs, A. J.; Maccallum, P.; Rankin, D. W. H.; Robertson, H. E.; Forsyth, G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1195. [ag] Gundersen, G.; Jonvik, T.; Seip, R. *Acta Chem. Scand.* **1981**, *35A,* 325. [ah] Chang, C. H.; Porter, R. F.; Bauer, S. H. *Inorg. Chem.* **1969**, *8,* 1689. [ai] Boese, R.; Polk, M.; Bläser. *Angew. Chem., Int. Ed. Engl.* **1987**, *26,* 245. [aj] Brock, C. P.; Minton, R.; Niedenzu, K., as quoted by L.-Y. Hsu et al. in *Inorg. Chem.* **1987**, *26,* 143. [ak] Hand, J. H.; Schwendeman, R. H. *J. Chem. Phys.* **1966**, *55,* 3349. [al] Kuribayashi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46,* 1045. [am] Ferguson, G.; Lough, A. J.; Sheehan, J. P.; Spalding, T. R. *Acta Crystallogr.* **1990**, *C46,* 1252. [an] Zvonkova, Z. V.; Glushkova, V. P. *Kristallografiya* **1958**, *3,* 559. [ao] Zeller, E.; Beruda, H.; Schmidbauer, H. *Chem. Ber.* **1993**, *126,* 2033.

boron (90 pm)[18] and oxygen (65 pm)[3] gives a value of 155 pm for the length of a covalent BO single bond, although essentially all formally single BO bonds are significantly shorter than this. In many cases they are much shorter and they vary over a wide range, for example, from 147.7 pm in $B(OH)_4^-$ to 136.1 pm in $B(OH)_3$ and to 132.4 pm in HO−BO (Table 3). To conform to the octet rule and to explain some of these bond lengths, resonance structures such as **I** and **II**, based on the concept of back-bonding, have commonly been suggested, indicating 33%


I


II

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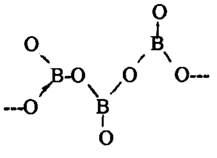
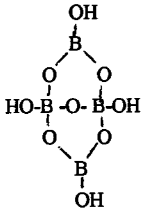
(18) The value of the covalent radius of boron of 90 pm is from: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993; p 292.

Table 2. Nonbonding 1,3 O- - -O Contact Distances in Some Polyborates

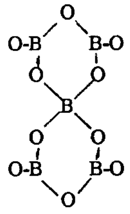
		BO$_3$ groups		BO$_4$ groups		
	type	O$_b$- - -O$_t$(H) (pm)	O$_b$- - -O$_b$ (pm)	O$_b$- - -O$_t$(H) (pm)	O$_b$- - -O$_b$ (pm)	ref
[Li$_2$BO$_2$]$_n$	A	243(1)	235(2)			*a*
[CaBO$_2$]$_n$	A	243(1)	234(1)			*b*
[B$_2$O$_3$]$_n$	A	242(2)	239(2)			*c*
Na$_2$[B$_4$O$_5$(OH)$_4$]·3H$_2$O	B	236(1)	239(1)	240(1)	241(1)	*d*
Na$_2$[B$_4$O$_5$(OH)$_4$]·5H$_2$O	B	235(4)	236(4)	242(3)	239(3)	*e*
Na$_2$[B$_4$O$_5$(OH)$_4$]·8H$_2$O	B	236(1)	239(1)	241(1)	240(1)	*f*
K$_2$[B$_4$O$_5$(OH)$_4$]·2H$_2$O	B	236(3)	240(1)	242(1)	241(2)	*g*
[Cs$_2$Na$_2$B$_{10}$O$_{17}$]$_n$	C		236(3)		240(3)	*h*
CaNa$_3$[B$_5$O$_{10}$]	C	238(2)	239(2)		240(3)	*i*
NH$_4$[B$_5$O$_6$(OH)$_4$]·2H$_2$O	D	233(2)	239(2)		239(2)	*j*



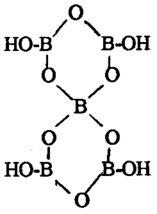
A



B



C



D

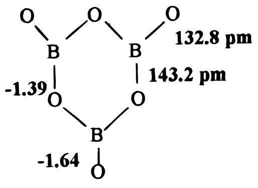
[a] Kirfel, A.; Will, G.; Stewart, R. F. *Acta Crystallogr.* **1983**, *B39*, 175. [b] Kirfel, A. *Acta Crystallogr.* **1987**, *B43*, 333. [c] Prewitt, C. T.; Shannon, R. D. *Acta Crystallogr.* **1968**, *24*, 869. [d] Powell, D. R.; Gaines, D. F.; Zerella, P. J.; Smith, R. A. *Acta Crystallogr.* **1991**, *C47*, 2279. [e] Giacovazzo, C.; Menchetti, S.; Scordari, F. *Am. Mineral.* **1973**, *58*, 523. [f] Levy, H. A.; Lisensky, G. C. *Acta Crystallogr.* **1978**, *B34*, 3502. [g] Marezio, M.; Plettinger, H. A.; Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 975. [h] Tu, J.-M.; Keszler, D. A. *Inorg. Chem.* **1996**, *35*, 463. [i] Fayos, J.; Howie, R. A.; Glasser, F. P. *Acta Crystallogr.* **1985**, *C41*, 1396. [j] Domenech, V.; Solans, J.; Solans, X. *Acta Crystallogr.* **1981**, *B37*, 643.

double-bond character in the BO bonds in these molecules. However, a comparison of the bond lengths of 137.3 pm in BO$_3^{3-}$ and 136.1 pm in B(OH)$_3$ with the estimated B−O single-bond length of 155 pm and the B═O double-bond length of 133 pm[19] requires a much greater double-bond character than is indicated by **I** and **II**. Another example of the unsatisfactory nature of covalent octet rule structures analogous to **I** and **II** is provided by the series B(OMe)$_3$, MeB(OMe)$_2$, (MeO)$_2$BB(OMe)$_2$, and Me$_2$BOMe for which such structures would correspond to 33%, 50%, 50% and 100% double-bond character for the BO bonds and yet the respective bond lengths of 136.8, 137.5, 136.9, and 136.1 pm (Table 1) have an almost constant value similar to the BO bond lengths in BO$_3^{3-}$ and B(OH)$_3$. Similarly, to satisfy the octet rule the structure of B(OH)$_2^+$ would have to be written as HO$^+$═B$^-$═O$^+$H, which would predict a value of 133 pm for the BO bond lengths which are, however, still shorter with a length of 125 pm.

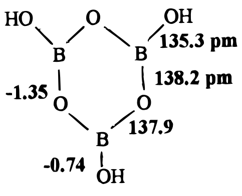
One- and Two-Coordinated Oxoboron Molecules. The nearly anionic O or OH ligands in the 3- and 4-coordinated molecules are attracted toward the cation-like central atom until they touch each other. When the constraint of close-packing is removed as in 1-coordinated and linear 2-coordinated molecules, the bonds are found to be still shorter than in 3- and 4-coordinated molecules, as shown by the following examples taken from Table 3: BO$^+$ (118.8 pm), BO (122.9 pm), FBO (120.6 pm), BO$_2^-$ (125.3 pm), OBOH (119.5 and 131.5 pm), and B(OH)$_2^+$ (124.5 pm). We noted previously[3] that the BF bonds in molecules in which the boron is two-coordinated are similarly much shorter than the BF bonds in 3- and 4-coordinated molecules. These observations provide further evidence that the lengths of the bonds in the 3- and 4-coordinated molecules are determined primarily by ligand−ligand interactions.

Although the atomic charges in 1- and 2-coordinated oxoboron molecules are smaller than would correspond to a fully ionic model, this extreme model is nevertheless very useful for understanding the variations in the bond lengths. Figure 1 shows the calculated bond lengths and charges as well as the charges for the fully ionic model. Using the fully ionic model we can interpret the bond lengths in terms of the electrostatic repulsions and attractions between the component ions. For example, the BO bond in BO$_2^-$ is longer than in FBO and HOBO because the O^{2-} ligand is repelled more strongly by the other O^{2-} ligand in BO$_2^-$ than by either an F$^-$ or an OH$^-$ ligand, while it is still shorter in BO$^+$ because there is no other ligand. In the radical BO the bond is somewhat longer than in BO$^+$ because the boron atom has only a +2 charge rather than a +3 charge. Similarly, the B−OH bond in HOBO is longer than in HOBOH$^+$ because the OH group is repelled by a doubly charged O^{2-} ligand but only by a singly charged OH$^-$ ligand in HOBOH$^+$. Finally we note that even the small difference in the BO bond lengths in FBO and HOBO can be accounted for in terms of the *actual* charges since the charge on F (−0.81) is slightly greater than that on the OH ligand (−0.74).

We can also use the ionic model to account for the differences in the bond lengths in the cyclic B$_3$O$_6^{3-}$ ion, **III**, and the cyclic acid B$_3$O$_3$(OH)$_3$, **IV**. The terminal B−O$_t$ bonds (132.8 pm) in **III** are shorter than the terminal B−OH bonds in **IV** (135.3 pm) because the charge on the terminal O ligand in **III** is larger than the charge on the terminal OH ligand in **IV**, and the bridging BO bonds are longer in **III** than in **IV** for the same reason; the bridging O in **III** is more strongly repelled by the terminal O ligand than is the bridging O in **IV** by the terminal OH ligand. The lines connecting the atoms in these structures



III



IV

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(19) Reference 1, page 228: The ratio of the CC double- and single-bond lengths is 0.86, and this same ratio is found to hold, somewhat surprisingly, for many other bonds. In this case it gives the same value of 133 pm for the B═O double bond.

Table 3. Results of ab Initio Calculations for Some Beryllium, Boron, and Carbon Oxo and Hydroxo Molecules

	A−O (pm)[a]		∠OAO (deg)	ρ_b (au)	$-q$(O)	q(H)	$-q$(OH)	q(A)	O- - -O (pm)
BeO	132.4 (133.1)[1]			0.1742	1.536			1.536	
BeO_2^{2-}	145.9		180.0	0.126	1.803			1.637	
$Be(OH)_2$	142.3		180.0	0.133	1.417	0.567	0.850	1.701	
$Be(OH)_3^-$	154.6 (154.0.3)		120.0	0.0954	1.365	0.469	0.896	1.690	268 HO- - -OH
$Be(OH)_4^{2-}$	168.8		107.8	0.0646	1.344	0.419	0.925	1.700	273 HO- - -OH
			110.3						277 HO- - -OH
$(HBe)_2O$[b]	139.6		180.0	0.148	1.79			1.74	
BO^+	118.8			0.2950	1.043			2.043	
BO[c]	120.3 (120.5)[1]			0.3194	1.553			1.553	
BO_2^-	126.4 (125.3)[2]		180.0	0.2707	1.576			2.150	
$OBOH$	121.2	-O	180.0	0.3082	1.436			2.179	
	132.4	-OH		0.2283	1.333	0.592	0.741		
$OBOH$[d]	119.5	-O	180.0						
	131.5	-OH							
$B(OH)_2^+$	125.5		180.0	0.2668	1.343	0.691	0.652	2.305	
	124.5[d]								
OBF	120.6	-O	180.0	0.3164	1.449			2.262	
	128.4	-F		0.2338					
BO_3^{3-}	141.8 (137.8)3		120.0	0.180	1.724			2.192	246 O- - -O
OBF_2^-	1 127.0	-O		0.2757	1.593			2.325	
	2 140.5	-F	2-2 106.4	0.1624					
$B(OH)_3$	136.9 (136.1)[3]		120.0	0.204	1.316	0.555	0.761	2.282	237 HO- - -OH
$B(OH)_3$[d]	135.8								235 HO- - -OH
$(HO)_2BOH_2^+$	132.2	-OH	141.2	0.231	1.331	0.618	0.713	2.296	249 HO- - -OH
	149.9	-OH_2	109.4	0.131	1.200	0.665			231 H2O- - -OH
$(HO)_2BOH_2^+$[d]	131.2	-OH	132						239 HO- - -OH
	150.2	-OH_2	114						236 HO- - -OH_2
$[OBO^-]_3$	1 132.8	-O_t	1-2 122.9 b-t	0.231	1.644			2.239	241 O_b- - -O_b
	2 143.2	-O_b-	2-2 114.2 b-b	0.171	1.592				242 O_b- - -O_t
$[OBOH]_3$	1 135.3 (135.5)[3]	-O_tH	2-3 119.8 b-b	0.2144	1.301	0.559	0.742	2.282	239 O_b- - -O_b
	2 138.2 (137.3)[3]	-O_b-	1-3 120.1 b-t	0.1964	1.546				238 O_b- - -O_tH
	3 137.9	-O_b-	1-2 121.1 b-t	0.1981	1.546				235 O_b- - -O_tH
$B(OH)_4^-$	148.7 (147.7)[3]		106.2	0.153	1.300	0.481	0.819	2.275	238 HO- - -OH
			111.1						245 HO- - -OH
$(H_2B)_2O$[b]	135.4		126.9	0.209	1.68			2.27	
CO	111.4[c] (112.8)[4]			0.5101	1.346			1.346	
	110.3[e]			0.5332	1.357				
CO_2	114.3[c] (116.0)4		180.0	0.4826	1.298			2.595	
	116.0			0.4637	1.076		x	2.151	
CO_3^{2-}	130.8 (129.4)[5]		120.0	0.3393	1.337			2.013	227 O- - -O
$HOCO_2^-$	1 123.3 (126.4)[5]	-O	1-2 132.8	0.3987	1.239			2.053	228 O- - -O
	2 125.1 (126.3)	-O	1-3 113.9	0.3846	1.258				226 O- - -OH
	3 145.4 (134.6)	-OH	2-3 113.3	0.2410	1.046	0.495	0.550		226 O- - -OH
$(HO)_2CO$	1 120.4 (120.3)[6]	-O	2-2 108.6	0.4268	1.166			2.129	218 HO- - -OH
	2 133.9 (134.3)	-OH	1-2 125.7	0.3138	1.047	0.568	0.598		226 O- - -OH
$(HO)_2CO$[f]	1 118.8	-O	2-2 109.2						214 HO- - -OH
	2 131.5	-OH	1-2 125.4						223 O- - -OH
$C(OH)_4$	139.3 (139.6)[7]		103.6	0.2893	1.040	0.544	0.496	1.985	219 HO- - -OH
			112.5						232 HO- - -OH
CO_4^{4-}	145.2		109.5	0.2510	1.405			1.617	237 O- - -O
$C(OH)_3^+$	128.1		120.0	0.3584	1.050	0.640	0.410	2.228	222 HO- - -OH
H_2CO	118.3[b] (120.9)[8]			0.4308	1.240			1.245	
	117.8[c]			0.4475	1.271			1.292	
Cl_2CO	117.2 (117.6)[9]		124.1	0.4584	1.05			1.248	
F_2CO	117.1 (117.0)[10]	-O		0.4667	1.088			2.297	
	132.0 (131.7)[8]	-F	107.7	0.2969					
F_3CO^-[g]	122.7 (121.4)[g]	-O		0.4369	1.260			2.160	
	139.2 (139.4)	-F	100.6	0.2278					
Me_2O[c]	139.0 (141.6)[11]			0.2730	1.288			0.776	

[a] Numbers in parentheses are experimental bond lengths: [1]Herzberg, G. *Molecular Spectra and Molecular Structure; Infrared Spectra of Diatomic Molecules*; van Nostrand: New York. [2]Calvo, C.; Faggiani, R.; Krishnamacari, N. *Acta Crystallogr.* **1975**, *B31*, 188. [3]See Table 2. [4]Sutton, L. E. Ed. *Tables of Interatomic Distances*; Chem. Soc. Special Publ. No. 11; Chemical Society: London, 1958. [5]See Table 4. [6]Experimental bond lengths are for $(MeO)_2CO$, see Table 4. [7]Experimental bond lengths are for $C(OMe)_4$, see Table 4. [8]Kato, C.; Konaka, S; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2148. [9]Nakata, M.; Fukuyama, T.; Kuchitsu, K.; Takeo, H.; Matsumura, C. *J. Mol. Spectrosc.* **1980**, *83*, 118; Nakata, M.; Kohata, K.; Fukuyama, T,; Kuchitsu, K. *J. Mol. Spectrosc.* **1980**, *83*, 105. [10]Nakata, M.; Kohata, K,; Fukuyama, T.; Kuchitsu, K.; Wilkins, C. J. *J. Mol. Struct.* **1980**, *68*, 271. [11]Blakis, V.; Kasa, P. H.; Myers, R. J. *J. Chem. Phys.* **1963**, *38*, 2753. [b] Gillespie, R. J.; Johnson, S. A. *Inorg. Chem.* **1997**, *36*, 3031. [c] Bader, R. F. W. *Atoms in Molecules*; Oxford University Press: Oxford, 1994. [d] Attina, M.; Cacace, F.; Ricci, A.; Grandinetti, F.; Occhiucci, G. *J. Chem. Soc., Chem. Commun.* **1991**, 66 (MO SCF calculations at the MP3/6-G**//6-31G* + 2PVE(6-31G*) level). [e] Bader, R. F. W.; Johnson, S.; Tang, T.-H.; Popelier, P. L. A. *J. Phys. Chem.* **1996**, *100*, 15398. [f] Hartz, N.; Rasal, G.; Olah, G. A. *J. Am. Chem. Soc.* **1993**, *115*, 1277; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767. [g] Farnham, W. B.; Smart, B. E.; Middleton, W. J.; Calebrese, J. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 4565.

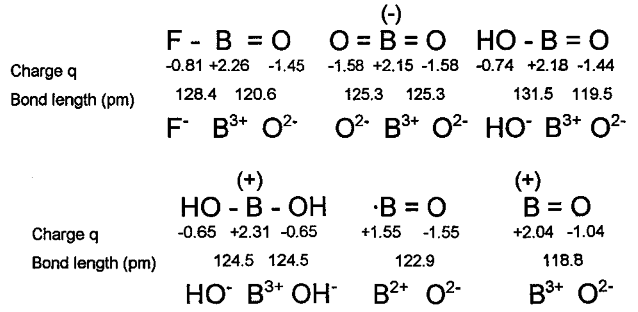

Figure 1. Covalent and ionic models for some 1- and 2-coordinated molelcules of boron.

should not be taken to represent conventional single bonds. They simply show which atoms are bonded together and they represent *bond paths* as defined by the Atoms in Molecules theory.[11]

An isolated BO_3^{3-} ion would be expected to have three equal bond lengths and angles of exactly 120°, but small differences in the bond lengths and angles are observed in most of the crystal structures. Moreover, the average observed BO bond length in the BO_3^{3-} ion (137.6 pm) is appreciably shorter than the calculated value of 141.8 pm for the free BO_3^{3-} ion in Table 3. This difference probably arises from the interaction of the ion with the surrounding cations which would be expected to slightly reduce the charge on each oxygen thus also slightly decreasing its radius which, in turn, allows the oxygens to move closer to the boron, hence decreasing the bond length.

Oxoberyllium Molecules. The results of our ab initio calculations for BeO, BeO_2^{2-}, Be $(OH)_2$, $Be(OH)_3^-$, $Be(OH)_4^{2-}$, and BeO_3^{4-} are given in Table 3. The large charges of −0.93 to −0.85 for the OH ligand and of −1.79 and −1.69 for the O ligand in these molecules show that BeO bonds are even closer to the fully ionic limit than BO bonds. Experimental structural data for oxoberyllium molecules are given in Table 4. Although the data is much more limited than that for boron compounds, it leads to the same conclusions. The seven examples of beryllium tetrahedrally coordinated by four oxygen ligands have bond lengths ranging from 162 to 165 pm with an average of 163.2 pm. The only two examples of trigonal planar BeO_3 groups both have a bond length of 154.3 pm. These lengths give an average d_4/d_3 ratio of 1.058 close to the geometrically predicted value of 1.061 for the ligand close-packing model. The tetrahedral $Be(OR)_4$ groups in molecules **3** and **4** both have a BeO bond length of 163.5 very close to the average value of 163.2 for the BeO_4 groups. Bonds from beryllium to Et_2O and H_2O range in length from 161 to 168 pm, consistent with the expected considerably smaller charge on oxygen in these cases. It is noteworthy that although there are two short bonds and one long bond in $(MesO)_2BeOEt_2$, the average value of 154.2 pm is almost exactly the same as in the other two BeO_3 groups and the largest bond angle is between the two short bonds, keeping the O- - -O distance nearly constant at an average value of 265 pm. The calculated bond length in $Be(OH)_3^-$ (154.6 pm) is essentially the same as that found experimentally in the two BeO_3 groups in Table 4, and the calculated O- - -O distance of 268 pm is close to the overall average value in Table 4. The calculated bond length and the O- - -O distance in $Be(OH)_4^{2-}$ are somewhat longer than expected, suggesting that the OH ligands are not closely packed and that this molecule is on the verge of instability, at least in the hypothetical isolated state. The O- - -O contact distances in all these molecules are close to the average value of 265 pm which is essentially equal to the O- - -O distance of 264−270 pm expected from the OH^- and O^{2-} ionic crystal radii as we discussed above, consistent with the nearly fully ionic charges on O and OH. According to our calculations, neither BeO_3^{4-} nor BeO_4^{6-} are stable as isolated anions.

As for oxoboron molecules, when the constraint of close-packing is removed still shorter bonds are found. For example the BeO bond length in $Be(OH)_2$ is 142.3 pm and in BeO_2^{2-} it is 145.9 pm. These bonds are longer than in the corresponding boron molecules $B(OH)_2^+$ (124.5 pm) and BO_2^- (123.5 pm) because the charge on Be is smaller than on B (+2 and +3, respectively in the fully ionic model).

Oxocarbon Molecules. The results of our calculations for CO_3^{2-}, $C(OH)_3^+$, HCO_3^-, H_2CO_3, CO_4^{4-}, and $C(OH)_4$ are given in Table 3. The charges on O (−1.1 to −1.4) and the charges on OH (−0.41 to −0.67) in these molecules show that it is less appropriate to regard these molecules as predominantly ionic and indeed the covalent model is more satisfactory than it is for BO and BeO bonds. Thus the single- and double-bond lengths estimated from covalent radii are 142 and 122 pm, respectively,[20] which are in fair agreement with the observed bond lengths although all the formally single C−O bonds are shorter than 142 pm, except the calculated value for CO_4^{4-} of 145.2 pm, where the O- - -O distances are also correspondingly long (237 pm) and appreciably longer than in the CO_3^{2-} ion, for example, showing that it is not truly close-packed and is probably on the verge of instability. Similarly, all the formal C=O double bonds are somewhat shorter than 122 pm. Nevertheless, the experimental data in Table 5 show that the O- - -O distance is approximately constant at an average value of 224 ± 5 pm. For example, for $C(OMe)_4$, $HC(OMe)_3$, and $MeC(OMe)_3$ the shortest contact distances are 224(1), 225(2), and 224(1) pm, respectively, for the carbonate ion the O- - -O distance is 222(1)−224(1) pm, and for the formate ion, HCO_2^-, it is 222(2) pm. In the hydrogen carbonate ion, $HOCO_2^-$, and in the computed structure of carbonic acid, $(HO)_2CO$, both the HO- - -OH and HO- - -O distances are similarly close to 224 pm, as they are also in $(MeO)_2CO$ and $(Cl_3CO)_2CO$ (Table 5), despite the large differences in the bond lengths to oxygen ($HOCO_2^-$, C−OH, 135 pm, and C−O, 126 pm; $(HO)_2CO$, C−OH, 132 pm, and C−O, 119 pm; $(MeO)_2CO$, C−OMe, 134.3(10) pm, C−O 120.3(9) pm; $(Cl_3CO)_2CO$, $C-OCCl_3$, 141.1(8) pm, average, C−O, 117.1(8) pm). This approximately constant O- - -O distance of 224 pm suggests that the ligand close-packing model is still valid even for these more covalent molecules. This O- - -O distance corresponds to a mean ligand radius of 112 pm. This value and the values of 120 pm for oxygen bonded to boron and 134 pm for oxygen bonded to beryllium show the expected increase with increasing charge on the oxygen ligand. These mean values decrease as the charge on the oxygen ligand decreases from Be to B to C and are compared with the corresponding fluorine radii in Table 6. The small variations in the oxygen and hydroxide ligand radii for a given central atom A also show the same trend, as can be seen in Figure 2.

Oxofluoroboron and Oxofluorocarbon Molecules. From the ligand radii of O and F bonded to boron of 120 and 112 pm, respectively (Table 6), we expect the O- - -F nonbonding distance in oxofluoroboron molecules to be (120 pm + 112 pm) = 232 pm. The experimental data in Table 7 give an average value of 232(2) pm despite considerable variations in BO and BF bond lengths between molecules. For example, F_2BOH and F_2BO^- both have an O- - -F distance of 234 pm close to the

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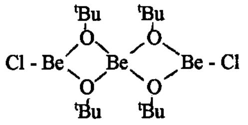
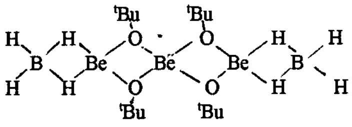
(20) $r(C) = 77$ pm, $r(O) = 65$ pm (ref 3), $d(C{=}O) = 0.86d(C-O)$ (ref 18).

Table 4. Average Bond Lengths, Bond Angles, and O- - -O Nonbonding Distances in Compounds with BeO_n Groups

	group	bond length (pm)	∠OBeO (deg)	O- - -O (pm)	ref
Y_2BeO_4	BeO_3	154.3(11)	120.0	267(2)	*a*
$SrBe_3O_4$	BeO_3	154.3(2)	120.0	266	*b*
	BeO_4	164(2)	109.5	268(3)	
BeO(s)	BeO_4	164	109.5	268	*c*
$Li_{14}Be_5B(BO_3)_9$	BeO_4	162(2)	109.4	265(3)	*d*
$LiBePO_4{\cdot}H_2O$	BeO_4	163(2)	109.5	266(3)	*e*
$Be_2AsO_4(OH)$	BeO_4	162(2)	109.4	264(5)	*f*
	BeO_4	163(2)	109.4	266(3)	
$(MesO)_2BeO'Et_2$	$Be(OR)_3$	148.1(2)	125.3(2)	263(1)	*g*
		148.1(2) 165.5(3)	117.4(1)	268(1)	
$Cl_2Be(OEt_2)_2$	$Be(OR)_2$	168.3(3)	101.8(3)	261(1)	*g*
$Be_2BO_3(OH)$	BeO_4	163(1)	109.5	266(2)	*h*
$Be(OH_2)_4{\cdot}SO_4$	$Be(OH_2)_4$	161.0(4)	109.5	263(1)	*i*
	$Be(OH_2)_4$	161.8(4)	109.5	264(1)	*j*
γ-Li_2BeSiO_4	BeO_4	164.7	109.5	269	*k*
A	$Be(OX)_2$	153.6	120.0	266	*l*
	$Be(OX)_4$	163.5	109.5	267	
B	$Be(OX)_2$	154.4(8)	120.0	267(2)	*m*
	$Be(OX)_4$	163.3(5)	109.5	267(1)	
			mean:	265(3)	



A



B

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expected value of 232, yet the BO bond is much shorter in the latter molecule (120.7 versus 134.4 pm). This short bond can be attributed to the much higher charge of the O ligand compared to OH. In F_2BO^- the oxygen is attracted relatively more strongly to the boron atom, pushing the fluorine ligands away but nevertheless keeping the O- - -F distance constant.

The very long B−O bond and the small deviation of the BF_3 moiety from planarity in the $F_3B{-}O{=}X$ and $F_3B{-}OX_2$ molecules indicate that these complexes are quite weak, in other words, that BF_3 is a weak Lewis acid. Despite the large differences between the B−O and B−F bond lengths, the O- - -O and O- - -F distances are close to the sum of the ligand radii, indicating that the oxygen and fluorine ligands are close-packed and that as the donor molecule approaches the BF_3 molecule the oxygen atom pushes the fluorine ligands away, distorting their geometry from planar toward tetrahedral and correspondingly increasing their length. The BF bonds in BF_3 are very strong (bond energy 613 kJ mol^{-1})[21] and, in particular, are considerably stronger than the BCl bonds in BCl_3 (bond energy 453 kJ mol^{-1}).[21] Thus the BCl bonds are more easily stretched than the BF bonds as the planar BX_3 molecule is distorted toward a tetrahedral geometry so that BF_3 complexes with oxygen donors are weaker than the analogous BCl_3 complexes. The same considerations apply to complexes with nitrogen donor molecules. For example, the BN bond is much longer in $F_3B{-}NH_3$ (167 pm) than in $Cl_3B{-}NH_3$ (158 pm), and the FBF angles (114.2°) are smaller than the ClBCl angles (111.2°).[22]

From the ligand radii of F and O to carbon of 108 and 112 pm, respectively, (Table 6) we expect the O- - -F nonbonding distance in oxofluorocarbon molecules to have a value of close to 220 pm. The experimental data in Table 8 give an average value of 222(2) pm, in close agreement with the predicted value. A particularly interesting structure is that of perfluorodimethyl ether, F_3COCF_3, where the CF bond length (132.7(2) pm) is only slightly longer than that in CF_4 (131.9 pm) but the CO bond length of 137 pm is unusually short for a CO single bond and the COC angle of 119.1(8)° is unusually large for an ether. (Compare, for example, 141.0(3) pm and 111.7(3)° in dimethyl ether[23]). Nevertheless, the experimental F- - -F and O- - -F contact distances (215.6 and 221.1 pm) are close to the predicted values. The short CO bond length and large COC angle can be attributed to the charges on C and O being appreciably larger than in dimethyl ether, for example.[24]

The F_3CO^- Anion. The structure of the $F_3\,CO^-$ determined by Farnham et al.[25] in the $(Me_2N)_3S^+$ salt has elicited great interest because the CO bond has a length (122.7 pm) very similar to that in, for example, formaldehyde (120.9 pm) which is usually assumed to be that appropriate for a CO double bond, apparently making carbon pentacovalent in this ion, as in **V**,

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(21) Reference 17, page A29.

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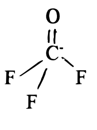
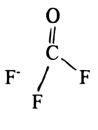
Table 5. Experimental and/Or Calculated Bond Lengths, Bond Angles, and O- - -O Nonbonding Distances for CO_n Groups in Some Oxocarbon Compounds

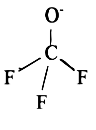
		bond length (pm)	∠OCO (deg)	O- - -O (pm)	ref
$C(OMe)_4$	(S_4)	139.6(1)	114.6(5) × 2	235(1) O_b- - -O_b	*a*
			106.9(5) × 4	224(1) O_b- - -O_b	
$C(OPh)_4$	(D_2)	1 139.2(2)	113.8(2) × 4	233(1) O_b- - -O_b	*b*
		2 139.5(2)	101.2(8) × 2	216(1) O_b- - -O_b	
$C(OC_6H_4Me_2\text{-}3,5)_4$	(D_2)	139.6(15)	114.3(14)	235(4) O_b- - -O_b	*b*
			101.3(12)	216(4) O_b- - -O_b	
$C(OH)_4$*	(S_4)	138.8	114.2 × 2	233 O_b- - -O_b	*c*
			107.2 × 4	223 O_b- - -O_b	
	(D_2)	138.9	112.1 × 4	230 O_b- - -O_b	*c*
			104.3 × 2	219 O_b- - -O_b	
	(D_2)	139.3	112.5 × 4	232 O_b- - -O_b	*d*
			103.6 × 2	219 O_b- - -O_b	
$HC(OMe)_3$		138.2(6)	115.0(10)	233(2) O_b- - -O_b	*e*
			109.2(6) × 2	225(2) O_b- - -O_b	
$H_3C{-}C(OMe)_3$		139.8(6)	1-2 106.7(9)	224(2) O_b- - -O_b	*f*
			1-3 110.8(9)	230(2) O_b- - -O_b	
			2-3 108.5(9)	227(2) O_b- - -O_b	
$HC(OH)_3$*	(C_3)	140.8	108.0	229 HO- - -OH	*c*
$H_2C(OMe)_2$	(C_2)	138.2(4)	114.3(7)	232(2) O_b- - -O_b	*g*
$Me_2C(OMe)_2$	(C_2)	142.3(6)	117.4(22)	243(4) O_b- - -O_b	*h*
$H_2C(OH)_2$*	(C_s)	142.0	114.4	239 HO- - -OH	*c*
	(C_2)	142.0	112.4	236 HO- - -OH	
$(HO)_2CO$*		1 131.5	1-1 109.2	214 HO- - -OH	*i*
		2 118.8	1-2 125.4	223 O- - -OH	
		1 133.9	1-1 108.6	218 HO- - -OH	*d*
		2 120.4	1-2 125.7	226 O- - -OH	
$(H_3CO)_2CO$		1 134.3(10)	1-1 107.0(1)	216(2) O_b- - -O_b	*j*
		2 120.3(9)	1-2 126.5(1)	227(2) O_b- - -O_t	
$(Cl_3CO)_2CO$		1 141.6(8)	1-2 101.2(3)	218(2) O_b- - -O_b	*k*
		2 140.5(7)	1-3 129.2(6)	233(3) O_b- - -O_t	
		3 117.1(8)	2-3 129.6(6)	232(2) O_b- - -O_t	
$Ca^{2+}CO_3^{2-}$		128.2(2)	120.0	222 O_t- - -O_t	*l*
		129.4(4)	120.0	224(1) O_t- - -O_t	*m*
CO_3^{2-}*		130.8	120.0	227 O_t- - -O_t	*d*
$Na^+HO{-}CO_2^-$		1 134.6	1-2 125.0	224 O_t- - -OH	*n*
		2 126.4	1-3 118.8	225 O_t- - -OH	
		3 126.3	2-3 116.3	222 O_t- - -O_t	
		1 134.5	1-2 125.5	224 O_t- - -OH	*o*
		2 124.9	1-3 119.9	225 O_t- - -OH	
		3 127.5	2-3 114.6	221 O_t- - -O_t	
$HO{-}CO_2^-$*		1 145.4	1-2 132.8	226 O_t- - -OH	*d*
		2 123.1	1-3 113.9	226 O_t- - -OH	
		3 125.1	2-3 113.3	226 O_t- - -O_t	
$NH_4^+HCO_2^-$		1 123.7(7)	1-2 126.3(6)	222(2) O_t- - -O_t	*p*
		2 124.6(7)			

*Calculated. [a] Mijlhoff, F. C; Geise, H. J.; Van Schaick. *J. Mol. Struct.* **1974**, *20*, 393. [b] Narasimhamurthy, N.; Manohar, H.; Samuelson, A. G.; Chandresekhar, J. *J. Am. Chem. Soc.* **1990**, *112*, 2937. [c] Reid, A. E.; Schade, C.; Schleyer, P. v. R; Kamath, P. V.; Chandrasekhar, J. *J. Chem. Soc. Chem. Commun.* **1988**, 67. [d] This work. [e] Spelbo, A.; Mijlhoff, F. C.; Faber, D. H. *J. Mol. Struct.* **1977**, *41*, 47. [f] Spelbos, A.; Mijlhoff, F. C.; Renes, G. H. *J. Mol. Struct.* **1978**, *44*, 73. [g] Astrup, E. E. *Acta Chem. Scand.* **1973**, *27*, 3271. [h] Astrup, E. E.; Admar, A. M. *Acta Chem. Scand.* **1975**, *29A*, 794. [i] Olah. G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767. [j] Mijlhoff, E. J. *J. Mol. Struct.* **1977**, *36*, 334. [k] Sørensen, A. M. *Acta Chem. Scand.* **1971**, *25*, 30. [l] Chessin, H.; Hamilton, W. C.; Post, B. *Acta Crystallogr.* **1965**, *18*, 689. [m] Sass, R. L.; Dale, R. V.; Donohue, J. *Acta Crystallogr.* **1957**, *10*, 567. [n] Sass, R. L.; Scheverman, R. F. *Acta Crystallogr.* **1962**, *15*, 77. [o] Sharma, B. D. *Acta Crystallogr.* **1965**, *18*, 818. [p] Nahringbauer, I. *Acta Crystallogr.* **1968**, *B24*, 565.

while the CF bonds (139.7 pm) are considerably longer than in F_2CO (131.7 pm). This "problem" is usually "solved" by writing resonance structures with ionic CF bonds such as **VI** in which the octet rule is obeyed. The alternative, and presumably approximately equally probable, octet rule structure **VII**, on the other hand, does not account for the short CO bond and so is usually neglected in this description of the bonding in this molecule. According to the ionic model (**VIII**) the O ligand forms the stronger shorter bond because of its higher charge, pushing the F ligands away to give longer CF bonds and small FCF angles, just as in the F_2BO^- ion discussed above. Nevertheless, the F- - -F and O- - -F contact distances in F_3CO^-


V


VI


VII

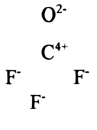

VIII

Table 6. Average Oxygen and Fluorine Intramolecular Ligand Radii (pm) for Bonds to Be, B, and C[a]

	Be	B	C
oxygen	134(1)	120(2)	112(3)
fluorine	128(1)	113(1)	108(2)

[a] Ligand radii are slightly variable for a particular A−X bond type because they vary with the ligand charge which itself is not exactly constant but depends to a small extent on the number and types of ligand coordinated to a central atom A (see Tables 3 and 8), which is also shown in Figure 2 for O and OH ligands.

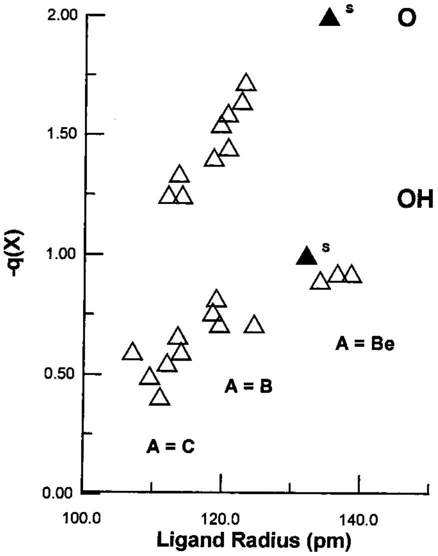


Figure 2. Plot of $-q$(O) and $-q$(OH) against ligand radius. (△) Data from Table 3; (▲) Shannon crystal radii.

Table 7. 1,3-Nonbonding O- - -F Distances in Some Oxofluoroboron Compounds

molecule	bond lengths (pm)	∠FBO (deg)	O- - -F (pm)	ref
F_3B-OH_2	BF(1) 138.2	1-4 105.9	233	*a*
	BF(3) 138.3	3-4 106.5	234	
	BO(4) 153.2			
$F_3B-OH_2\cdots OH_2$	BF(1) 137.7(3)	1-4 107.3(1)	233(1)	*b*
	BF(3) 138.2(3)	3-4 108.3(2)	235(1)	
	BO(4) 151.2(2)			
$F_3B-O(H)Me$	BF(1) 139.9	1-4 105.7	233	*a*
	BF(3) 135.5	3-4 106.0	230	
	BO(4) 152.4			
$F_3B-OPPh_3$	BF(1) 135.7(5)	1−4 105.7(3)	229(1)	*c*
	BF(2) 135.3(6)	2-4 108.1(4)	233(2)	
	BF(3) 133.4(6)	3-4 109.2(4)	233(2)	
	BO(4) 151.6(6)			
$F_3B-OAsPh_3$	BF(1) 135.4(5)	1-4 106.4(3)	228(1)	*c*
	BF(2) 136.2(5)	2-4 109.0(3)	232(1)	
	BF(3) 135.2(5)	3-4 109.0(3)	231(1)	
	BF(4) 148.6(5)			
F_2B-OH	BF 132.3	122.8	234	*d*
	BO 134.4			
F_2B-O^-*	BF 140.5	126.8	234	*e*
	BO 120.7			
		average	232(2)	

*Calculated structure. [a] Mootz, D.; Steffen, M. *Z. Anorg. Allg. Chem.* **1981**, *483*, 171. [b] Mootz, D.; Steffen, M. *Acta Crystallogr.* **1981**, *37B*, 1110. [c] Burford, N.; Spence, R. E. v. H.; Linden, A.; Cameron, T. S. *Acta Crystallogr.* **1990**, *C46*, 92. [d] Takeo, H.; Curl, R. F. *J. Chem. Phys.* **1972**, *56*, 4314. [e] This work.

have the expected values of 215 and 223 pm, respectively. The experimental bond distances in F_3CO^- are all longer than in F_2CO because it is four-coordinated rather than three-coordinated, even though the atomic charges in F_3CO^- are slightly larger than in F_2CO. The ratio of the average bond length in F_3CO^- (135.5 pm) to that in F_2CO (123.0 pm) has a value of 1.066, which is close to the expected d_4/d_3 ratio of 1.061. It appears that the bond lengths and bond angles in F_3CO^- are most satisfactorily accounted for in terms of the ligand close-packing model even though in this case the atomic charges are considerably less than the fully ionic values. It is in any case clear that an O ligand is always more strongly bound than an OH or an F ligand, which is most simply explained in terms of the fully ionic model according to which the O ligand has a charge of −2 whereas an F or OH ligand has a charge of only −1. Although the charges in F_3CO^- are smaller (O, −1.260; F, −0.633), the charge on O is nevertheless almost exactly twice the charge on F.

An analogous explanation based on the packing of the ligands can be given for the similar geometry of the isoelectronic molecule F_3NO[26] which has an NO bond length of only 116.0 pm and very long NF bonds of 143.4 pm even though the bonding in this molecule is still less ionic. The strongly bonded oxygen pushes the more weakly held fluorine ligands still further from the nitrogen than from the carbon in F_3 CO^-, giving NF bonds that are still longer than the CF bonds and correspondingly small FNF angles of only 100.5°.

Geometry of $A(OH)_4$ and $A(OX)_4$ Molecules. In contrast to the exactly tetrahedral bond angles in AX_4 molecules the OAO bond angles in $A(OH)_4$ and $A(OX)_4$ molecules are not tetrahedral (Table 9). Either two of the angles are larger and the other four are smaller than tetrahedral so that the molecule has a geometry that can be described as a squashed tetrahedron, or two of the angles are smaller than tetrahedral and the other four are larger so that the geometry of the molecule can be described as an elongated tetrahedron. Depending on the orientation of the OH groups the molecule then has either D_2 or S_4 symmetry.

No completely satisfactory explanation of these deviations of the bond angles from tetrahedral appears to have been given. Interactions between the OX dipoles and negative hyperconjugation (back-bonding) have, for example, been suggested as possible explanations.[27] But according to the back-bonding model different OXO angles would have to correspond to different bond lengths, yet all the XO bonds in these molecules have the same length. Moreover, very similar deviations in the bond angles from tetrahedral are also observed (Table 9) in tetrakis(chloromethyl)methane, $C(CH_2Cl)_4$, and in pentaerythritol, $C(CH_2OH)_4$, in which all four CC bonds have a normal single-bond lengths of 154.8 and 153.9 pm, respectively, and in which the ligand carbon has no lone pairs to take part in negative hyperconjugation (back-bonding).

We suggest that the explanation for these unexpected OAO bond angles is to be found in the electron density distribution around the O atom. Unlike a terminal oxygen or fluorine ligand, the electron density of a bridging oxygen in an $A(OH)_4$ or $A(OX)_4$ molecule does not have cylindrical symmetry and therefore has a ligand radius that varies with direction. In particular it has a slightly smaller ligand radius in the directions of the lone pairs, that is, on the opposite side of the oxygen atoms from the two bonds. This gives it a nonbonding radius that differs slightly in different directions so that the intramolecular contact distance with the other O ligands varies with the orientation of the OX groups leading to correspondingly different OAO bond angles.

When the A−O bond is very ionic, as it is in $Be(OH)_4^{2-}$, the OH ligands are nearly fully ionic and still have close to cylindrical symmetry around the A−O axis, producing only very small deviations of the OAO angles from the ideal angle of 109.5° (Table 10). But as the A−O bond becomes more covalent and the lone pairs become more localized, the electron density distribution around oxygen becomes progressively flattened in the direction of the lone pairs. The O- - -O distances and the corresponding OAO angles then depend on the relative

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(26) Plato, V.; Hartford., W. D.; Hedberg, K. *J. Chem. Phys.* **1970**, *53*, 3488.

(27) Reed, A. E.; Schade, C.; Schleyer, P. v. R.; Kamath, P. V.; Chandrasekhar, J. *J. Chem. Soc., Chem. Commun.* **1988**, 67.

Table 8. 1,3-Nonbonding O- - -O, F- - -F, and O- - -F Contact Distances in Some Oxfluorocarbon Molecules and O and F Ligand Radii

	bond length (pm)		bond angle (deg)		$[X\text{- - -}X']_{obs}$ (pm)		$[X\text{- - -}X']_{pred}$ (pm)[#]	r_F (pm)	r_O (pm)	ref
CF_4	CF	131.9	FCF	109.5	215.4	F- - -F	216	107.7		*a*
$CF_3^{+\ \#}$	CF	123.5	FCF	120.0	213.9	F- - -F	216	107.0		3
	CF	124.6	FCF	120.0	215.8	F- - -F	216	107.9		*b*
$CF_3^{-\ \#}$	CF	141.7	FCF	99.5	216.3	F- - -F	216	108.2		*c*
	CF	143.4	FCF	99.6	219.1	F- - -F	216	109.6		*d*
CF_3OCF_3	CF	132.7	FCF	108.7	215.6	F- - -F	216	107.8		*e*
	CO	136.9	OCF	110.2	221.1	O- - -F	223		113.3	
$CF_3CO_2^-$	CF	131.4	FCF	107.2	216.7	F- - -F	216	108.4		*f*
	CO	126.9	OCO	128.2	228.3	O- - -O	230		114.2	
CF_3O^-	CF	139.2	FCF	101.3	215.3	F- - -F	216	107.7		*c*
	CO	122.7	OCF	116.2	222.5	O- - -F	223		114.8	
$CF_3O^{-\ \#}$	CF	139.4	FCF	101.3	215.6	F- - -F	216	107.8		*c*
	CO	121.4	FCO	116.8	222.3	O- - -F	223		114.5	
CF_3OF	CF	131.9	FCF	109.5	215.3	F- - -F	216	107.7		*g*
	CO	139.5	OCF	109.6	221.9	O- - -F	223		114.2	
COF_2	CF	131.7	FCF	109.5	215.3	F- - -F	216	106.3	115.6	*h*
	CO	117.0	OCF	126.2	221.9	O- - -F	223			
$COF_2^{\ \#}$	CF	132.0	FCF	107.6	213.0	F- - -F	216	106.5	115.7	3
	CO	117.1	OCF	126.2	222.2	O- - -F	223			
MeC(O)F	CF	134.8	OCF	121.4	220.7	O- - -F	223			*i*, *j*
	CO	118.1								
FC(O)OF	CF	132.4	OCF	126.5	222.8	O- - -F	223			*j*
trans	CO	117.0								
FC(O)OF	CF	132.0	OCF	126.4	222.5	O- - -F	223			*j*
cis	CO	117.2								
$FC(O)NO_3$	CF	132.0	OCF	128.8	224.2	O- - -F	223			*k*
	CO	116.5								
F(O)C−C(O)F	CF	132.9	OCF	124.2	221.8	O- - -F	223			*l*
	CO	118.0								
$CF_2(OF)_2$	CF	131.7	FCF	113.0	219.6	F- - -F	216	109.8		*m*
	CO	138.7	OCO	115.0	234.0	O- - -O	230		117	
			OCF	112.1	224.3	O- - -F	223			
			OCF	102.1	210.3	O- - -F	223			
							mean:	108(1)	115(1)	

[#] Calculated structure. [a] Fink, M.; Schmeidekamp, C. W.; Gregory, D. *J. Chem. Phys.* **1976**, *71*, 258. [b] Olah, G. A.; Rasul, G.; Yudin, A. K.; Burrichter, A.; Surya Prakash, G. K.; Chistyakov, A. L.; Stankevich, I. V.; Akhrem, I. S.; Gambaryan, N. P.; Vol'pin, M. E.; *J. Am. Chem. Soc.* **1996**, *118*, 1446. [c] Farnham, W. B.; Smart, B. E.; Middleton, W. J.; Calebrese, J. C.; Dixon, D. A.; *J. Am. Chem. Soc.* **1985**, *107*, 4565. [d] Marynick, D. S. *J. Mol. Struct.* **1982**, *87*, 161. [e] Lowrey, A. H.; George, C.; D'Antonio, P. *J. Mol. Struct.* **1980**, *63*, 243. [f] Cruickshank, D. W. J.; Jones, P. W.; Walker, G. J. *J. Chem. Soc.* **1964**, 1303. [g] Diodati, F. R.; Bartell, L. S.; *J. Mol. Struct.* **1971**, *8*, 395. [h] Carpenter, J. H. *J. Mol. Spectrosc.* **1974**, *50*, 182; Nakata, M.; Kohata, K.; Fukuyama, T.; Kuchitsu, K.; Wilkins, C. J. *J. Mol. Struct.* **1980**, *68*, 271. [i] Pierce, L.; Krisher, L. C. *J. Chem. Phys.* **1959**, *31*, 875. [j] Argüello, G. A.; Ülicher, B. J.; Ulic, S. J.; Willner, H.; Casper, B.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **1995**, *34*, 2089. [k] Scheffler, D. Schaper, I.; Willner, H.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **1997**, *36*, 339. [l] See: Möller, G.; Olmstead, M. M.; Tinti, D. S. *J. Am. Chem. Soc.* **1987**, *109*, 95. [m] Gobbato, K. J.; Mack, H.-G; Oberhammer, H.; Della Védova, C. O. *J. Am. Chem. Soc.* **1997**, *119*, 803.

Table 9. Symmetries and Average Bond Angles (deg) in Some $A(XY)_4$ Molecules with Distorted Tetrahedral Structures

	symmetry	∠XAX		ref		symmetry	∠XAX		ref
$^*Be(OH)_4^{2-}$	D_2	107.8 × 2	110.3 × 4	*a*	$C(OC_6H_5)_4$	D_2	101.2 × 2	113.8 × 4	*i*
$^*B(OH)_4^-$	D_2	106.2 × 2	111.1 × 4	*a*	$C(OC_6H_3Me_2\text{-}3,5)_4$	D_2	100.9 × 2	114.0 × 4	*i*
$LiB(OH)_4$		106.6 × 2	112.8 × 2	*b*	$^*Si(OH)_4$	D_2	104.8 × 2	111.8 × 4	*g*
		109.1 × 2				S_4	107.1 × 4	114.2 × 2	*g*
$NaB(OH)_4{\cdot}2H_2O$		106.4 × 2	112.6 × 2	*c*	$C(SC_6H_5)_4$	S_4	106.3 × 4	116.0 × 2	*j*
		108.0 × 2			$C(CH_2OH)_4$	S_4	106.7 × 2	110.9 × 4	*k*
$Na_2B(OH)_4Cl$	D_2	105.1 × 2	111.7 × 4	*d*	$C(CH_2Cl)_4$	S_4	106.1 × 2	112.9 × 2	*l*
$B(OMe)_4^-$	D_2	101.7 × 2	113.5 × 4	*e*		D_2	108.3 × 2	111.9 × 4	*l*
$KB(OSO_2Cl)_4$	S_4	107.4 × 4	113.8 × 2	*f*	$^*Ti(NH_2)_4$	S_4	107.2 × 4	114.2 × 2	*m*
$^*C(OH)_4$	D_2	103.6 × 2	112.5 × 4	*a*	$Ti(NMe_2)_4$	S_4	107.2 × 4	114.2 × 2	*m*
	D_2	104.3 × 2	112.1 × 4	*g*	$V(NMe_2)_4$	D_2	100.6 × 2	114.1 × 4	*m*
	S_4	107.2 × 4	114.2 × 2	*g*	$V(O^tBu)_4$	S_4	106.7 × 4	115.1 × 2	*m*
$C(OMe)_4$	S_4	106.9 × 4	114.6 × 2	*h*					

*Calculated structure. [a] This work. [b] Höhne, E. *Z. Anorg. Allg. Chem.* **1966**, *342*, 188. [c] Block, S.; Perloff, A. *Acta Crystallogr.* **1963**, *16*, 1233. [d] Effenberger, H. *Acta Crystallogr.* **1982**, *B38*, 82. [e] Alcock, N. W.; Hagger, R. M.; Harrison, W. D.; Wallbridge, M. G. H. *Acta Crystallogr.* **1982**, *B38*, 676. [f] Mairesse, G.; Drache, M. *Acta Crystallogr.* **1978**, *B34*, 1771. [g] Reed, A. E.; Schade, C.; Schleyer, P. v. R.; Kamath, P. V.; Chandrasekhar, J. *J. Chem. Soc., Chem. Commun.* **1988**, 67. [h] Mijlhoff, F. C.; Geise, J. J.; Van Schaick, E. J. M. *J. Mol. Struct.* **1974**, *20*, 393. [i] Narasimhamurthy, N.; Manohar, H.; Samuelson, A. G.; Chandrasekhar, J. *J. Am. Chem. Soc.* **1990**, *112*, 2937. [j] Kato, K. *Acta Crystallogr.* **1972**, *B28*, 606. [k] Shiono, R.; Cruichshank, D. W. J.; Cox, E. G. *Acta Crystallogr.* **1958**, *11*, 389. [l] Stølevik, R. *Acta Chem. Scand.* **1974**, *28A*, 327. [m] Haaland, A.; Rypdal, H.; Volden, H. V.; Andersen, R. A. *J. Chem. Soc., Dalton Trans.* **1992**, 891.

Table 10. Analysis of the ab Initio Structural Data for $A(OH)_3$ and $A(OH)_4$ Molecules

	$Be(OH)_3$	$Be(OH)_4^{2-}$	$B(OH)_3$	$B(OH)_4^{-}$	$C(OH)_3^{+}$	$C(OH)_4$
A−O (pm)	154.6	168.8	136.9	148.7	128.1	139.3
$-q_{OH}$ (au)	0.90	0.93	0.76	0.82	0.43	0.50
∠OAO (deg)	120.0 × 3	107.8 × 2	120.0 × 3	106.2 × 2	120.0 × 3	103.6 × 2
∠OAO (deg)		110.3 × 4		111.1 × 4		112.5 × 4
O- - -O (pm)	268 × 3	273 × 2	237 × 3	238 × 2	222 × 3	219 × 2
O- - -O (pm)		277 × 4		245 × 4		232 × 4
Δ(O- - -O) (pm)[a]		4				13

[a] Difference in the two contact distances in the $A(OH)_4$ molecules.

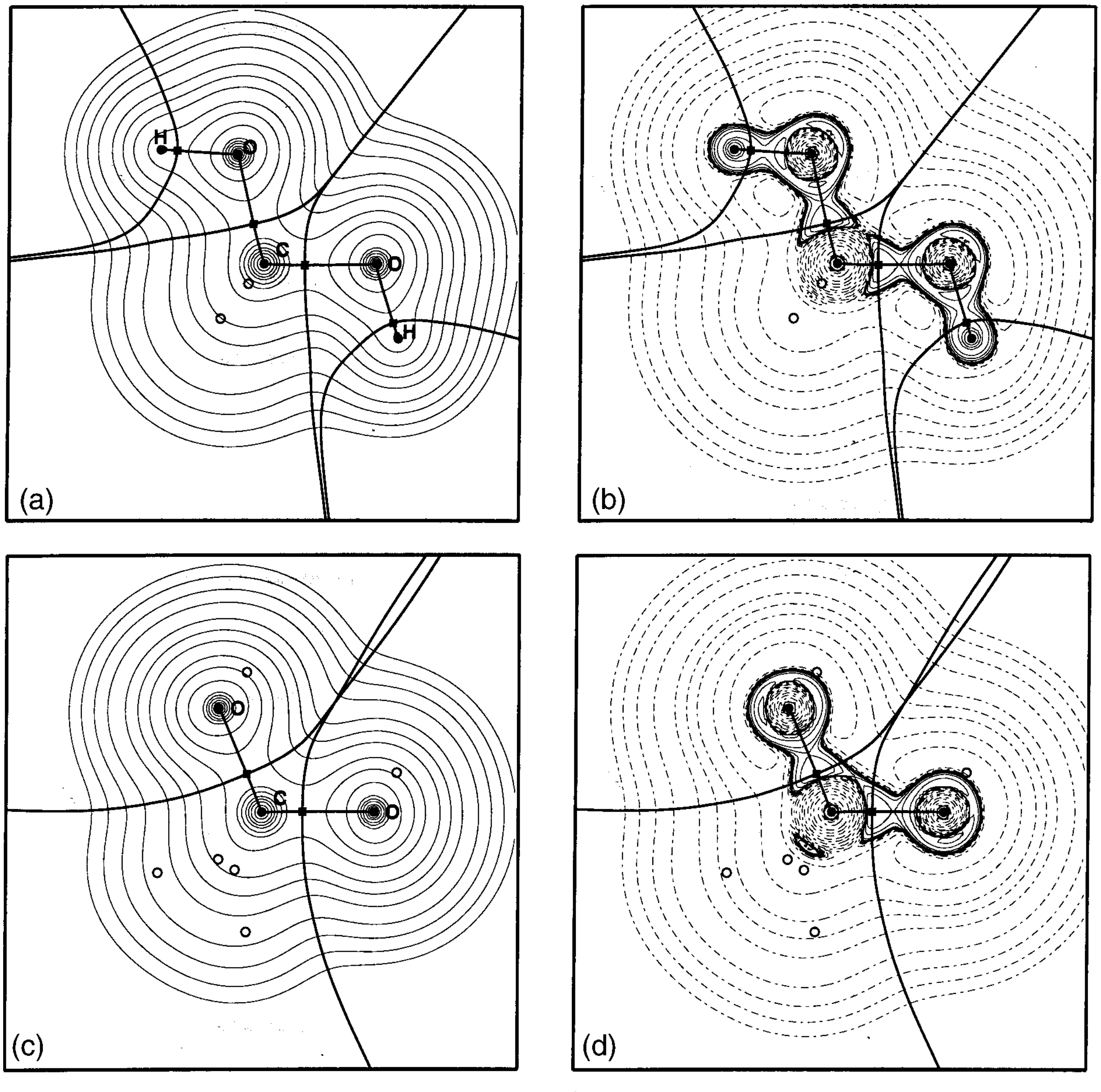

Figure 3. Plots of the Electron Density, ρ, and of the Laplacian, $L = -\nabla^2\rho$, for the two nonequivalent COC planes in $C(OH)_4$. (a and b) ρ and L for the 103.6° OCO plane; (c and d) ρ and L for the 112.5° plane.

orientation of the two adjacent OH ligands and have their smallest values when the H atoms point away from each other and the lone pair regions point toward each other. Other relative orientations of the OH ligands give larger O- - -O distances so that the OAO angles depend on the relative orientations of the OX bonds. The differences in these distances are expected to increase as the ionicity of the A−OH bonds decreases and the electron density distribution around oxygen becomes increasingly less symmetric, as is found to occur progressively from $Be(OH)_4^{2-}$ to $B(OH)_4^{-}$ to $C(OH)_4$ (Table 10). In $A(OH)_3$ molecules, which all have C_{3h} symmetry with the OH bonds lying in the molecular plane and having the same orientation, the three O- - -O distances (Table 10) are all the same and are very similar to the smaller distances in the corresponding $A(OH)_4$ molecules.

The calculated electron density distributions for the two COC planes associated with the two different OCO angles in the D_2 conformation of $C(OH)_4$ are shown in Figure 3. The distortion of the distribution around the oxygen atoms can be seen in both cases. For the larger COC angle the regions around the O atom that have a slightly higher electron density and therefore a "bulge" in the density in this region point toward each other giving a correspondingly large OCO angle. For the smaller OCO angle these regions of higher electron density are parallel to each other. Although these distortions of the electron density are very small, they are made more evident in the Laplacian[11] (Figure 3) where the regions of increased electron density appear as charge concentrations and they cause correspondingly small but nevertheless significant deviations of the angles from the tetrahedral angle.

Similar deviations from tetrahedral symmetry have also been observed for the transition metal molecules $Ti(NMe_2)_4$, $V(NMe_2)_4$ and $V(O^tBu)_4$.[28] A similar explanation can be given for the bond angles in these molecules in terms of an unsymmetrical electron density at the N or O atom as we will discuss in detail in a following paper.[29]

Covalent and Ionic Character of Polar Bonds. The constancy of the intramolecular F- - -F, O- - -O, and O- - -F contact distances in the fluorides, hydroxides, and oxides of the less electronegative elements such as Be, B, and C, independent of coordination number and the presence of other ligands, shows that the ligands are essentially close-packed around the central atom. The large calculated charges on the atoms indicate that the bonds have considerable ionic character, and the ligand radii obtained from the contact distances, although smaller than ionic crystal radii, are consistent with the smaller ligand charge. These results form the basis for our model for these molecules as consisting of anion-like ligands of nearly constant size and charge close-packed around a cation-like central atom. Thus A−F and A−O bond lengths decrease with decreasing coordination number for a given central atom and from Li to C as the charge on the central atom increases and its size decreases.

However, as the charges are less than the fully ionic charges, the bonds clearly have some covalent character, in other words, there is some shared density. The bond density at the critical point, which would be zero in a hypothetical truly ionic bond, is presumably a function of the amount of shared density and therefore may be considered to be a measure of the covalent character of the bond. We see from Figure 4, which is based on the data in Table 3, that ρ_b increases remarkably smoothly as the bond length decreases for Be−O(X), B−O(X), and C−O(X) bonds and that bonds to carbon have larger ρ_b values and therefore greater covalent character than bonds to boron, which are more covalent than bonds to beryllium. It appears that for a given bond type, ρ_b and the covalent character of the bond depend primarily on the bond length which in turn is determined by the packing of the anion-like ligands around the cation-like central atom. However, it is not clear that either covalent character or ionic character can be defined in unambiguous or precise way. An alternative definition of covalent character might, for example, be given in terms of bond order as determined from $\rho(r)$.[30] Ionic character could be defined in terms of the charge on the ligand, being equal to 100% in the case of a purely ionic bond and 0% in the case of a pure covalent bond. However, it is not clear that there is any quantitative relationship between covalent and ionic character, even if they can be precisely defined, except in the extreme cases.

The difficulty of defining ionic and covalent character in a meaningful way is illustrated by the ρ_b value for the C−OH bond in $C(OH)_4$ of 0.289 au, which is larger than the value for the C−C bond in ethane (0.252 au), suggesting that the C−OH bond is both more covalent and more ionic than a C−C bond. Consistent with its greater ρ_b and relatively large atomic charges, the C−OH bond has a length of only 139 pm compared to 154 pm for the C−C bond in ethane.

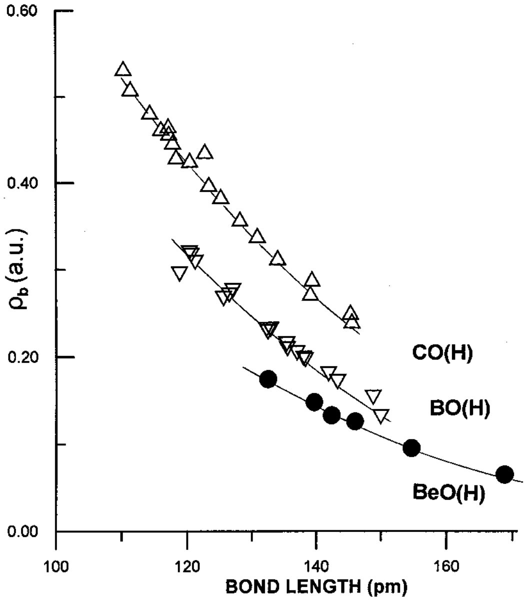

Figure 4. Correlation of bond length with the electron density at the bond critical point, ρ_b for AO bonds: BeO (○), BO (▽), CO (△).

According to our ionic model, the marked decrease in bond length from $Be(OH)_2$ to $C(OH)_4$ and from LiF to CF_4 correlates with the increasing charge on the central atom, or more exactly with the product of the charges on the central atom and the ligand, and the consequently increased attraction between the cation-like central atom and the anion-like ligands.

Conclusions and Summary

In this paper we have shown the following:

1. In the oxides, hydroxides, and alkoxides of Be, B, and C the ligands have considerable negative charges and the bond lengths and bond angles in these molecules can be better understood in terms of an ionic model than a covalent model, just as we have previously shown for fluorides.
2. Oxygen−oxygen contact distances for a given central atom A are remarkably constant and essentially the same in both three- and four-coordinated molecules. The ligand radii for O and OH obtained from these contact distances, decrease in the series Be−O(H) > B−O(H) > C−O(H) with decreasing charge on the ligand.
3. The length of an A−O bond for a given central atom A depends primarily on the coordination number of A and decreases with decreasing coordination number.
4. The observations summarized in (2) and (3) can be most satisfactorily explained in terms of close packing of anion-like O, OH, or OX ligands around a cation-like central atom, the same model that we have previously used to account for the bond lengths and bond angles in molecular fluorides.
5. As the length of an A−O(H) bond decreases, the electron density at the bond critical point increases correspondingly.
6. Terminal O atoms are bound more strongly and have considerably shorter A−O bonds than OH or OR ligands primarily, it appears, because the charge on a terminal O atom is considerably larger than the O atom in an OH or OX ligand.
7. The unusual bond lengths in the F_3CO^- molecule can be accounted for by the same ligand close-packing model. Oxygen,

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because of its much higher charge, is more strongly bound than fluorine and hence forms a considerably shorter bond.

8. The nontetrahedral OAO bond angles that are observed in $A(OH)_4$ and $A(OR)_4$ molecules may be attributed to the noncylindrical symmetry of the electron density around the O atom that leads to two different O- - -O contact distances and hence to two different bond angles—one larger than tetrahedral and the other smaller than tetrahedral.

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