Geometrical Parameters of Hydroxo and Related Molecules of Be, B, and C

Table 8.5 Geometrical Parameters, Atomic Charges, and ρ_b Values for Some Be, B, and C Hydroxo Molecules and Ions

	Bond Lengths (pm)			Atomic Charges			
Molecule	***Calc.***	***Exp.***	ρ_b***(au)***	$-q(O)$	$q(H)$	$-q(OH)$	$q(A)$
$Be(OH)_2$	142.3		0.133	1.42	0.57	0.85	1.70
$Be(OH)_3^-$	154.6	154.0	0.095	1.37	0.47	0.90	1.69
$Be(OH)_4^{2-}$	168.8		0.065	1.34	0.42	0.93	1.70
$B(OH)_2^+$	125.5		0.267	1.34	0.69	0.65	2.31
$B(OH)_3$	136.9	136.3	0.204	1.32	0.56	0.76	2.28
$B(OH)_4^-$	148.3	147.7	0.153	1.30	0.48	0.82	2.28
$C(OH)_3^+$	128.1		0.358	1.05	0.64	0.41	2.23
$C(OH)_4$	139.3	139.6[a]	0.289	1.04	0.54	0.50	1.99

[a] $C(OMe)_4^-$.

- ✔ High charges on A and both O and OH indicate very polar bonds.
- ✔ Low ρ_b values for $Be(OH)_2$, $Be(OH)_3^-$, and $Be(OH)_4^{2-}$ suggest mostly ionic bonding.
- ✔ Bond lengths increase with coordination number (CN) for a given central atom.
  - Nearly constant charges with CN change suggests that bond polarity is not responsible for bond length changes.
  - Bond lengthening with increasing CN is consistent with LCP model, in which ligands maintain a relatively constant interligand distance due to close packing and a constant ligand radius with a given central atom.

Calculated Geometries, Charges, and Bond Critical Point Densities for $A(OH)_n$ Species[1,2]

Molecule	A–O (pm)	∠O–A–O (°)	∠A–O–H (°)	q(OH)	q(A)	ρ_b (au)
LiOH	158.2		180.0	–0.91	+0.91	0.073
$Be(OH)_2$	142.3	180.0	134.5	–0.85	+1.70	0.133
$B(OH)_3$	136.8	120.0	112.8	–0.76	+2.28	0.204
$C(OH)_4$	139.3	103.6, 112.5	106.9	–0.50	+1.99	0.289
$N(OH)_3$	141.3	103.8	102.6	–0.13	+0.40	0.311
$O(OH)_2$	144.4	100.3	98.7	+0.04	–0.08	0.281
FOH	143.2		98.6	+0.19	–0.19	0.269

✔ ∠A–O–H decreases with increasing electronegativity of A as oxygen valence shell electrons are increasingly localized with approximately tetrahedral geometry.
- When poorly localized, the geometry is linear as in LiOH.
- When oxygen nonbonding electrons become more localized with increasing electronegativity of A, the angle decreases towards 109.5° and becomes still smaller as the lone pairs increasingly dominate the geometry.

✔ Bonds become increasingly covalent (rising ρ_b) from LiOH to $N(OH)_3$, falling only slightly through $O(OH)_2$ and FOH.

✔ Bond polarity falls through the series {declining q(OH)}, rising slightly at HOF.

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[1]E. A. Robinson, G. L. Heard, R. J. Gillespie, *J. Mol. Struct.*, **1999**, *485-486*, 305-319.

[2]G. L. Heard, R. J. Gillespie, D. W. H. Rankin, *J. Mol. Struct.*, **2000**, *520*, 237-248.

Geometry of $A(OX)_3$ and $A(OX)_4$ Molecules

✔ Non-linear A–O–X unit determines geometry about A and the point group of the molecule.

Table 8.6 Geometry of $A(OX)_3$ and $A(OX)_4$ Molecules

Molecule	Bond Length (pm)	Bond Angles (°)	Symmetry
$Be(OH)_3^{-}$ [a]	154.0	120	C_{3h}
$Be(OH)_4^{2-}$ [a]	168.8	107.8 × 2 110.3 × 4	D_{2d}
$B(OH)_3$	136.3	120	C_{3h}
$B(OMe)_3$	136.8	120	C_{3h}
$B(OH)_4^{-}$	147.7	106.2 × 2 111.1 × 4	D_{2d}
$C(OH)_3^{+}$ [a]	128.1	120	C_{3h}
$C(OH)_4$ [a]	139.3	104.3 × 2 112.1 × 4	D_{2d}
$C(OH)_4$ [a]	139.3	107.2 × 4 114.2 × 2	S_4
$C(OMe)_4$	139.6	106.9 × 4 114.6 × 2	S_4
$C(OPh)_4$	139.4	101.2 × 4 113.8 × 4	D_{2d}

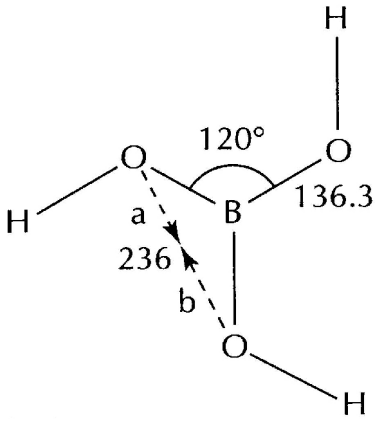
[a]Calculated data.

Symmetry of $B(OH)_3$ and Related Species

✔ Non-linear A–O–H leads to two ligand radii for O, r_a and r_b, depending on direction of contact with neighboring ligands.

✔ Radius in the direction between the bonds (r_a) is greater than in the direction of the oxygen lone pairs (r_b)

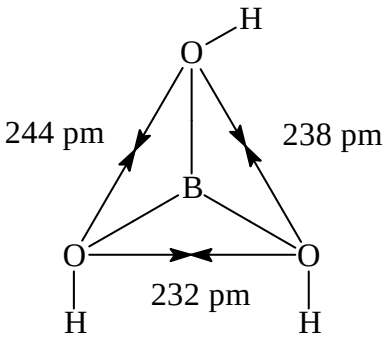
✔ Optimal configuration of $A(OX)_3$ molecules is C_{3h}, as with $B(OH)_3$.



C_{3h}

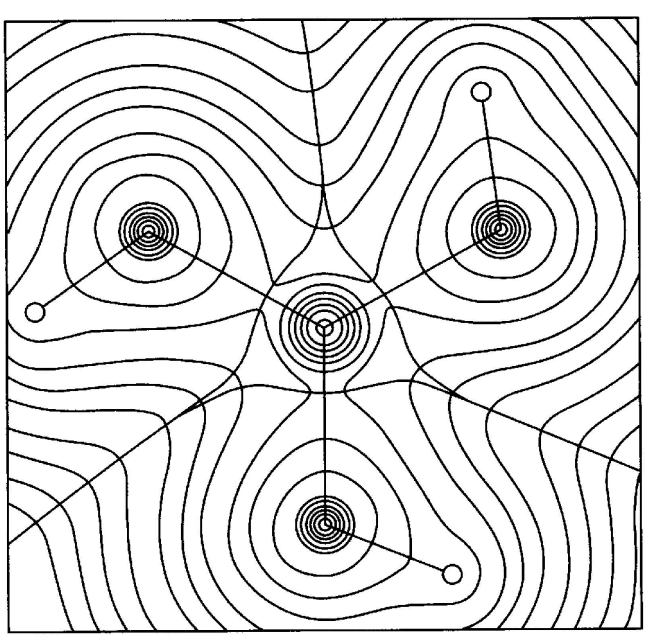
✔ For $B(OH)_3$, r_a = 122 pm and r_b = 116 pm.

✔ The C_s structure, which has unequal bond angles, is not the minimum energy configuration.

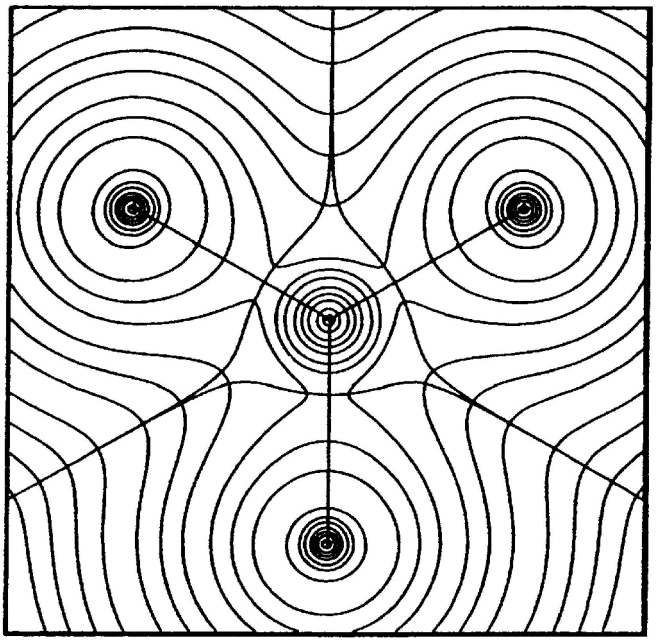


C_s

Bonding in $B(OH)_3$



$B(OH)_3$



BF_3

✔ Bonding in $B(OH)_3$ is very similar to that in BF_3.

BX_3	ρ_b	$-q(X)$	$q(B)$	Bond Length (pm)
$B(OH)_3$	0.204	0.76	2.28	136.9
BF_3	0.217	0.81	2.43	130.7

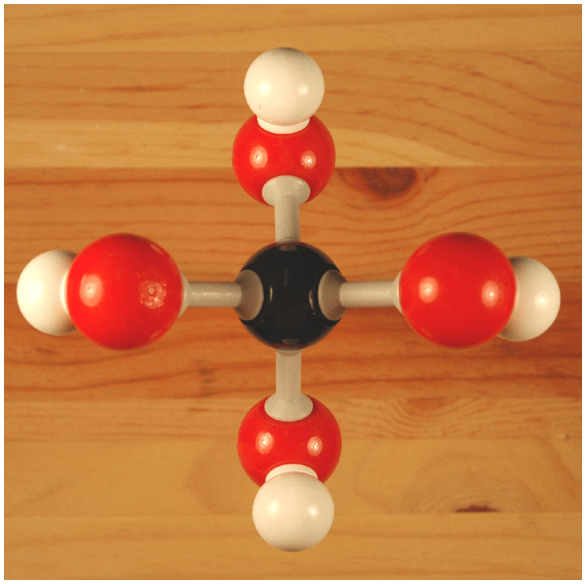
✔ Contours and ρ_b values indicate covalent bonds with high polarity.

✔ Bond length in $B(OMe)_3$ (136.8 pm) is similar to $B(OH)_3$, indicating that bond lengths in both are determined by oxygen ligand close packing.

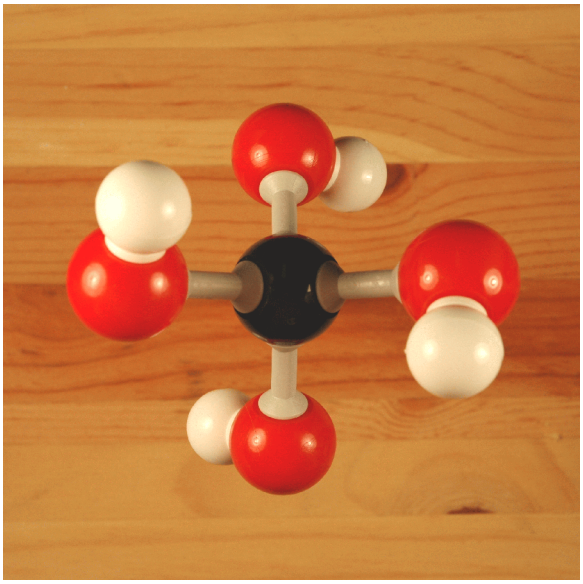
Symmetry of $A(OX)_4$ Molecules

✔ Asymmetry of electron density around the ligand oxygen in –OX prevents $A(OX)_4$ molecules from having perfect T_d symmetry.

✔ $A(OX)_4$ molecules may be D_{2d} or S_4, depending on the orientations of the O–X groups.



D_{2d}



S_4

✔ All A–O distances are equal, but there are four ∠O–A–O <109.5° and two ∠O–A–O >109.5°, or vice versa.

✔ Geometry is non-tetrahedral because if all six interligand distances were the same the ligands could not be in contact with each of their neighbors and thus be as close as possible to the central atom.[3]

✔ Both D_{2d} and S_4 structures have nearly equal energy in some cases; e.g., $C(CH_2Cl)_4$ is an equal mixture of both.

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[3]G. L. Heard, R. J. Gillespie, D. W. H. Rankin, *J. Mol. Struct.* **2000,** *520*, 237-248.

Distorted Tetrahedral $A(XY)_4$ Molecules

Table 8.7 Symmetries and Bond Angles in Some $A(XY)_4$ Molecules with Distorted AX_4 Tetrahedral Structures

		Bond Angles (°)	
Molecule	***Symmetry***	***XAX***	***XAX***
$Be(OH)_4^{2-}$ [a]	D_{2d}	107.8 × 2	110.3 × 4
$B(OH)_4^-$ [a]	D_{2d}	106.2 × 2	111.1 × 4
$B(OMe)_4^-$	D_{2d}	101.7 × 2	113.5 × 4
$B(OSO_2Cl)_4^-$	S_4	107.4 × 4	113.8 × 2
$C(OH)_4$[a]	D_{2d}	104.3 × 2	112.1 × 4
$C(OH)_4$[a]	S_4	107.2 × 4	114.2 × 2
$C(OMe)_4$	S_4	106.9 × 4	114.6 × 2
$C(OC_6H_5)_4$	D_{2d}	101.2 × 2	113.8 × 4
$C(OC_6H_3Me_2{-}3,5)_4$	D_{2d}	100.9 × 2	114. 0 × 4
$C(SC_6H_5)_4$	S_4	106.3 × 4	116.0 × 2
$C(CH_2OH)_4$	S_4	106.7 × 2	110.9 × 4
$C(CH_2Cl)_4$	S_4	106.1 × 2	~~112.9 × 2~~ 111.2 × 4
$C(CH_2Cl)_4$	D_{2d}	108.3 × 4	111.9 × 2

[a]Calculated data.

✔ $B(OH)_4^-$ (D_{2d}) has two106.2° angles and four 111.1° angles.