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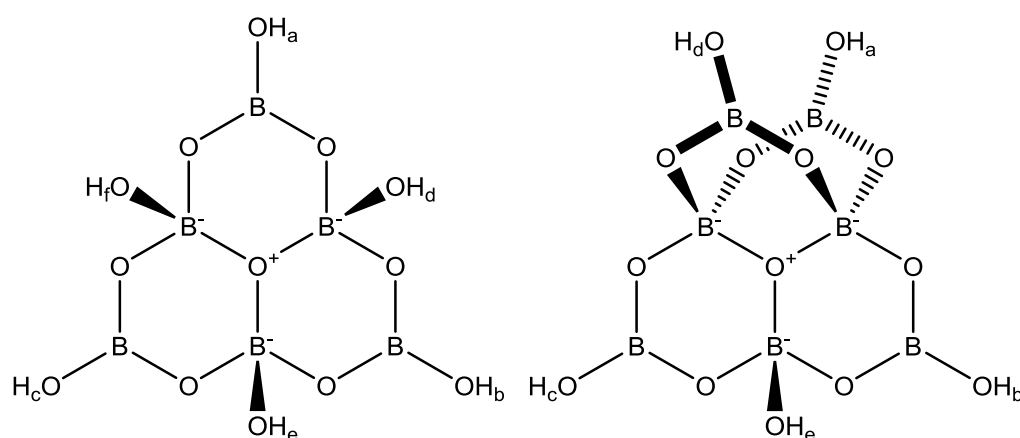
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## DFT studies on hexaborate(2-) and heptaborate(2-) anions

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### GRAPHICAL ABSTRACT



**Abstract** Bond counting rules allow chemists to unearth low-energy structures by sequentially sieving undesirable interactions whilst maximizing stabilizing interactions. The approach is applied to model hydrogen-bonding in polyborate anions.

**Keywords** Polyborate anions; hydrogen bonding; polyhydroxybenzoquinones

### INTRODUCTION

Conformational analysis is a painstaking task even with advances in computing power. Bond counting rules (BCR) have been used to identify low-energy structures for B/C/N superhard materials,<sup>1,2</sup> and doped fullerenes,<sup>3</sup> based upon observations<sup>4</sup> that stable structures had no B-B nor N-N bonds, whilst the number of C-C and B-N bonds were maximized. The BCR works well for B/C/N systems due to the large energetic differences (*ca.* 100-200 kJ mol<sup>-1</sup>) between the weakest and strongest covalent bonds. It should be possible to extend BCRs to hydrogen-bonded systems,<sup>5,6</sup> as typical hydrogen-bond energies (*ca.* 20 kJ mol<sup>-1</sup>) are far greater than either thermal energy or computational error.

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Polyborate anions can form a myriad of structures including isolated rings or cages, 1-D chains, 2-D sheets and 3-D networks due to corner sharing linked triangular  $\text{BO}_3$  and tetrahedral  $\text{BO}_4$  units.<sup>7-11</sup>

## RESULTS AND DISCUSSION

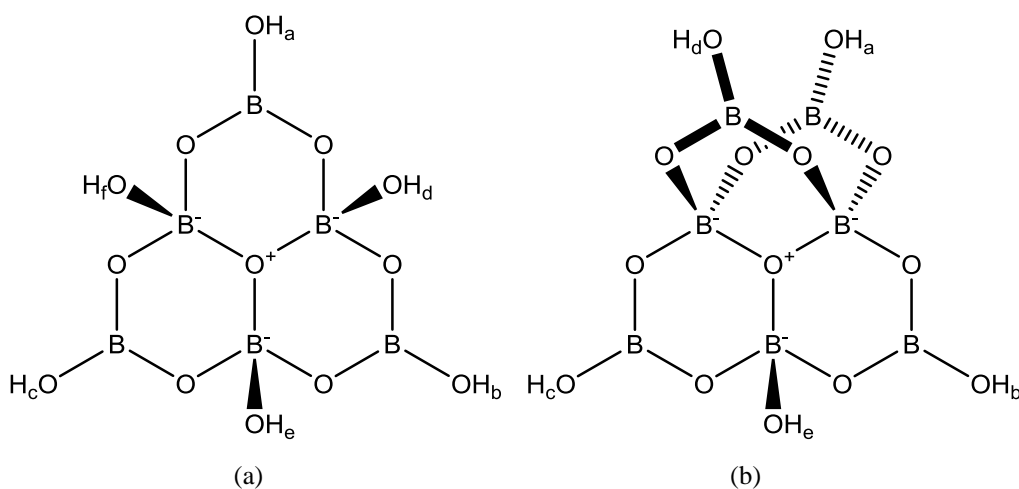
### Computational Methodology

Gas-phase B3LYP/6-311++G(*d,p*) DFT calculations were performed using *Gaussian09*.<sup>12</sup>

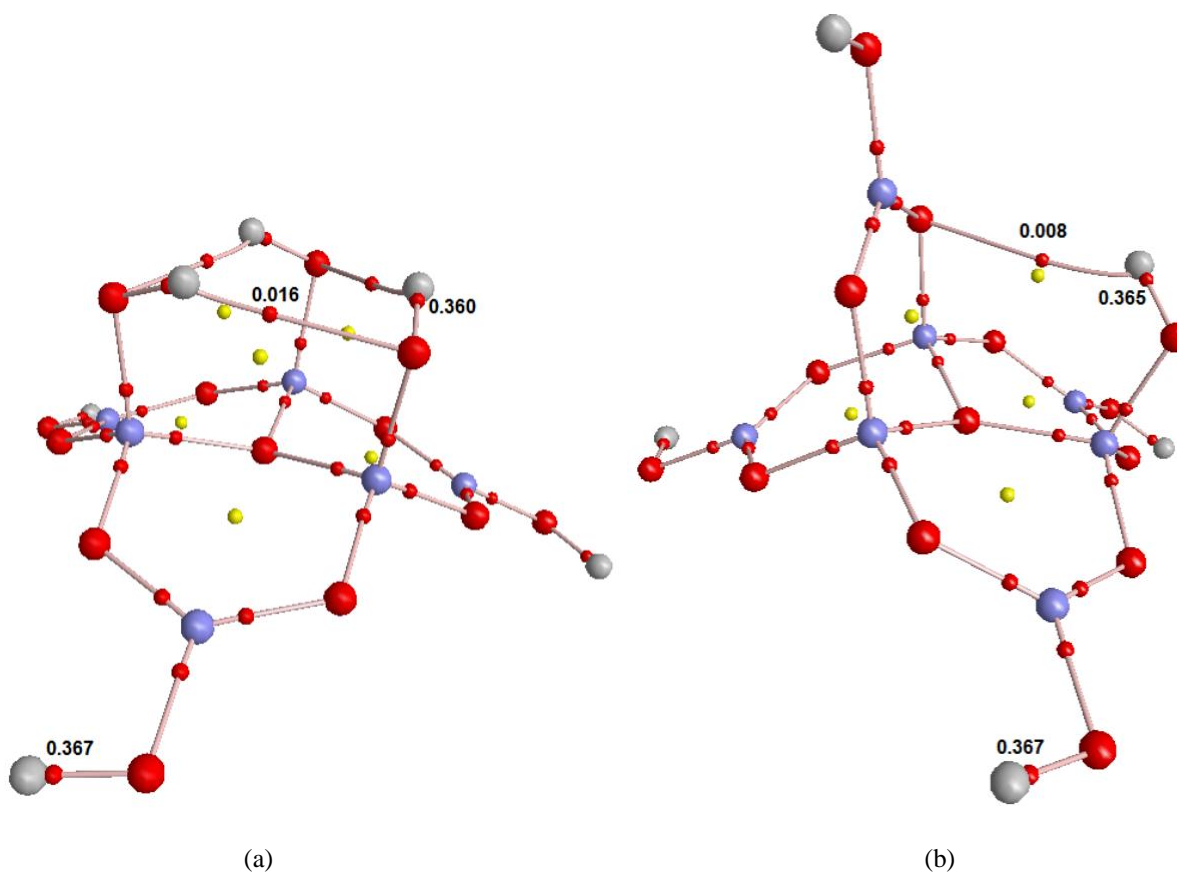
### Hexaborate

The  $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$  anion consists of  $\text{BO}_3$  triangles ( $\Delta$ ) &  $\text{BO}_4$  tetrahedra (T) linked by vertices and a central 3-coordinate O atom to form three 6-membered rings containing 3- and 4-coordinate borons (Figure 1a) with a Christ and Clark description of  $6:3\Delta + 3\text{T}$ .<sup>7</sup> The calculations suggest that *exo* OH groups attached to tetrahedral borons will preferentially orientate *anti-* to the ring B-O bonds. The most stable structures (Figure 2a) possess an unbroken, quasi-triangular cyclic network ( $r_{\text{O-H}} = 0.967 \text{ \AA}$ ;  $r_{\text{O...H}} = 2.25 \text{ \AA}$ ;  $\angle_{\text{O-H...O}} = 135.7^\circ$ ;  $r_{\text{O...O}} = 3.02 \text{ \AA}$ ) of cooperative intramolecular hydrogen bonds (IHBs). The cyclic network maximizes the number of stabilizing interactions in complete accord with bond counting rule approaches. Breaking an IHBs (so that two remain) *via* B-O bond rotation, raises the conformational energy by *ca.*  $15 \text{ kJ mol}^{-1}$  (Table 1), which is consistent with hydrogen bond energies.<sup>6</sup> In complete contrast, rotation of the planar hydroxyl groups attached to a trigonal boron atom has a negligible energetic effect due to absence of H-bonding (no bond critical point) coupled with almost identical electrostatic attractions between the electropositive hydrogen of the OH group and the electronegative ring O atoms.

QTAIM analyses (Figure 2a) confirm the covalent nature of the OH groups with large  $\rho_{\text{BCP}}$  and -ve  $\nabla^2$  values (*ca.*  $0.36 \text{ a.u.}$  and  $-2.40 \text{ a.u.}$  respectively). The closed-shell IHBs have much smaller  $\rho_{\text{BCP}}$  and  $\nabla^2$  values (*ca.*  $0.02 \text{ a.u.}$  and  $0.05 \text{ a.u.}$  respectively) reflecting their weaker nature. A  $0.007 \text{ a.u.}$  reduction in  $\rho_{\text{BCP}}$ , a  $0.006 \text{ \AA}$  elongation in  $r_{\text{OH}}$  and a *ca.*  $100 \text{ cm}^{-1}$  red shift in  $\nu_{\text{OH}}$  are observed for *exo* vs planar OH groups, reflecting the loss in electron density that occurs during hydrogen bond formation.



**Figure 1** Polyborate anion skeletal structures: (a)  $[B_6O_7(OH)_6]^{2-}$ ; (b)  $[B_7O_9(OH)_5]^{2-}$



**Figure 2** QTAIM bond graph (AIM2000) and selected  $\rho_{BCP}$  values (a.u.): (a)  $[B_6O_7(OH)_6]^{2-}$ ; (b)  $[B_7O_9(OH)_5]^{2-}$ .

Small red and yellow dots represent bond and ring critical points respectively.

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**Table 1** Gas phase B3LYP/6-311++G(*d,p*) relative energies (kJ mol<sup>-1</sup>) for the [B<sub>6</sub>O<sub>7</sub>(OH)<sub>6</sub>]<sup>2-</sup> hexaborate anion. Initial hydrogen atom orientations C = clockwise, A = anticlockwise and sites (a-f) relative to Figure 1a. Sixty four (2<sup>6</sup>) different combinations were generated giving rise to twelve unique enumerations.

Outer (Trigonal) OH groups			Inner (Tetrahedral) OH groups			$\Delta E$ (kJ mol <sup>-1</sup> )
a	b	c	d	e	f	
C	C	C	A	A	A	0
C	C	C	C	C	C	0
C	C	A	A	A	A	1
C	C	A	C	C	C	1
C	C	A	A	A	C	14
C	C	A	C	C	A	14
C	C	C	C	A	A	15
C	C	C	C	C	A	16
C	C	A	C	A	A	16
C	C	A	A	C	C	17
C	C	A	A	C	A	18
C	C	A	C	A	C	19

**Table 2** Gas phase B3LYP/6-311++G(*d,p*) relative energies (kJ mol<sup>-1</sup>) for the [B<sub>7</sub>O<sub>9</sub>(OH)<sub>5</sub>]<sup>2-</sup> heptaborate anion. Initial hydrogen atom orientations C = clockwise, A = anticlockwise and sites (a-e) relative to Figure 1b. Thirty two (2<sup>5</sup>) different combinations were generated giving rise to sixteen unique enumerations.

OH groups					$\Delta E$ (kJ mol <sup>-1</sup> )
a	b	c	d	e	
C	C	C	C	C	0
C	A	C	A	A	0
C	A	A	C	A	1
C	A	C	A	C	1
C	A	A	C	C	1
C	C	C	C	A	1
C	C	A	A	A	1
C	C	A	A	C	2
C	C	C	A	A	2
C	A	A	A	A	2
C	C	A	C	A	2
C	A	A	A	C	2
C	C	A	C	C	3
C	C	C	A	C	3
C	A	C	C	C	3
C	A	C	C	A	4

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## Heptaborate

The  $[\text{B}_7\text{O}_9(\text{OH})_5]^{2-}$  anion is related to  $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$  by condensing two *exo* OHs with a  $\text{B}(\text{OH})_3$  unit, forming an additional 6-membered ring (Figure 1b). It has a Christ and Clark descriptor of  $7:4\Delta + 3\text{T}$ .<sup>7</sup> An IHB is formed between the *exo*-OH and either O atom situated on the new ring (Figure 2b), giving rise to similar energies for all rotamers (Table 2). The weaker nature of the IHB ( $r_{\text{O-H}} = 0.962 \text{ \AA}$ ;  $r_{\text{O}\cdots\text{H}} = 2.59 \text{ \AA}$ ;  $\angle_{\text{O-H}\cdots\text{O}} = 128.3^\circ$ ;  $r_{\text{O}\cdots\text{O}} = 3.27 \text{ \AA}$ ) is highlighted in the low ( $< 0.01$  a.u.)  $\rho_{\text{BCP}}$  value together with a much shorter BCP-RCP distance (almost to the point of BCP/NCP coalescence). A small (*ca.* 0.002 a.u.) reduction in  $\rho_{\text{BCP}}$ , together with a *ca.* 20  $\text{cm}^{-1}$  red shift in  $\nu_{\text{OH}}$  and negligible ( $< 0.001 \text{ \AA}$ ) elongation in  $r_{\text{OH}}$  for *exo* vs planar hydroxyl groups confirms the weaker nature of the IHB. Rotation of the planar hydroxyl groups attached to trigonal boron atoms again have a negligible energetic effect due to absence of hydrogen bonding.

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