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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,^{1,2} and doped fullerenes,³ based upon observations⁴ 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⁻¹) between the weakest and strongest covalent bonds. It should be possible to extend BCRs to hydrogen-bonded systems,^{5,6} as typical hydrogen-bond energies (*ca.* 20 kJ mol⁻¹) 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 BO_3 and tetrahedral BO_4 units.⁷⁻¹¹

RESULTS AND DISCUSSION

Computational Methodology

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

Hexaborate

The $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$ anion consists of BO_3 triangles (Δ) & 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 $6:3\Delta + 3\text{T}$.⁷ 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 kJ mol^{-1} (Table 1), which is consistent with hydrogen bond energies.⁶ 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 ρ_{BCP} and -ve ∇^2 values (*ca.* 0.36 a.u. and -2.40 a.u. respectively). The closed-shell IHBs have much smaller ρ_{BCP} and ∇^2 values (*ca.* 0.02 a.u. and 0.05 a.u. respectively) reflecting their weaker nature. A 0.007 a.u. reduction in ρ_{BCP} , a $0.006 \text{ \AA}$ elongation in r_{OH} and a *ca.* 100 cm^{-1} red shift in ν_{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) $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$; (b) $[\text{B}_7\text{O}_9(\text{OH})_5]^{2-}$

Figure 2 QTAIM bond graph (AIM2000) and selected ρ_{BCP} values (a.u.): (a) $[\text{B}_6\text{O}_7(\text{OH})_6]^{2-}$; (b) $[\text{B}_7\text{O}_9(\text{OH})_5]^{2-}$.

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⁻¹) for the [B₆O₇(OH)₆]²⁻ hexaborate anion. Initial hydrogen atom orientations C = clockwise, A = anticlockwise and sites (a-f) relative to Figure 1a. Sixty four (2⁶) different combinations were generated giving rise to twelve unique enumerations.

Outer (Trigonal) OH groups			Inner (Tetrahedral) OH groups			ΔE (kJ mol ⁻¹)
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⁻¹) for the [B₇O₉(OH)₅]²⁻ heptaborate anion. Initial hydrogen atom orientations C = clockwise, A = anticlockwise and sites (a-e) relative to Figure 1b. Thirty two (2⁵) different combinations were generated giving rise to sixteen unique enumerations.

OH groups					ΔE (kJ mol ⁻¹)
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 $7:4\Delta + 3\text{T}$.⁷ 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 ($r_{\text{O-H}} = 0.962 \text{ \AA}$; $r_{\text{O...H}} = 2.59 \text{ \AA}$; $\angle_{\text{O-H...O}} = 128.3^\circ$; $r_{\text{O...O}} = 3.27 \text{ \AA}$) is highlighted in the low ($< 0.01 \text{ a.u.}$) ρ_{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 ρ_{BCP} , together with a *ca.* 20 cm^{-1} red shift in ν_{OH} and negligible ($< 0.001 \text{ \AA}$) elongation in r_{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.

REFERENCES

1. Mattesini, M.; Matar, S. F. *Comput. Mater. Sci.*, **2001**, 20, 107-119.
2. Mattesini, M.; Matar, S.F. *Int. J. Inorg. Mater.*, **2001**, 3, 943-957.
3. Fan, X. F.; Zhu, Z.; Shen, Z. X.; Kuo, J.-L. *J. Phys. Chem. C*, **2008**, 112, 15691–15696.
4. Tateyama, Y.; Ogitsu, T.; Kusakabe, K.; Tsuneyuki, S.; Itoh, S. *Phys. Rev. B*, **1997**, 55, 10161
5. Beckett, M. A.; Davies, R. A.; Thomas, C.D. *Comput. Theor. Chem.*, **2014**, 1044, 74-79.
6. Beckett, M. A.; Coles, S. J.; Davies, R. A.; Horton, P. N.; Jones, C.L. *Dalton Trans.*, **2015**, 44, 7032-7040.
7. Christ, C. L.; Clark, J. R. *Phys. Chem. Miner.*, **1977**, 2, 59-87.
8. Farmer, J. B. *Adv. Inorg. Chem. Radiochem.*, **1982**, 25, 187-237.
9. Heller, G., *Top. Curr. Chem.*, **1986**, 131, 39-98.
10. Schubert, D. M.; *Struct. Bond.*, **2003**, 105, 1-40.
11. Belokoneva, E. L.; *Crystallogr. Rev.*, 2005, 11, 151-198.
12. Gaussian 09, Revision **D.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.