Structural similarity between boron oxide $\text{B}_n\text{(BO)}_n^{2-}$ and boron hydride $\text{B}_n\text{H}_n^{2-}$ dianions ($n = 4–12$)

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The boron oxide dianions $\text{B}_n\text{(BO)}_n^{2-}$ ($n = 4–12$) are studied using DFT (B3LYP) method. Geometries of the global minima of $\text{B}_n\text{(BO)}_n^{2-}$ with $n = 4–12$ are found to be analogous to those of boron hydrides. All boron oxides considered exhibit large HOMO-LUMO gaps and high vertical detachment energies. Similar to $\text{B}_n\text{H}_n^{2-}$, the enhanced thermodynamic stabilities are established for $\text{B}_n\text{(BO)}_n^{2-}$ at $n = 6, 10$ and 12. Due to the strength of BO bonds, oxidation of boron clusters thus consistently leads to formation of exohedral boronyls that in turns behave as substituents replacing the hydrogen atoms. This structural similarity allows the shape of boron oxides to be predicted from boron hydrides. Nevertheless, the BO bonds are expected to be the preferred reaction sites of boron oxides.

Keywords: Theoretical chemistry, Boron oxides, Boron hydrides, Exohedral boronyls, Structural similarity

Although the boronyl (-BO) group is isoelectronic with the cyano (-CN) group, it is relatively less known and used as a substituent. While both substituents exert a strong electron-withdrawing effect,$^1$ their overall behaviour is much different from each other. A case in point concerns $\text{O(CN)}_2$ and $\text{O(BO)}_2$, that are both derived from water upon hydrogen substitution. While the dicyano species is rigidly bent, the diboronyl derivative turns out to be quasi-linear having a very small barrier to linearity.$^2$

More recently, the $\text{B}_n\text{O}_m$ compounds have attracted considerable interest, in part due to the fact that they are oxide derivatives of the boron clusters ($\text{B}_n$). The latter possess many interesting physical and chemical properties, and also potential applications.$^3,6$ Boron oxides have been studied both experimentally and theoretically in a number of previous studies.$^7–9$

Recently, we examined the electronic structure, chemical bonding nature and thermochemical parameters of a series of small boron oxides $\text{B}_n\text{O}_m$ ($n = 1–10$ and $m = 1–2$) in both neutral and anionic states using the G3B3 and also the high accuracy CCSD(T)/CBS methods.$^{10,11}$ Our findings pointed out that the growth mechanism of $\text{B}_n\text{O}_m$ is mainly governed by formation of new BO bonds, and planar boron cyclic $\text{B}_n$. A special feature is that a similarity between boron hydrides $\text{B}_n\text{H}_2$ and boron oxides $\text{B}_n\text{O}_2$ is established.

Substitution of hydrogen atoms in simple organic compounds by boronyl radicals has further been considered in recent studies. Li et al.$^{12}$ investigated the carbon boronyl compounds ($\text{CBO})_n (n = 3–7)$ derived from hydrocarbons by boronyl groups substitution. These carbon boronyls are found to be thermodynamically more stable than their boron carbonyl ($\text{BCO})_n$ isomers, and also exhibit a certain aromatic character. Considering the boron hydrides $\text{B}_n\text{H}_n^{2-}$, Cederbaum and co-workers$^{13,14}$ also reported that the structures $\text{B}_n\text{(BO)}_2^{2-}$ ($D_{2h}, A_1$)$^{13}$ and $\text{B}_n\text{(BO)}_6^{2-}$ ($\text{O}_h, T_{d}$)$^{14}$ that are analogous to the $\text{B}_n\text{H}_n^{2-}$ and $\text{B}_n\text{H}_6^{2-}$ dianions, respectively, are electronically stable systems. However, these authors did not search for the global minima of these systems. Wang and co-workers$^{15,16}$ investigated the small boron oxides $\text{B(BO)}_2^{2-}$, $\text{B(BO)}_3^{2-}$ and $\text{B}_2\text{(BO)}_2^{2-}$ using photoelectron spectroscopy and $ab$ initio calculations, and the calculated structures are consistent with spectroscopic data. Yao et al.$^{17}$ subsequently showed that the $\text{B}_3\text{O}_4$ anion in fact possesses a tetrahedral ($T_d$) shape $\text{B(BO)}_3^{2-}$, which is analogous to $\text{BH}_3^{2-}$ with four equivalent BO attached around the central B atom. In a recent report on the $\text{B}_3\text{(BO)}_3$ clusters,$^{18}$ we found that the global energy minimum of the $\text{B}_3\text{(BO)}_3^{2-}$ dianion has a triangular planar structure ($D_{3h}$), that is directly derived from the boron hydride $\text{BH}_3^{2-}$ by replacement of all H atoms by BO groups. Some other boron oxides were also recently studied.$^{19–21}$
In this context, a question arises as to whether such a substitution and analogy can generally be applied to boron hydrides in order to generate oxygen-rich boron oxides. Since \( B_4 H_4 \) are well-known compounds, a generalized similarity between boron oxides and boron hydrides could lead to important insights into the understanding of structural properties and chemical reactivity of boron oxides, and in the design of materials containing BO groups. Motivated by this consideration, we set out to perform a theoretical investigation of the electronic structure, thermodynamic stability and aromatic character of a series of clusters \( B_n(BO)_2^- (n = 4-12) \), that are formally derived from the boron hydrides \( B_n(H)_2^- \). Calculations on \( B_4 H_2^- \) were also carried out for a more detailed comparison with the corresponding \( B_4(BO)_2^- \). Thus, an analogous pattern between boronyl group in boron oxides and hydrogen atom in boron hydrides can be established.

**Computational Methods**

All electronic structure calculations were carried out by using the Gaussian 03 suite of programs. Geometry optimizations and calculations of harmonic vibrational frequencies of all possible isomers were fully performed using density functional theory with the hybrid B3LYP functional in conjunction with the 6-311+G(d) basis set. Structures having imaginary frequencies were re-investigated by geometry relaxation in order to obtain the local minima. In addition, the isomers for \( B_4 H_2^- \) were also constructed from the reported structures of \( B_n H_n \) at various charged states. In such a way, we were able to locate the global minima. Relative energies were obtained at the B3LYP/6-311+G(d) + ZPE level.

Analysis of the electronic structure was done using the electron localization function (ELF) supplemented by a determination of the ELF topological bifurcation. The ELF can be viewed as a local measure of the Pauli repulsion between electrons owing to the exclusion principle in a 3D space. This localization technique allows the total density to be partitioned into different local basins, which contain electrons and correspond to the classical concepts such as cores, lone pairs and bonds. While the total ELF was mapped out using the TOPMOD software, all ELF isosurfaces were plotted using the Gopenmol software.

**Results and Discussion**

**Optimized geometries and the Wade’s rule**

**\( B_4 H_2^- \) and \( B_4(BO)_2^- \)**

Let us mention again that all isomers are fully optimized and their harmonic vibrational frequencies calculated at the B3LYP/6-311+G(d) level of theory. By combining different approaches, we can locate the global minima. Let us first consider these simplest hydrides and oxides in some details. The boron hydride dianions \( B_n H_n^- (n = 5-12) \) have been extensively studied. The isomers of \( B_4(BO)_4^- \) are constructed in different ways including (i) binding four BO moieties to the lowest forms of \( B_4 \), (ii) connecting three BO radicals with the low-lying \( B_4O \) isomers and, (iii) binding two BO radicals to the low-lying \( B_9O_2 \) isomers. While the shape of the local minima without imaginary frequencies for both \( B_4 H_2^- \) and \( B_4(BO)_2^- \) are displayed in Fig. 1, the corresponding geometrical parameters, point groups, and vibrational frequencies of the lower-lying isomers are given in Table 1.

The dianion \( B_4 H_2^- \) presents an exception in the series of boron hydride dianions as it has never been experimentally observed. Dreuw et al. reported that the global minimum of dianion \( B_4 H_2^- \) is the \( D_{2d} \) structure \( H4.2 \) (Fig. 1) that is distorted from a higher symmetry \( H4.3 (T_d) \). Our findings do not concur with this result, but point towards a \( C_4 \) structure \( H4.1 \) as the most stable isomer that is 7.7 kcal/mol more stable than \( H4.2 \). The form \( H4.3 (T_d) \) turns out to be the local minimum with a relative energy of 36.9 kcal/mol with respect to \( H4.1 \).

Our calculations for \( B_4 O_2^- \) show that the \( C_4 \) structure in which BO groups substitute H atoms of the global minimum \( H4.1 \) is the most stable isomer. Both structures \( 4.2 (D_{2d}) \) and \( 4.3 (S_d) \) are degenerate with the same content in energy, and are 2.7 kcal/mol less stable than \( 4.1 \). The high-spin structure \( 4.4 (T_d) \) is the next isomer with a relative energy of 27.5 kcal/mol, while the remaining isomers are much less stable, being at least 40 kcal/mol above the global minimum.

**\( B_5(BO)_5^- \) and larger \( B_n(BO)_n^- \)**

Similarly, the lower-lying isomers of the larger systems \( B_n(BO)_n^- (n = 5-12) \) are constructed by substituting the H-atoms of the different \( B_n H_n^- \) isomeric forms by BO radicals. Our calculated results summarized in Fig. 1 show that the \( D_{2h} \) structure \( 5.1 \) is the global minimum for \( B_5(BO)_5^- \).
TAI et al.: STRUCTURAL SIMILARITY BETWEEN BORON OXIDE & BORON HYDRIDE DIANIONS

Fig 1—Shape of the optimized structures and relative energies (kcal/mol) obtained using B3LYP/6-311+G(d) + ZPE computations) of $\text{B}_4\text{H}_4^2\text{–}^4.1-4.3$, $\text{B}_8\text{O}_4^2\text{–}^4.1-4.9$ and $\text{B}_{10}\text{O}_5^2\text{–}^5.1-5.3$.

Table 1—Selected geometrical parameters ($r$), charges ($q$) and BO stretching frequencies of the lower-lying isomers (at B3LYP/6-31+G(d))

<table>
<thead>
<tr>
<th>Structure</th>
<th>State</th>
<th>$r_{\text{B–BO}}$ (Å)</th>
<th>$r_{\text{B–O}}$ (Å)</th>
<th>$q$(O) (electron)</th>
<th>$Q$(B(BO)) (electron)</th>
<th>BO frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO</td>
<td>$^3\Sigma^+$</td>
<td>1.203</td>
<td></td>
<td></td>
<td></td>
<td>1916</td>
</tr>
<tr>
<td>BO$^-$</td>
<td>$^1\Sigma^+$</td>
<td>1.235</td>
<td></td>
<td></td>
<td></td>
<td>1736</td>
</tr>
<tr>
<td>BBO</td>
<td>$^1\Sigma^+$</td>
<td>1.777</td>
<td>1.204</td>
<td></td>
<td></td>
<td>1986</td>
</tr>
<tr>
<td>BBO$^-$</td>
<td>$^2\Pi$</td>
<td>1.701</td>
<td>1.233</td>
<td></td>
<td></td>
<td>1795</td>
</tr>
<tr>
<td>$\text{B}_4(\text{BO})_4^2\text{–}^{-}$</td>
<td>$C_s$</td>
<td>~1.648</td>
<td>~1.228</td>
<td></td>
<td></td>
<td>1879</td>
</tr>
<tr>
<td>$\text{B}_5(\text{BO})_5^2\text{–}^{-}$</td>
<td>$D_{5h}$</td>
<td>1.616</td>
<td>1.224</td>
<td>-0.90</td>
<td>+0.96</td>
<td>1914</td>
</tr>
<tr>
<td>$\text{B}_6(\text{BO})_6^2\text{–}^{-}$</td>
<td>$O_h$</td>
<td>1.638</td>
<td>1.220</td>
<td>-0.88</td>
<td>+0.97</td>
<td>1935</td>
</tr>
<tr>
<td>$\text{B}_7(\text{BO})_7^2\text{–}^{-}$</td>
<td>$D_{5h}$</td>
<td>1.638</td>
<td>1.217</td>
<td>-0.87</td>
<td>+0.98</td>
<td>1949</td>
</tr>
<tr>
<td>$\text{B}_8(\text{BO})_8^2\text{–}^{-}$</td>
<td>$D_{4d}$</td>
<td>1.639</td>
<td>1.215</td>
<td>-0.85</td>
<td>+0.98</td>
<td>1961</td>
</tr>
<tr>
<td>$\text{B}_9(\text{BO})_9^2\text{–}^{-}$</td>
<td>$D_{5h}$</td>
<td>1.649</td>
<td>1.212</td>
<td>-0.83</td>
<td>+0.99</td>
<td>1976</td>
</tr>
<tr>
<td>$\text{B}<em>{10}(\text{BO})</em>{10}^2\text{–}^{-}$</td>
<td>$D_{4d}$</td>
<td>1.652</td>
<td>1.211</td>
<td>-0.82</td>
<td>+0.99</td>
<td>1986</td>
</tr>
<tr>
<td>$\text{B}<em>{11}(\text{BO})</em>{11}^2\text{–}^{-}$</td>
<td>$C_{1v}$</td>
<td>1.655</td>
<td>1.210</td>
<td>-0.81</td>
<td>+0.99</td>
<td>1991</td>
</tr>
<tr>
<td>$\text{B}<em>{12}(\text{BO})</em>{12}^2\text{–}^{-}$</td>
<td>$I_h$</td>
<td>1.660</td>
<td>1.207</td>
<td>-0.80</td>
<td>+0.99</td>
<td>2000</td>
</tr>
</tbody>
</table>
The next isomer is a non-symmetric structure 5.3 with a high energy of 42.7 kcal/mol, whereas the $D_{5h}$ structure 5.2 is a transition structure with one imaginary frequency.

Increase of the number of B-atoms gives similar results, in that the $O_h$ structure 6.1, which is analogous to the global minimum of $B_6H_{12}^2-$ ($O_h$), is the global minimum of $B_n(BO)_{n}^{2-}$ (Fig. 2). The next isomer is a $C_{2v}$ structure 6.2 with a relative energy of 59.5 kcal/mol, whereas the $C_1$ structure 6.3 is much less stable than 6.1 (being 88.4 kcal/mol higher in energy).

The shapes and point groups of the energy minima $B_n(BO)_{n}^{2-}$ ($n = 6–12$) are predicted in Fig. 2. While geometry optimization of various initial structures of $B_7(BO)_{7}^{2-}$, $B_{10}(BO)_{10}^{2-}$ and $B_{11}(BO)_{11}^{2-}$ obtained by replacing H-atoms of the corresponding $B_nH_{n}^{2-}$ by BO radicals, leads to only one low-lying isomer, two different isomers are found for other $B_n(BO)_{n}^{2-}$ ($n = 8$, 9 and 12) (Fig. 2). It is interesting that all global energy minima for these $B_n(BO)_{n}^{2-}$ species reveal an analogy with the $B_nH_{n}^{2-}$ global minima reported previously. This lends further support for the above prediction in the structural analogy between oxides and hydrides.

**Wade’s rule and growth mechanism**

The structure of boron hydrides is well characterized using the electron-counting scheme, known as Wade’s rules. Accordingly, the boron hydride dianions $B_nH_{n}^{2-}$ possessing $(n+1)$ electron pairs exhibit polyhedral structures with triangular faces. The charge populations obtained from NBO analysis (Table 1) show that the two extra electrons of the dianion $B_n(BO)_{n}^{2-}$ are mainly distributed in the cage boron atoms. This population is consistent with the assumption that each dianion cage contains $(n+1)$ electron pairs. In fact, if each BO radical gives one electron to the $B_n$ cage, the $B_n(BO)_{n}^{2-}$ system has $(n+1)$ electron pairs, and thus satisfies the Wade’s electron counting rule. In other words, the BO radical simply behaves as a substituent of the hydrogen.

![Figure 2](image-url)
Geometrical parameters and vibrational frequencies

A comparison of the geometrical parameters and vibrational frequencies of $B_n(BO)^{-2-}$ with smaller BO and BBO systems are tabulated in Table 1. It is interesting to note that the B-O distance of 1.23 Å of the diatomic anion BO$^-$ is slightly longer than those of the larger species $B_n(BO)^{-2-}$, and the BO stretching frequencies of 1736 cm$^{-1}$ is lower than those of the $B_n(BO)^{-2-}$. These frequencies tend to increase with the increasing size of the dianion.

Relative stabilities of clusters

To evaluate the stability of the dianions considered, the vertical detachment energies (VDEs), which is defined as a energy difference between the total energies of $B_n(BO)^{-2-}$ and $B_n(BO)^{-}$ at the dianion geometry, were examined. The calculated results given in Table 2 and the VDE plot displayed in Fig. 3 clearly show that all $B_n(BO)^{-2-}$-dianions are stable with respect to electron ejection.

The HOMO-LUMO gap of a molecular system is usually considered as a measure of its kinetic stability. A large gap indicates a stable system with respect to chemical interactions. The HOMO-LUMO gaps of the dianions are quite high, and get remarkably high peaks for $n = 6, 7, 10$ and 12.

Another indicator of cage stability is the second-order difference in total energy (disproportionation energy) $\Delta^2 E$, that is defined as the energy required for a cage to transform into the immediately larger and smaller cages. This indicator has proven to be effective for boron hydride cages, and is defined as given in Eq. (1).

$$\Delta^2 E = E(B_{n+1}(BO)_{n+1}^{-2-}) + E(B_{n-1}(BO)_{n-1}^{-2-}) - 2E(B_n(BO)_n^{-2-})$$

(1)

The plot of second order differences $\Delta^2 E$ given in Fig. 3 reveal the enhanced stability at the sizes of $n = 6, 10$ and 12, that are internally consistent with large frontier orbital gaps of these systems. This trend of stability is also similar to that of boron hydrides $B_nH_n^{-2-}$ reported in previous studies.$^{28,29}$

Chemical bonding and aromatic character

The dianions $B_n(BO)_n^{-2-}$ can simply be viewed as composed of a $B_n$ cage bound to $n$ BO groups. The MO picture of $B_6(BO)_6^{-2-}$ can thus be compared to that of the corresponding hydrides $B_nH_n^{-2-}$. Let us consider the smallest species with enhanced stability, namely $B_6(BO)_6^{-2-}$. While the full MO pictures of both $B_6(BO)_6^{-2-}$ and $B_6H_6^{-2-}$ are given as Supplementary Data (Fig. S1), their selected MOs are depicted in Fig. 4. Thirteen orbitals of $B_6(BO)_6^{-2-}$ including the HOMO(3), HOMO-1(3), HOMO-9(2), HOMO-10(1), HOMO-11(3) and HOMO-12(1) play the role of those of the $B_6H_6^{-2-}$-counterpart, and form bonds not only within the $B_6$ cage but also single bonds between the $B_6$ cage and BO groups. The remaining MOs are responsible for BO triple bonds. This result is consistent with the Wiberg bond orders shown in Table 3. The total bond indices of B-atoms of the $B_n$ cage vary in the range of 3.6-3.8 that is consistent with a Lewis electronic structure.
One of the important features of small boron clusters is their high aromatic character (see ref. 6). We have earlier shown that the planar structure $B_3(BO)_3^{2-}$ is highly aromatic. To probe the aromatic character of the $B_n(BO)_n^{2-}$ cages, we herein perform the nucleus-independent chemical shifts (NICS). The NICS values at central positions of the $B_n(BO)_n^{2-}$ cages shown in Table 2 suggest that they indeed have high aromatic character (with negative values).

Electron localization function (ELF)

A topological analysis of the electron localization function (ELF) for $B_4(BO)^{2-}$ ($n = 4–6$) has been carried out using B3LYP/6-311+G(d) densities and the obtained plots are given in Fig. 5. At first glance, a similar electron population at BBO moieties in all structures can be noted. While electrons are populated on disynaptic basins of $B_4(BO)_4^{2-}$ (both $C_1$ and $D_{2d}$ structures), there is presence of trisynaptic basins on $B_5(BO)_5^{2-}$ and $B_6(BO)_6^{2-}$ cages, that suggests the existence of multi-center bonds. Moreover, a good electron delocalization is also found in all structures considered. These multi-center bonds and electron delocalization lend a further support for the high stability of $B_n(BO)_n^{2-}$ dianions.

Concluding Remarks

In this work, we performed a theoretical study on a series of boron oxide dianions. The global minima of the small species $B_4(BO)_4^{2-}$ ($n = 4–6$) are found to be analogous to those of boron hydride dianions, $B_nH_n^{2-}$. 

<table>
<thead>
<tr>
<th>Structures</th>
<th>$WBI_{B-BO}$ (electron)</th>
<th>$WBI_{B(BO)}$ (electron)</th>
<th>$WBI_B$ (electron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_4(BO)_4^{2-}$</td>
<td>1.0</td>
<td>2.3</td>
<td>3.5–3.8</td>
</tr>
<tr>
<td>$B_4(BO)_5^{2-}$</td>
<td>1.0</td>
<td>2.9</td>
<td>3.8</td>
</tr>
<tr>
<td>$B_4(BO)_6^{2-}$</td>
<td>1.0</td>
<td>2.9</td>
<td>3.7–3.4</td>
</tr>
<tr>
<td>$B_4(BO)_7^{2-}$</td>
<td>0.9</td>
<td>2.9</td>
<td>3.7–3.7</td>
</tr>
<tr>
<td>$B_4(BO)_8^{2-}$</td>
<td>0.9</td>
<td>2.9</td>
<td>3.7–3.7</td>
</tr>
<tr>
<td>$B_{10}(BO)_{10}^{2-}$</td>
<td>0.9</td>
<td>2.9</td>
<td>3.7–3.7</td>
</tr>
<tr>
<td>$B_{11}(BO)_{11}^{2-}$</td>
<td>0.9</td>
<td>2.9</td>
<td>3.7–3.7</td>
</tr>
<tr>
<td>$B_{12}(BO)_{12}^{2-}$</td>
<td>0.9</td>
<td>2.9</td>
<td>3.7–3.7</td>
</tr>
</tbody>
</table>
Similar local minima of the larger species $B_n(BO)_n^{2-}$ ($n = 7$–$12$) are located and expected to be among the lowest-lying isomers. All systems considered are characterized by large HOMO-LUMO gaps and high vertical detachment energies (VDEs). The enhanced stabilities are also found for dianionic clusters, $B_n(BO)_n^{2-}$ at $n = 6$, 10 and 12, with trend similar to that of the boron hydride dianions, $B_nH_n^{2-}$. Oxidation of boron clusters thus consistently leads to formation of boronyl groups that behave predominantly as substituents replacing hydrogen atoms. These structures could be relevant in the investigation of bulk materials of boron oxides. Nevertheless, it can be expected that the chemical reactivities of both classes of boron compounds differ much from each other. Reactions of boron oxides are likely to occur at the B-O bond site due to its high polarity.

**Supplementary Data**

Supplementary data associated with this article, i.e., Fig S1 is available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_53A(8-9)978-984_SupplData.pdf.

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