Carbon Boronyls: Species with Higher Viable Possibility Than Boron Carbonyls at the Density Functional Theory

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Abstract: Density functional theory investigations indicate that carbon boronyls \((\text{CBO})_n\) \((n = 3–7)\) are considerably more stable in thermodynamics than their boron carbonyl isomers \((\text{BCO})_n\) and exhibit aromaticity throughout the whole series. The extra stabilities of \((\text{CBO})_n\) originate from their frontier \(\pi\) molecular orbitals delocalized over the \(D_{nh}\) \(C_n\) central rings which are absent in \((\text{BCO})_n\). It is expected that experimental characterization of these \((\text{CBO})_n\) species may open a new branch of chemistry on carbon boronyls.


Key words: boron carbonyls; carbon boronyls; structures; stability; density functional theory; aromaticity

Introduction

The recent proposal of monocyclic boron carbonyls \((\text{BCO})_n\) \((n = 3–7)\)\(^{1,2}\) at the density functional theory (DFT) level provides intriguing examples to derive new aromatic compounds from the prototypic benzene, and may open a branch of chemistry on boron carbonyls. In these monocyclic systems, the \(n\) B atoms in BCO groups form the structural core and the \(n\) carbonyl tails (\(-\text{CO}\)) are attached to the central \(B_n\) rings from outside. No direct \(C=C\) bonds exist in these planar structures. However, it is well known that C atoms strongly favor direct \(C=C\) interactions in chains, rings, or cages in organic compounds, fullerences, and mixed semiconductor clusters.\(^3,4\) The reason is obvious: \(C=C\), \(C=\equiv C\), and \(C=\equiv C\) bonds are among the strongest interactions in chemistry, and are well favored in energies in most compounds. As already noticed in ref.1, the \((\text{CBO})_n\) isomer is indeed 213.6 kcal/mol more stable than \((\text{BCO})_n\) at DFT. With such a huge energy difference between the two isomers in thermodynamics, \((\text{BCO})_n\) would be very difficult to be observed in experiments if there exist(s) no high enough energy barrier(s) on the reaction path to prevent the structural transition from \((\text{BCO})_n\) to \((\text{CBO})_n\). A detailed and reliable \textit{ab initio} study on the reaction dynamics of such big systems is beyond the reach of available computing resources.

At this stage, we think it is necessary and important to perform a comprehensive and comparable investigation on the geometrical and electronic properties of \((\text{CBO})_n\) systems \((n = 2–7)\) at the DFT level to further facilitate future characterization of these species. This is the goal designed to achieve in this report.

Computational Method

Structural optimizations and frequency analyses are performed at the DFT B3LYP/6-311+G** level\(^3\) on \((\text{BCO})_n\) \((n = 2–7)\) and the results obtained in the size range of \(n = 2–6\) further refined with the second-order Moller–Plesset perturbation procedure (MP2/6-311+G**).\(^5\) Starting from \((\text{BCO})_n\) initial structures with C and B exchanged in positions, the optimized results indicate that carbon boronyl series \((\text{CBO})_n\) \((n = 2–7)\) lie considerably lower in energies than their boron carbonyl isomers \((\text{BCO})_n\) and therefore have higher viable possibility to be observed in experiments. These carbon boronyls contain a monocyclic \(C_n\) ring at the center with \(n\) boronyl groups —\(BO\) attached to the structural cores from outside. The calculated negative nucleus independent chemical shifts (NICS)\(^1,2\) at the \(C_n\) ring centers indicate that \(D_{nh}\) \((\text{CBO})_n\) systems are aromatic in nature. Natural bond orbital (NBO) analyses were carried out to reveal the difference in bonding nature between boron carbonyls and the corresponding carbon boronyls. All the calculations in this work were performed using the Gaussian 03 program package.\(^7\)

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Results and Discussions

Figure 1 depicts the optimized structures of carbon boronyls (CBO)_n, in which the n carbon atoms form the planar regular polygons and n —BO groups are attached to the central rings through B atoms at the n apices. Similar to the situation in benzene, COCO interactions in these systems exhibit obvious double bond characteristics as shown in Figure 1, except D_{4h} (CBO)_2\^{2+}, in which the COC bond lengths are elongated due to the strong Coulomb repulsion existing in this dianion. As can be seen in Figure 1, MP2 method produces essentially the same structures as DFT with MP2 bond lengths slightly longer (within 0.02 Å). The traditional bonding requirements for all component atoms are fully satisfied in these structures, as demonstrated by the calculated total Wiberg bond indices\(^7\)^\(^8\) (WBIs) of WBIC\(_{\text {C}}\)\(^{2+}\)\(^{3.73}\)\(^{3.96}\), WBIB\(_{\text {C}}\)\(^{2.93}\)\(^{3.00}\), and WBIO\(_{\text {C}}\)\(^{1.77}\)\(^{2.20}\). More importantly, as shown in Table 1, carbon boronyls are all considerably more stable than the corresponding boron carbonyls. For instance, D_{5h} (CBO)_5\(^{2+}\) lies 10.36 eV (238.9 kcal/mol) lower in energy than D_{5h} (BCO)_5\(^{2+}\) at DFT (or 10.95 eV (252.5 kcal/mol) at MP2), implying that the reaction of D_{5h} (BCO)_5\(^{2+}\) → D_{5h} (CBO)_5\(^{2+}\) is strongly exothermic.

Obviously, the metastable (BCO)_n series are much less stable in thermodynamics when compared to their (CBO)_n boron carbonyl isomers. Whether they can survive the structural transitions of D_{nh}.

### Table 1

<table>
<thead>
<tr>
<th>(CBO)_n</th>
<th>N e</th>
<th>NICS(0)</th>
<th>NICS(1)</th>
<th>ΔE</th>
<th>(E_b)*</th>
<th>(v_{\text{min}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CBO)_2</td>
<td>2</td>
<td>-24.1</td>
<td>-15.4</td>
<td>-4.15</td>
<td>-10.52(2×1)</td>
<td>90</td>
</tr>
<tr>
<td>(CBO)^{2+}_3</td>
<td>6</td>
<td>-7.2</td>
<td>-4.3</td>
<td>-8.01</td>
<td>-0.43(2×2)</td>
<td>47</td>
</tr>
<tr>
<td>(CBO)^{2-}_3</td>
<td>6</td>
<td>-12.4</td>
<td>-11.3</td>
<td>-10.36</td>
<td>-11.75(2×2+1\textsuperscript{+})</td>
<td>56</td>
</tr>
<tr>
<td>(CBO)_5</td>
<td>6</td>
<td>-6.8</td>
<td>-4.1</td>
<td>-9.26</td>
<td>-3.68(3×2)</td>
<td>45</td>
</tr>
<tr>
<td>(CBO)_6</td>
<td>6</td>
<td>-3.5</td>
<td>-7.5</td>
<td>-5.97</td>
<td>-7.54(3×2+1\textsuperscript{+})</td>
<td>20</td>
</tr>
</tbody>
</table>

*The binding energies \(E_b\) (eV) relative to singlet (CBO)_2 and quadruplet BCO neutrals or their charged ions in different dissociation channels are also tabulated.
(BCO)$_n$ does depend on specific reaction dynamics, which require more powerful computing resources unavailable at current stage. The infrared resonance (IR) active vibrational frequencies of D$_{nh}$ (CBO)$_n$ are summarized in Table 2 to facilitate future spectroscopic characterization of these isomers. Concerning the stability of these high symmetry D$_{nh}$ structures, D$_{6h}$ (CBO)$_6$ has the binding energies of 3.68 eV (84.9 kcal/mol) with respect to the reaction of 3(CBO)$_2$ and D$_{5h}$ (CBO)$_5$ has a much higher binding energy of 11.75 eV (271.0 kcal/mol) with respect to the process of 2(CBO)$_2$ + CBO$^-$ = (CBO)$_5^-$. The binding energies of other (CBO)$_n$ species relative to different combinations of the quadruplet CBO (1) and singlet (CBO)$_2$ (2)$^9,10$ and their charged ions are tabulated in Table 1. It should also be mentioned that all carbon boronyls have higher lowest vibrational frequencies

![Figure 2](image-url). Delocalized $\pi$ valence orbitals of D$_{nh}$ (CBO)$_n$ neutrals and charged ions ($n = 2–7$) at DFT-B3LYP/6-311+G**.
than the corresponding boron carbynols.\textsuperscript{1} Obviously, there is an isological relationship\textsuperscript{1} between carbon boronyl (CBO)\textsubscript{n} series and the corresponding hydrocarbons (CH)\textsubscript{n} with a \(\text{−CBO}\) group equivalent to a \(\mathrm{−CH}\) fragment in valence electrons. Even in the case of one \(\text{−CH}\) substituted with a \(\text{−CBO}\) group in benzene, C\textsubscript{2v}, (CH)\textsubscript{2}BCO also turned out to be substantially more stable (2.23 eV) than its isomer C\textsubscript{2v}, (CH)\textsubscript{2}BCO.

NBO analyses indicate that carbon boronyls exhibit “sandwich” charge distributions with C atoms negatively charged on the central rings, O atoms carrying negative charges at the outmost ends of the tails, and B atoms with positive charges lying between. For example, in D\textsubscript{5h} \((\text{CBO})_5\) inner isolated relationship\textsuperscript{1} between carbon boronyl (CBO)\textsubscript{n} series and boron carbonyl series. Both MO pictures and coefficient analyses clearly implying that these systems are aromatic in nature (compare the corresponding data of NICS(0) = −8.0 and NICS(1) = −10.2 ppm obtained for benzene at the same theoretical level). The obvious irregularity at (CBO)\textsubscript{n} (which has the most negative NICS) is caused by the \(\sigma\) aromaticity of the extremely small C\textsubscript{3} ring in the cation.\textsuperscript{2}

In summary, (CBO)\textsubscript{n} carbon boronyls have higher viable possibility to be observed in experiments than their (BCO)\textsubscript{n} boron carbonyl isomers and exhibit aromaticity throughout the whole series \((n = 3–7)\). The \(\mathrm{C−B}\) exchanges (or \(\text{BCO} \rightleftharpoons \text{CBO}\) rearrangements) in (BCO)\textsubscript{n} form the D\textsubscript{nh} \(\text{C}_n\) rings covered by the delocalized frontier \(\pi\) MOs in (CBO)\textsubscript{n} and produce the extra stabilities in carbon boronyls over boron carbynols. Similar exchanges are expected to exist in two-dimensional multicyclic systems and three-dimensional cages with boron carbonyl groups. It is anticipated that experimental characterization of (CBO)\textsubscript{n} species may open a new branch of chemistry on carbon boronyls.

References