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

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Introduction

The recent proposal of monocyclic boron carbonyls $(BCO)_n$ ($n = 3–7$)[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 (—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, fullerenes, and mixed semiconductor clusters.[3,4] The reason is obvious: C—C, C=C, and C≡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 $(CBO)_6$ isomer is indeed 213.6 kcal/mol more stable than $(BCO)_6$ at DFT. With such a huge energy difference between the two isomers in thermodynamics, $(BCO)_6$ 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 $(BCO)_6$ to $(CBO)_6$. A detailed and reliable *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 $(CBO)_n$ 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[5] on D_{nh} $(CBO)_n$ ($n = 2–7$) 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**).[6] Starting from $(BCO)_n$ initial structures with C and B exchanged in positions, the optimized results indicate that carbon boronyl series $(CBO)_n$ ($n = 2–7$) lie considerably lower in energies than their boron carbonyl isomers $(BCO)_n$, 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} $(CBO)_n$ 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]
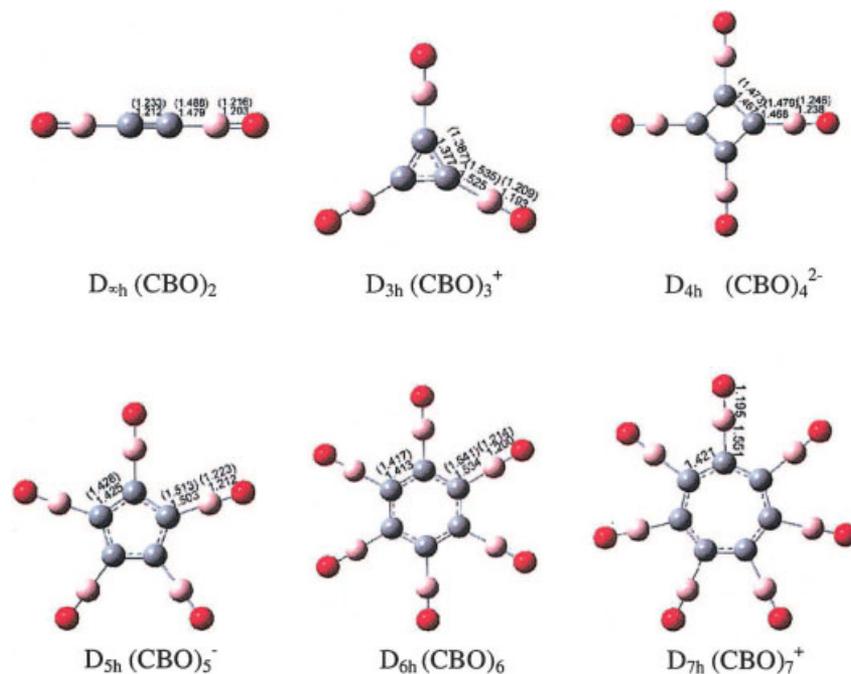
Figure 1. Optimized structures of $D_{\infty h}$ $(CBO)_2$, D_{3h} $(CBO)_3^+$, D_{4h} $(CBO)_4^{2-}$, D_{5h} $(CBO)_5^-$, D_{6h} $(CBO)_6$, and D_{7h} $(CBO)_7^+$ with necessary bond lengths indicated at DFT-B3LYP/6-311+G** level. MP2 bond lengths are also quoted in the size range of $n = 2-6$ in parentheses. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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, C—C interactions in these systems exhibit obvious double bond characteristics as shown in Figure1, except D_{4h} $(CBO)^{2-}$, in which the C—C 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 $WBI_C = 3.73\sim3.96$, $WBI_B = 2.93\sim3.00$, and $WBI_O = 1.77\sim2.20$. More importantly, as shown in Table 1, carbon boronyls are all considerably more stable than the corresponding boron carbonyls. For instance, D_{5h} $(CBO)_5^-$ lies 10.36 eV (238.9 kcal/mol) lower in energy than D_{5h} $(BCO)_5^-$ at DFT (or 10.95 eV (252.5 kcal/mol) at MP2), implying that the reaction of D_{5h} $(BCO)_5^- \rightarrow D_{5h}$ $(CBO)_5^-$ 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. Energy Differences ΔE (eV) between Carbon Boronyls and the Corresponding Boron Carbonyls, the Calculated NICS(0) and NICS(1) Values (ppm), and the Lowest Vibrational Frequencies ν_{min} (cm^{-1}) of $(CBO)_n$ ($n = 2-7$) Neutrals and Charged Ions at the DFT-B3LYP Level.

$(CBO)_n$	N_π	NICS(0)	NICS(1)	ΔE	E_b*	ν_{min}
$(CBO)_2$				−4.15	−10.52(2*1)	90
$(CBO)_3^+$	2	−24.1	−15.4	−1.61	−5.00(2+1$^+$)	71
$(CBO)_4^{2-}$	6	−7.2	−4.3	−8.01	−0.43(2*2$^-$)	47
$(CBO)_5^-$	6	−12.4	−11.3	−10.36	−11.75(2*2+1$^-$)	56
$(CBO)_6$	6	−6.8	−4.1	−9.26	−3.68(3*2)	45
$(CBO)_7^+$	6	−3.5	−7.5	−5.97	−7.54(3*2+1$^+$)	20

*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.

Table 2. IR Active Vibrational Frequencies ν (cm^{-1}) of (CBO)$_n$ Carbon Boronyls Obtained at the DFT-B3LYP Level with the Corresponding Vibrational Intensities (km · mol^{-1}) Quoted in Parentheses.

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
$C_{n\nu}$ BCO	483(0.5)	1131(14)	2048(403)				
D_{nh} (CBO)$_2$	90(14)	494(83)	980(15)	2055(755)			
D_{3h} (CBO)$_3^+$	71(13)	84(46)	416(33)	425(72)	700(4)	1331(77)	2090(46)
D_{4h} (CBO)$_4^{2-}$	76(3)	88(2)	497(101)	517(82)	766(2)	1244(345)	1836(2914)
D_{5h} (CBO)$_5^-$	94(9)	95(20)	486(47)	530(155)	758(21)	1391(48)	1985(1528)
D_{6h} (CBO)$_6$	89(17)	94(41)	455(46)	484(148)	734(25)	1353(5)	2053(718)
D_{7h} (CBO)$_7^+$	79(25)	88(58)	420(37)	439(137)	713(13)	1242(99)	2067(151)

(BCO)$_n$ → D_{nh} (CBO)$_n$ depends 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)$_2$ = (CBO)$_6$ 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
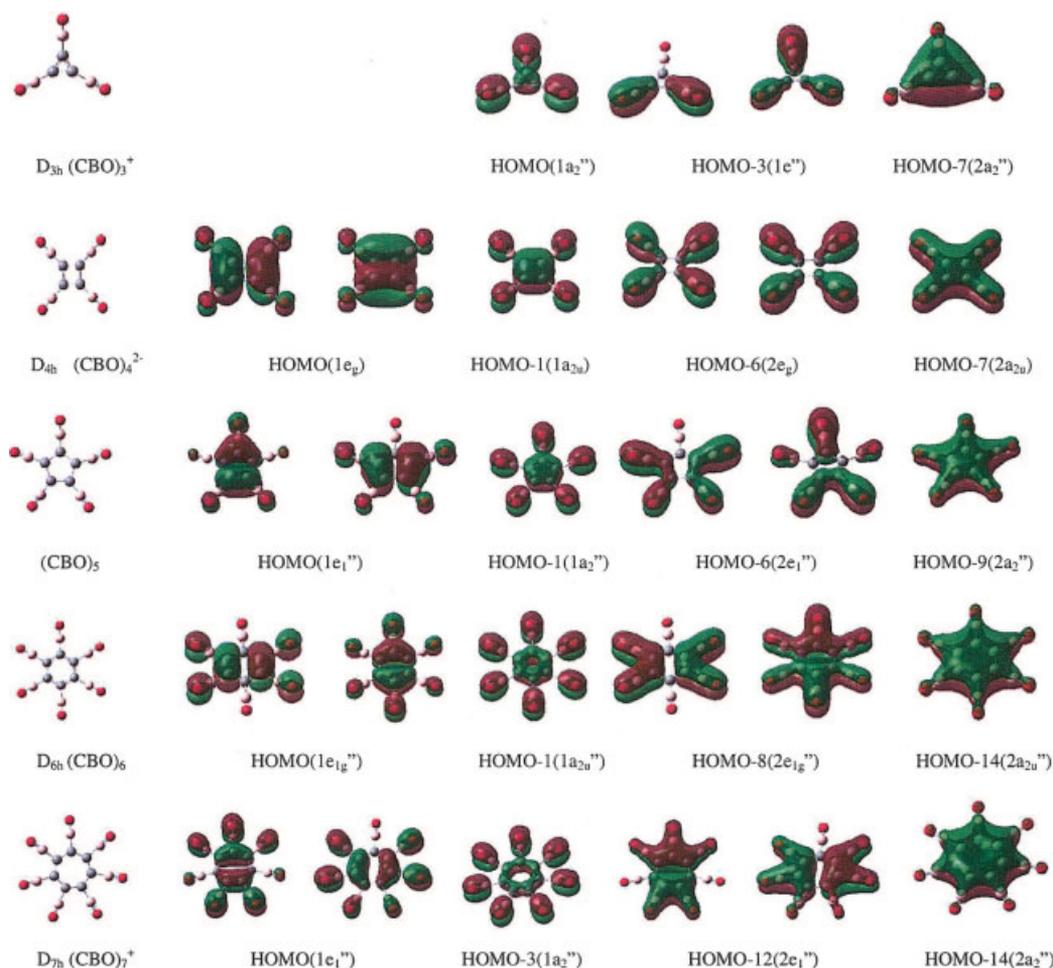
Figure 2. Delocalized π valence orbitals of D_{nh} (CBO)$_n$ neutrals and charged ions (n = 2–7) at DFT-B3LYP/6-311+G**.

than the corresponding boron carbonyls.[1] Obviously, there is an isolobal relationship[1] between carbon boronyl $(CBO)_n$ series and the corresponding hydrocarbons $(CH)_n$ with a —CBO group equivalent to a —CH fragment in valence electrons. Even in the case of one —CH substituted with a —CBO group in benzene, C_{2v} $(CH)_5CBO$ also turned out to be substantially more stable (2.23 eV) than its isomer C_{2v} $(CH)_5BCO$.

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_{5h} $(CBO)_5^-$, C, B, and O atoms carry the natural charges of -0.45, $+1.06$, and $-0.80|e|$, respectively, corresponding to the electron configurations of C $[He]2s^{0.97}2p_x^{1.09}$ $2p_y^{1.26}2p_z^{1.12}$, B $[He]$ $2s^{0.52}2p_x^{0.40}2p_y^{0.56}2p_z^{0.43}$, and O $[He]$ $2s^{1.75}$ $2p_x^{1.63}2p_y^{1.77}2p_z^{1.65}$. Here, each C atom hybridizes in sp^2 to form the three in-plane bonds and contributes one unpaired electron in p_z orbital to form the delocalized π molecular orbitals (MOs). Figure 2 shows the pictures of the delocalized π MOs of the carbon boronyl series. Both MO pictures and coefficient analyses clearly indicate that there exist two sets of delocalized π MOs in these molecules. For instance, in the much concerned D_{5h} $(CBO)_5^-$ and D_{6h} $(CBO)_6$, the six electrons occupying the top three delocalized π MOs [the first set of π MOs: the degenerate $1e_1''$ and $1a_2''$ of $(CBO)_5^-$ and degenerate $1e_{1g}''$ and $1a_{2u}''$ of $(CBO)_6$ mainly come from the p_z orbitals of the C atoms on the central rings. These three π MOs are similar in electron density distribution to the three delocalized π MOs of benzene. Similar situations exist in $(CBO)_4^{2-}$ and $(CBO)_7^+$ which also have 6 π electrons (but $(CBO)_3^-$ has only two π electrons to occupy its $HOMO(1a_2'')$]. Interestingly, as demonstrated in Figure 2, carbon boronyls have three additional delocalized π MOs lying much lower in energies than the first set of π MOs. In the cases of $(CBO)_5^-$ and $(CBO)_6$, these inner πMOs are the degenerate $HOMO-6(2e_1'')$ and $HOMO-9(2a_2'')$ and degenerate $HOMO-8(2e_{1g}'')$ and $HOM-14(2a_{2u}'')$, respectively. MO analyses show that these inner shell π orbitals are occupied by electrons mainly coming from the $2p_z$ orbitals of the —BO groups. They help to maintain the planarity of the systems, but contribute little to the aromaticity of the systems. It is interesting and important to notice that the second set of πMOs of D_{6h} $(CBO)_6$ are very similar to the degenerate π HOMO and HOM-1 of D_{6h} $(BCO)_6$ shown as Scheme 1 in ref. 1. In both cases, the six electrons occupying the second set of π MOs of $(CBO)_n$ and the HOMO and HOM-1 of $(BCO)_6$ mainly originate from the structural tails (—BO or —CO) attached to the central rings. We conclude that the extra stability of carbon boronyls $(CBO)_n$ over boron carbonyls $(BCO)_n$ mainly comes from their delocalized frontier π MOs composed of the contribution from C atoms on the C_n rings which do not exist in $(BCO)_n$.

As indicated in Table 1, the whole $(CBO)_n$ series with $(4n + 2)$ π electrons have both negative NICS(0) and NICS(1) values, 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 $(CBO)_3^+$ (which has the most negative NICS) is caused by the σ aromaticity of the extremely small C_3 ring in the cation.[2]

In summary, $(CBO)_n$ carbon boronyls have higher viable possibility to be observed in experiments than their $(BCO)_n$ boron carbonyl isomers and exhibit aromaticity throughout the whole series ($n = 3–7$). The C–B exchanges (or BCO → CBO rearrangements) in $(BCO)_n$ form the D_{nh} C_n rings covered by the delocalized frontier π MOs in $(CBO)_n$ and produce the extra stabilities in carbon boronyls over boron carbonyls. 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 $(CBO)_n$ species may open a new branch of chemistry on carbon boronyls.

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