Density functional theory investigations on boronyl-substituted ethylenes $C_2H_{4-m}(BO)_m$ ($m = 1$–4) and acetylenes $C_2H_{2-m}(BO)_m$ ($m = 1, 2$)

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Abstract

The geometrical and electronic structures and electron detachment energies of boronyl-substituted ethylenes $C_2H_{4-m}(BO)_m$ ($m = 1$–4) and acetylenes $C_2H_{2-m}(BO)_m$ ($m = 1, 2$) have been comparatively studied with the corresponding cyano substitutes at density functional theory level. ─B═O boronyl groups are found to serve basically as σ-radicals in these covalent systems, similar to ─H in hydrocarbons and ─C≡N in cyanocarbons. The electron affinities of boronyl dimer $(BO)_2$ and boronyl-substituted ethylenes and acetylenes and the first and second vertical detachment energies of their anions have been predicted for the first time. The thermodynamic quantity changes of carbon boronyls turned out to be parallel with the corresponding values of cyanocarbons. The typical symmetrical stretching frequencies of ─B═O functional groups at about 2000 cm^{-1} feature the vibrational properties of boronyl compounds. The results obtained in this paper and our previous work [S.-D. Li, C.-Q. Miao, J.-C. Guo, G.-M. Ren, J. Comp. Chem. 26 (2005) 799] complete the $C_n(BO)_n$ carbon boronyl series with $n = 2$–7 and provide more partially BO-substituted ethylene and acetylene species possible to be synthesized in future experiments.
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1. Introduction

In a recent work [1], our group presented a density functional theory (DFT) investigation on cyclic carbon boronyls D$_{nh}$ (CBO)$_n$ which are found to be considerably more stable than their boron carbonyl isomers (BCO)$_n$ [2,3] and exhibit π aromaticity throughout the whole series ($n = 3$–7). These novel clusters possess two sets of delocalized π molecular orbitals (MOs) to stabilize the systems, with the first set mainly originating from the C $2p_z$ orbitals cycling the C$_n$ perimeters and the second from the $2p_z$ orbitals of the surrounding ─BO boronyl groups [1]. Based upon the observation that ─BO groups in (CBO)$_n$ ape

─H atoms in C$_n$H$_n$ hydrocarbons, these carbon boronyls should be more accurately formulated as C$_n$(BO)$_n$. In another recent work [4], we employed the 6π-electron aromatic D$_{4h}$ C$_4$(BO)$_4^{2-}$, D$_{5h}$ C$_5$(BO)$_5^-$, and D$_{6h}$ C$_6$(BO)$_6$ ligands to coordinate transition metal centers (M) to form D$_{nd}$ M[C$_n$(BO)$_n$]$_2$ sandwich-type complexes. Very recently, based upon a combined photoelectron spectroscopy (PES) and DFT investigation on gas-phase BO$^-$ and BO$_2^-$ [5], Zhai and coworkers conceived the possibility that ─BO groups possess similar chemistry with ─CN. In this work, we expand the investigation to boronyl-substituted ethylenes $C_2H_{4-m}(BO)_m$ ($m = 1$–4) and acetylenes $C_2H_{2-m}(BO)_m$ ($m = 1, 2$) and compare them with the corresponding iso-electronic cyano substitutes. These boronyl substitutes turn out to possess linear or planar ground-state structures, similar to the corresponding cyano compounds in both geometrical and electronic structures. ─BO groups

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are found to serve basically as σ-radicals directly coordinating C atoms at the molecular centers. The electron affinities (EAs) of the neutrals and the first and second vertical detachment energies (VDEs) of their anions have also been predicted at DFT level to facilitate future experiments. Given the iso-electronic relationship and close similarities between —BO and —CN, —BO groups are expected to coordinate a wide range of metal and nonmetal atoms to form a new class of boronyl compounds.

2. Computational procedure

Structural optimization, frequency analyses, and time-dependent DFT (TD-DFT) [6] calculations were performed using the hybrid DFT-B3LYP procedure [7] with Dunning's all-electron basis (aug-cc-pVTZ) implemented in Gaussian 03 [8]. Extensive searches produced no structures with lower energies than the lowest-lying structures presented in this work. As closed-shell systems, all the ground-states of boronyl-substituted ethylenes and acetylenes are singlet and possess the same symmetries as the corresponding cyano substitutes. In most cases, their anions prove to share the same symmetries as the neutrals with only slight structural relaxations. EAs of the neutrals were calculated as the energy differences between the neutrals and the anions at their ground states and the VDEs of the anions approximated with the TD-DFT procedure. The TD-DFT procedure has proven to be a reliable method in predicting the electron detachment energies of boron compounds in reproducing the PES spectra of BO^- and BO_2^- [5]. Fig. 1 compares BO, CN, $(BO)_2$, and $(CN)_2$ neutrals and their anions. Fig. 2 shows the optimized structures of $C_2H_{4-m}(BO)_m$ ($m = 1$–4) and $C_2H_{2-m}(BO)_m$ ($m = 1,\ 2$) and their anions. Fig. 3 depicts the pictures of the highest occupied MOs (HOMOs) and π-typed valence MOs of typical boronyl compound anions, including BO^-, $(BO)_2^-$, cis-C_2H_2 $(BO)_2^-$, $C_2(BO)_4^-$, and $C_2(BO)_2^-$. The corresponding cyano compound anions CN^-, $(CN)_2^-$, cis-$C_2H_2(CN)_2^-$, $C_2(BO)_4^-$, and $C_2(CN)_2^-$ prove to possess similar MOs with different energy orders. Table 1 tabulates the calculated adiabatic detachment energies (ADEs) and the first and the second VDEs (corresponding to X- and A-bands in PES spectra [5]) of the boronyl compound anions. The ADEs of the anions are equivalent to the EA

values of the corresponding neutrals in definitions. The symmetrical vibrational frequencies of the corresponding neutrals which may be vibrationally resolved in future PES spectra are also listed in Table 1. Table 2 tabulates the calculated thermodynamic quantity changes of $C_n(BO)_m$ neutrals ($n = 0, 2; m = 2, 4$) compared with that of the corresponding cyanocarbons $C_n(CN)_m$.

3. Results and discussion

As shown in Fig. 2, the optimized boronyl-substituted ethylenes $C_2H_{4-m}(BO)_m$ ($m = 1$–4) and acetylenes $C_2H_{2-m}(BO)_m$ ($m = 1, 2$) follow the structural patterns of their parent hydrocarbons C_2H_4 and C_2H_2, respectively. Most of their anions share the same symmetries as the neutrals at DFT, except the slightly distorted C_s $C_2H(BO)^-$ (22). The slight structural relaxations from the anions to their neutrals in Fig. 2 suggest that the first ADE and VDE of the anions be close in energies to form sharp X-bands in PES spectra. This is supported by the calculated ADE and VDE values in Table 1.

3.1. $(BO)_2$ and $(BO)_2^-$

Both BO (1) and CN (5) groups have doublet ground states and their dimers $(BO)_2$ (2) and $(CN)_2$ (6) possess linear singlet ground-states [5,9,10]. Our DFT bond lengths of $r_{BO} = 1.203$ Å, $r_{BO^-} = 1.235$ Å, $r_{CN} = 1.162$ Å, and $r_{CN^-} = 1.171$ Å agree well with the corresponding measured values of $r_{BO} = 1.2049$ Å [10], $r_{BO^-} = 1.236$ Å [11], $r_{CN} = 1.171$ Å, and $r_{CN^-} = 1.177$ Å [9], respectively. The DFT structures of $(BO)_2$ (2) and $(CN)_2$ (6) and their valence MO orderings of $(BO)_2$ $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4$ and $(CN)_2$ $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^2 3\sigma_g^2 1\pi_g^4$ agree nicely with experiments [12,13] and theory [14,15]. The calculated bond lengths of $r_{B\text{-}B} = 1.636$ Å in $D_{\infty h}$ $(BO)_2$ and $r_{C\text{-}C} = 1.375$ Å in $D_{\infty h}$ $(CN)_2$ exhibit certain double bond characteristics originated from the effective π delocalization effects in these systems, well in line with the calculated Wiberg bond indexes (WBI) of $WBI_{B\text{-}B} = 1.20$ and $WBI_{C\text{-}C} = 1.29$.

As shown in Fig. 1, adding one extra electron to BO or CN slightly elongates the bond lengths of BO^- and CN^-, but the added electron causes symmetry changes to the
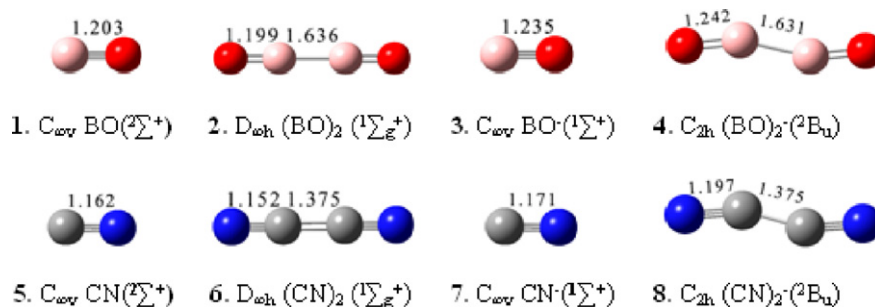

Fig. 1. Comparison between the ground-state structures of BO, CN, $(BO)_2$, and $(CN)_2$ and their anions.
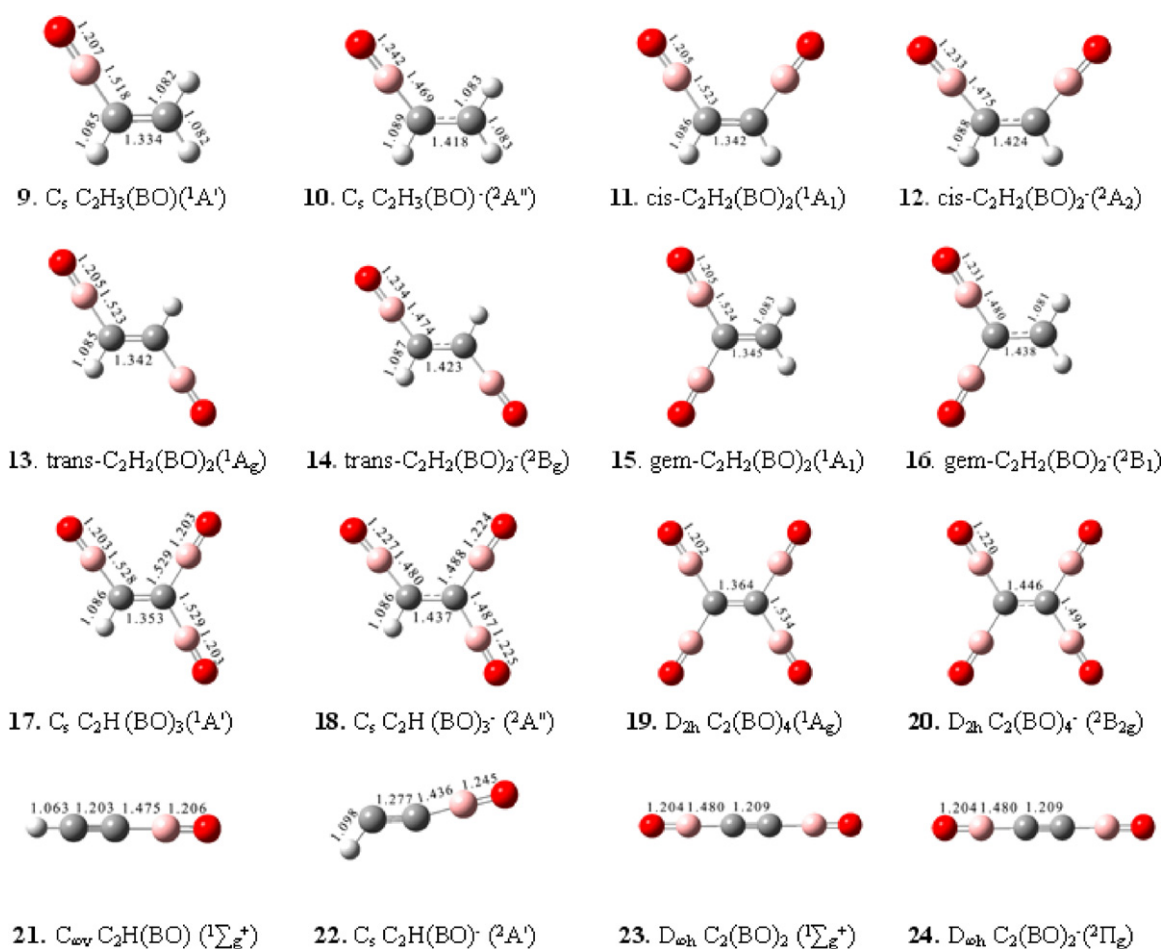
Fig. 2. DFT structures of $C_2H_{4-m}(BO)_m$ ($m = 1$–4) and $C_2H_{2-m}(BO)_m$ ($m = 1, 2$) and their anions.

anions of their dimers. Both $(BO)_2^-$ (**4**) and $(CN)_2^-$ (**8**) anions have been slightly distorted from the perfectly linear neutrals to the tetra-atomic C_{2h} chains due to the existence of the unpaired electrons in their singly occupied HOMOs (SOMOs, see Fig. 3(b)). These distorted SOMOs (b_u) are mainly π interactions localized on the B—B or C—C bonds at the molecular centers. The nearly degenerate HOMO-1(b_g) and HOMO-2(a_u) of $(BO)_2^-$ represent the two B≡O π bonds localized on the BO terminals (compare with the HOMO-1(π) of BO^- in Fig. 3(a)), while HOMO-3(a_u) and HOMO-4(b_u) are two π-typed strong bonding MOs totally delocalized over the penta-atomic chain. It is these totally delocalized π MOs that provide extra stabilities to linear $D_{\infty h}$ $(BO)_2$ and $(CN)_2$ and their slightly distorted C_{2h} anions. The second set π MOs of the cyclic $C_n(BO)_n$ clusters ($n = 4$–7) provide typical such delocalized π interactions [1,4] and $C_2(BO)_4$ (**19**) and $C_2(BO)_2$ (**23**) discussed in the following part possess similar delocalized π MOs. No such delocalized π bonding exists in H_2 molecule.

3.2. $C_2H_{4-m}(BO)_m$ and $C_2H_{4-m}(BO)_m^-$ ($m = 1$–4)

All boronyl-substituted ethylenes $C_2H_{4-m}(BO)_m$ and their anions $C_2H_{4-m}(BO)_m^-$ (**9–20**) possess planar struc-

tures inherited from the parent ethylene C_2H_4, similar to the corresponding cyano substitutes of $C_2H_{4-m}(CN)_m$ [16–20]. These structures agree well with chemical intuition that introduction of —BO or —CN groups to C_2H_4 results in σ-substitutions of —H atoms while the C=C frame keeps unchanged. It should be pointed out that, although cis-$C_2H_2(BO)_2$ (**11**) possesses the lowest energy in the three isomers of the diboronylethylenes, $trans$-$C_2H_2(BO)_2$ (**13**) and gem-$C_2H_2(BO)_2$ (**15**) lie very close to cis-$C_2H_2(BO)_2$ (**11**) (within 0.05 eV). They are practically iso-energetic isomers expected to co-exist in experiments, analogous to the situation in dicyanoethylenes [18,20].

To simplify the situation, the highly symmetrical carbon boronyls $C_n(BO)_m$ will be the main focus of our discussions in the following parts. Planar D_{2h} $C_2(BO)_4$ (**19**) and $C_2(BO)_4^-$ (**20**) possess exactly the same symmetries as ethylene C_2H_4 with a C=C double bond at the center. $C_2(CN)_4$ [16,19,20] and $C_2(CN)_4^-$ share the same symmetry of D_{2h}. Among the π-typed MOs of D_{2h} $C_2(BO)_4^-$ (Fig. 3(d)), the HOMO(b_{2g}) mainly involves C–B interactions, HOMO-1(b_{3u}) is a typical localized C=C π bond (similar to the C=C interaction in C_2H_4), HOMO-6(a_u) and HOMO-7(b_{1g}) belong to localized B≡O π interactions (compare with the HOMO-1(π) of BO^- in Fig. 3(a)), while
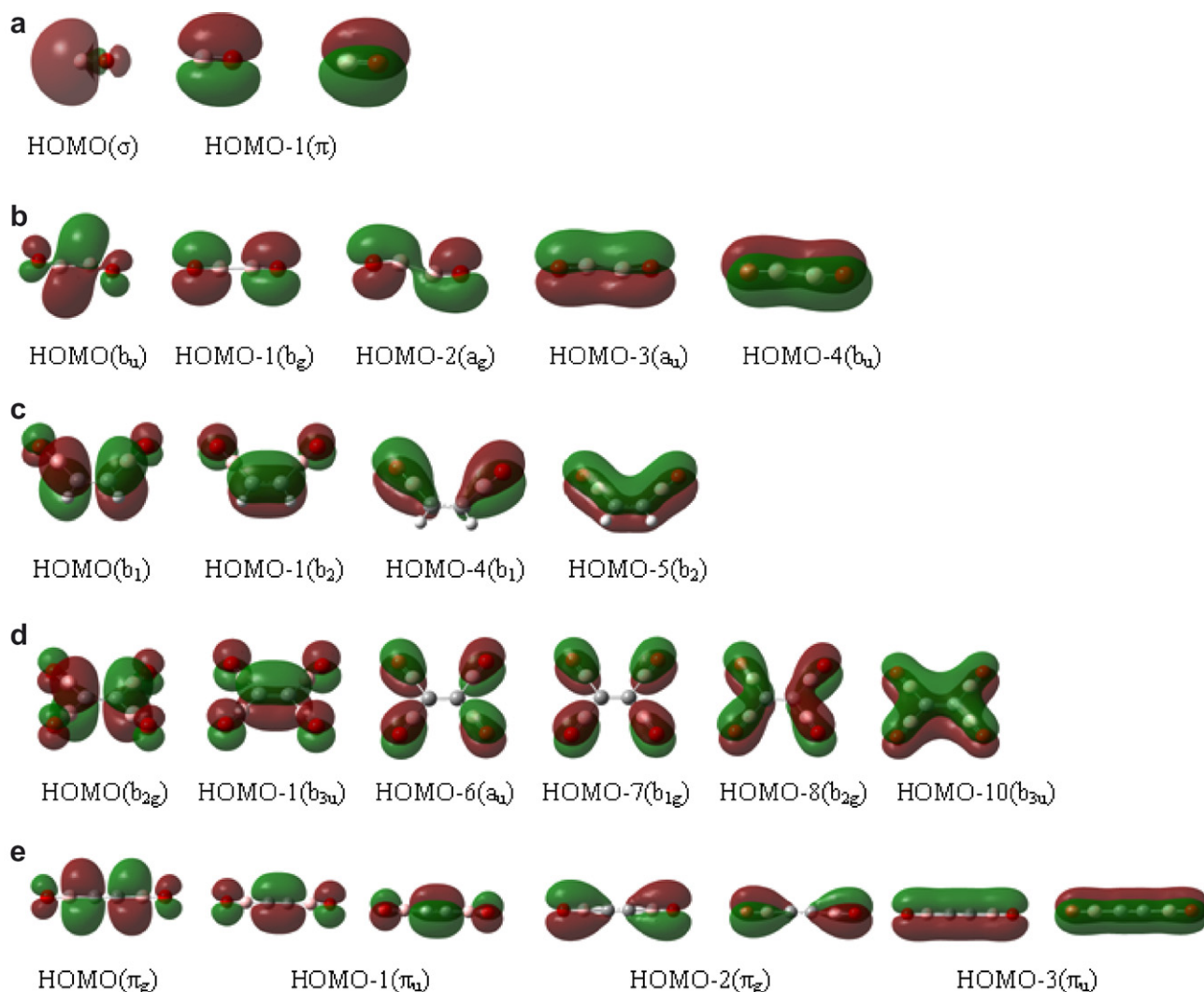
Fig. 3. Pictures of the singly occupied HOMOs and doubly occupied π-typed valence MOs of $C_{\infty v}$ BO^- (a), C_{2h} $(BO)_2^-$ (b), C_{2v} *cis*-$C_2H_2(BO)_2^-$ (c), D_{2h} $C_2(BO)_4^-$ (d), and $D_{\infty h}$ $C_2(BO)_2^-$ (e).

HOMO-8(b_{2g}) and HOMO-10(b_{3u}) are totally delocalized π interactions covering the whole molecular plane. It is these delocalized π MOs that feature the bonding pattern of carbon boronyls.

A browse of the MOs of $C_2H_3(BO)$ (**9**), *cis*-$C_2H_2(BO)_2$ (**11**), *trans*-$C_2H_2(BO)_2$ (**13**), *gem*-$C_2H_2(BO)_2$ (**15**), and $C_2H(BO)_3$ (**17**) indicates that —H groups are not involved in the delocalized π MOs of these partially substituted ethylenes. Typical situation is demonstrated in HOMO-5(b_2) of *cis*-$C_2H_2(BO)_2$ (**11**) in Fig. 3(c). Obviously, —BO and —CN radicals are σ similar to but π different with —H groups. In addition to σ bonding, —BO and —CN radicals also form delocalized π interactions with the C=C or C≡C main frames to further stabilize the systems. Such delocalized MOs stop at —H terminals.

3.3. $C_2H_{2-m}(BO)_m$ and $C_2H_{2-m}(BO)_m^-$ (m = 1, 2)

BO-substituted acetylenes $C_{\infty v}$ $C_2H(BO)$ (**21**) and $D_{\infty h}$ $C_2(BO)_2$ (**23**) and their anions C_s $C_2H(BO)^-$

(**22**) and $D_{\infty h}$ C_2 $(BO)_2^-$ (**24**) all contain a C≡C triple bond at the center inherited from the parent acetylene C_2H_2. The penta-atomic chain $C_sC_2H(BO)^-$ (**22**) is the only case in these BO-substituted anions whose structure has been distorted from its neutral at DFT. However, the formation of strong C≡C bonds is fully guaranteed in these substituted acetylenes, as clearly demonstrated in the case of diboronylacetylene O=B—C≡C—B=O (**23**) which lies much lower in energy (4.15 eV) than its boron carbonyl isomer of O≡C—B=B—C≡O [1].

For linear $D_{\infty h}$ C_2 $(BO)_2^-$ (**24**), the singly occupied HOMO(π_g) (Fig. 3(e)) mainly involves B–C interactions between the —BO groups and C=C frame, the nearly degenerate HOMO-1(π_u) represent typical C≡C π interactions, HOMO-2(π_g) belong to two localized B=O π bonds, while HOMO-3(π_u) prove to be totally delocalized π MOs distributed over the whole hexa-atomic chain. There is no such totally delocalized π bonding in the partially substituted $C_sC_2H(BO)^-$.

Table 1
Calculated ADEs and the first and second VDEs of BO^-, $(BO)_2{}^-$, $C_2H_{4-m}(BO)_m{}^-$ ($m = 1$–4), and $C_2H_{2-m}(BO)_m{}^-$ ($m = 1, 2$) anions at B3LYP/aug-cc-pvtz level

	Feature	Final state	ADE (eV)	VDE (eV)	Frequency (cm^{-1})
$C_{\infty v}$ BO^-	X	$^2\Sigma^+$	2.588 $(2.510 \pm 0.015)^5$	2.627 $(2.510 \pm 0.015)^5$	$1913(\sigma)$ $(1940 \pm 30)^5$ (B=O)
	A	$^2\Pi$		5.900 $(5.63 \pm 0.02)^5$	
C_{2h} $(BO)_2{}^-$	X	$^1\Sigma_g^+$	0.58	0.952	$611(\sigma_g)$, $2119(\sigma_g)$ $(585)^{12}$, $(2060)^{12}$
	A	$^3\Pi_u$		5.410	(B—B) (B=O)
C_s $C_2H_3(BO)^-$	X	$^1A'$	0.005	0.256	$557(a')$, $799(a_1)$, $1661(a')$, $2017(a')$
	A	$^3A'$		3.096	(C—B) (C=C) (B=O)
cis-$C_2H_2(BO)_2{}^-$	X	$^1A_1$	1.396	1.699	$485(a_1)$, $768(a_1)$, $1627(a_1)$, $2036(a_1)$
	A	$^3B_2$		4.159	(C—B) (C=C) (B=O)
$trans$-$C_2H_2(BO)_2{}^-$	X	^1A_g	1.436	1.732	$497(a_g)$, $891(a_g)$, $1635(a_g)$, $2032(a_g)$
	A	^3B_u		4.210	(C—B) (C=C) (B=O)
gem-$C_2H_2(BO)_2{}^-$	X	$^1A_1$	1.275	1.591	$544(a_1)$, $670(a_1)$, $1631(a_1)$, $2027(a_1)$
	A	$^3A_1$		4.129	(B—C) (C=C) (B=O)
$C_2H(BO)_3{}^-$	X	$^1A'$	2.538	2.839	$483(a')$, $552(a')$, $1593(a')$, $2040(a')$
	A	$^3A'$		5.044	(B—C) (C=C) (B=O)
D_{2h} $C_2(BO)_4{}^-$	X	^1A_g	3.523	3.803	$476(a_g)$, $575(a_g)$, $1550(a_g)$, $2041(a_g)$
	A	$^3B_{1u}$		5.750	(B—C) (C=C) (B=O)
C_s $C_2H(BO)^-$	X	$^1A'$	2.538	2.839	$766(\sigma)$, $1989(\sigma)$, $2231(\sigma)$
	A	$^3A'$		5.044	(B—C) (B=O) (C≡C)
$D_{\infty h}$ $C_2(BO)_2{}^-$	X	$^1\Sigma_g^+$	1.403	1.660	$515(\sigma_g)$, $1990(\sigma_g)$, $2327(\sigma_g)$
	A	$^3\Pi_u$		4.760	(B—C) (B=O) (C≡C)

The calculated symmetrical vibrational frequencies of the corresponding neutrals are also listed.

Table 2
Calculated DFT energy changes ΔE^0, enthalpy changes ΔH^0, and Gibbs free energy changes ΔG^0 of $C_n(BO)_m$ ($n = 0,2$; $m = 2, 4$) with respect to the processes of $C_n + mBO = C_n(BO)_m$

	ΔE (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
$D_{\infty h}$ $(BO)_2$	−474	−478	−431
$D_{\infty h}$ $(CN)_2$	−588	−593	−544
$D_{2h}C_2$ $(BO)_4$	−1703	−1718	−1536
$D_{2h}C_2$ $(CN)_4$	−1900	−1917	−1730
$D_{\infty h}C_2$ $(BO)_2$	−1137	−1145	−1052
$D_{\infty h}$ C_2 $(CN)_2$	−1205	−1214	−1119

The corresponding values of $C_n(CN)_m$ are listed for comparison.

3.4. Symmetrical vibrational frequencies

As indicated in Table 1, the unscaled DFT symmetrical vibrational frequencies at $1913\ cm^{-1}$ for BO and 611 and $2119\ cm^{-1}$ for $(BO)_2$ all agree nicely with available experimental values with the averaged discrepancies of less than +5%. Vibrational analyses indicate that the harmonic vibrational frequencies at $2119\ cm^{-1}$ for $(BO)_2$, $2041\ cm^{-1}$ for $C_2(BO)_4$, and $1990\ cm^{-1}$ for $C_2(BO)_2$ all mainly correspond to symmetrical stretching vibrations of the —B=O terminals. The B—B single bond in $(BO)_2$, C=C double bond in $C_2(BO)_4$, and C≡C triple bond in $C_2(BO)_2$ stretches at 611, 1550, and $2327\ cm^{-1}$, respectively. As indicated in Table 1, in other partially substituted ethylenes and acetylenes, —B=O groups vibrate in the frequencies between 2017 and $2040\ cm^{-1}$, C=C between 1593

and $1661\ cm^{-1}$, and C≡C at 2231 in $C_{\infty v}$ $C_2H(BO)$. The vibrational frequencies in the range of 476–$891\ cm^{-1}$ belong to the coupled vibrational modes of the systems mainly involving the stretching vibrations of B—C single bonds. Obviously, B=O bonds in these substitutes vibrate in higher energies than B—C, B—B, and C=C bonds, but in lower frequencies than C≡C triple bonds. The DFT tretching vibrational frequencies of —B=O functional groups at about $2000\ cm^{-1}$ agree well with the measured value of $1935 \pm 30\ cm^{-1}$ for BO [5] and feature the vibrational properties of boronyl compounds.

3.5. One-electron detachment energies

Our calculated electron affinities for BO at 2.588 eV, CN at 4.044 eV, $trans$-$C_2H_3(CN)_2$ at 1.488 eV, $C_2(CN)_4$ at 3.464 eV, and $C_2H_3(CN)$ at 0.029 eV all show agreement of better than +0.3 eV with the corresponding experimental values at $2.510 \pm 0.015\ eV^5$, $3.862 \pm 0.004\ eV$ [9,18], $1.249 \pm 0.087\ eV$ [18], $3.17 \pm 0.2\ eV$ [18,19], and 0.01–0.02 eV [20,21], respectively. The experimentally determined A-band of $BO(^2\Pi)$ at 5.63 eV [5] and $CN(^2\Pi)$ at 5.008 eV [9,10] have also been well reproduced at 5.900 and 5.120 eV, respectively. The singlet ground-states of $(BO)_2$ and $(CN)_2$ dimers $(^1\Sigma_g^+)$ can be easily reached by detaching one electron from the HOMOs of their anions with the ADE values of 0.580 and 0.531 eV, respectively. Their first triplet excited states $(^3\Pi_u)$ are expected to lie quite high in energies above the ground-states (4.46 and

3.20 eV at DFT). It is interesting to notice that, although BO radical has a much lower electron affinity (2.510 eV) than CN (3.862 eV), the tetra-substituted $C_2(BO)_4$ possesses approximately the same EA (3.523 eV) with $C_2(CN)_4$ (3.464 eV) at DFT. This suggests that $C_2(BO)_4^-$ be similar with $C_2(CN)_4^-$ in stability. Their first triplet excited states ($^3B_{1u}$) are found to lie 1.95 and 1.55 eV above the ground-states, respectively. These results provide a viable possibility to produce $C_2(BO)_4^-$ in experiments. The DFT thermodynamic data listed in Table 2 well support this possibility. The similarity between $C_2(BO)_2$ and $C_2(CN)_2$ is also obvious, with the EA value of 1.403 eV for $C_2(BO)_2$ and 1.511 eV for $C_2(CN)_2$. The first VDE of $C_2(BO)_2^-$ is only 0.20 eV higher than its first ADE, but the first VDE of $C_2(CN)_2^-$ lies considerably higher (0.60 eV) than its ADE for the reason that the $C_2(CN)_2^-$ anion has been distorted from the linear neutral to a C_{2h} structure. The first excited states ($^3\Pi_u$) of $C_2(BO)_2$ and $C_2(CN)_2$ lies 3.10 and 2.02 eV above their ground-states ($^1\sum_g^+$), respectively. As $C_2(CN)_2$ [17], $C_2(CN)_4$ [18,19], $C_2H_3(CN)$ [20,21], and trans-$C_2H_2(CN)_2$ [18,19] have all been experimentally known, we expect their iso-electronic BO-substituted species $C_2(BO)_2$, $C_2(BO)_4$, $C_2H_3(BO)$, and trans-$C_2H_2(BO)_2$ to be experimentally synthesized and characterized in future. Our calculated EA values for $C_2H_3(BO)$ (9), cis-$C_2H_2(BO)_2$ (11), trans-$C_2H_2(BO)_2$ (13), gem-$C_2H_2(BO)_2$ (15), and $C_2H(BO)_3$ (17) at 0.005, 1.396, 1.436, 1.275, and 2.538 eV well parallel the reported theoretical values of the corresponding cyano-substituted ethylenes at 0.06, 1.45, 1.53, 1.36, and 2.59 eV [20].

The first VDEs (X-bands) of $(BO)_2^-$, cis-$C_2H_2(BO)_2$, $C_2(BO)_4^-$, and $C_2(BO)_2^-$ anions all originate from detaching one electron from their singly occupied π HOMOs (see Fig. 3), mainly involving the B–B interaction in $(BO)_2^-$ and B–C interactions in $C_2(BO)_4^-$, cis-$C_2H_2(BO)_2$, and $C_2(BO)_2^-$, respectively. The second VDEs (A-bands) correspond to detaching one electron from their π-typed HOMO-1 orbitals, i.e., the localized B=O π bonds in $(BO)_2^-$, C=C π bonds in cis-$C_2H_2(BO)_2$ and $C_2(BO)_4^-$, and C≡C π interaction in $C_2(BO)_2^-$. The strong π bonding effects in these HOMO-1 MOs result in the considerably wide X–A energy gaps (1.9–4.5 eV) in the anions, as indicated in Table 1.

We now turn to discuss the substitution effect of ─BO radicals on C─C bond lengths, their vibrational frequencies, and the electron detachment energies in $C_2H_{4-m}(BO)_m$ and $C_2H_{2-m}(BO)_m$ series. Fig. 2 and Table 1 clearly indicate that when the number of ─BO radicals increases in these systems, their C─C bond lengths increase and the corresponding C─C vibrational frequencies decrease. For example, with $m = 1$–4, the C=C bond lengths in $C_2H_{4-m}(BO)_m$ neutrals increase from 1.334, 1.342, 1.353, to 1.364 Å, and the corresponding C=C stretching frequencies decrease from 1661, 1627, 1593, to 1550 cm^{-1}, respectively. This observation agrees well with the situation in the corresponding cyano substitutes of $C_2H_{4-m}(CN)_m$ [20]. Similar changes happen to $C_2H_{2-m}(BO)_m$. These results

can be understood based on the fact that both ─BO and ─CN radicals possess π-accepting characteristics. The delocalized inner-shelled π MOs mainly from the 2p atomic orbitals of the surrounding ─BO groups reduce, in certain degree, the electronic density and therefore the strengths of the π-typed HOMO-1 MOs of the systems (These HOMO-1 MOs are mainly localized between C and C, see Fig. 3 and Appendix A). As also indicated in Table 1, the ADEs of $C_2H_{4-m}(BO)_m$ anions increase dramatically from EA = 0.005, 1.396, 2.538, to 3.523 eV with $m = 1$–4, respectively. This variation originates from the fact that with the number of ─BO groups increasing from 1 to 4, the π-typed HOMOs of these anions are more and more effectively delocalized to cover the whole molecular frames (see Fig. 3).

3.6. Thermodynamic stabilities

Concerning the thermodynamic stabilities of carbon boronyls, Table 2 indicates that, with respect to their component fragments (free C_2 and BO), the thermodynamic quantity changes (ΔE^0, ΔH^0, and ΔG^0) of $C_n(BO)_m$ neutrals ($n = 0, 2$; $m = 2, 4$) all possess huge negative values which are parallel with that of the corresponding $C_n(CN)_m$ (about 4–10% lower). In the case of $C_2(BO)_4$ (19) (which has the highest EA value of 3.523 eV at DFT), with zero-point correction included, the following formation process

$$C_2(^1\Sigma_g^+) + 4OB(^2\Sigma^+) = C_2(BO)_4(^1A_g) \tag{1}$$
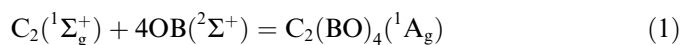
possesses the energy change of $\Delta E^0 = -1703$ kJ/mol, thermal enthalpy change of $\Delta H^0 = -1718$ kJ/mol, and Gibbs free energy change of $\Delta G^0 = -1536$ kJ/mol (The singlet state of $C_2{}^1\Sigma_g^+$ has been chosen in Eq. (1). It is the ground-state of C_2 lying 0.09 eV lower than the triplet state of $C_2{}^3\Sigma_g^+$ [18]). These values are about 10% smaller than the corresponding values of $\Delta E^0 = -1900$ kJ/mol, $\Delta H^0 = -1917$ kJ/mol, $\Delta G^0 = -1730$ obtained for $C_2(CN)_4$ at the same DFT level. We notice from Table 2 that the corresponding thermodynamic data of the experimentally known $(BO)_2$ dimer [12,14] are about 20% smaller than that of cyanogen $(CN)_2$ [13,15,17] at DFT level.

4. Summary

A systematical DFT investigation on the geometrical and electronic structures and one-electron detachment energies of boronyl-substituted ethylenes $C_2H_{4-m}(BO)_m$ ($m = 1$–4) and acetylenes $C_2H_{2-m}(BO)_m$ ($m = 1, 2$) has been presented in this work. ─B≡O σ-radicals in these covalent molecules and their anions behave similar to ─CN in cyanocarbons and ─H in hydrocarbons. The symmetrical harmonic vitrabional frequencies of ─B≡O groups at about 2000 cm^{-1} feature these boronyl compounds in vibrational properties. As can be judged from the EA difference (1.35 eV) between BO and CN discussed above, BO$^-$ anions are expected to be much less stable than

CN^- in aqueous solutions and ionic solids. However, as demonstrated in this work, $-B=O$ groups possess similar bonding abilities with $-C\equiv N$ in covalent molecules and anions. The results obtained in this paper and our previous work [1,4] complete the $C_n(BO)_n$ carbon boronyl series with $n = 2$–7 and provide more partially BO-substituted ethylene and acetylene species which are possible to be synthesized and characterized in future experiments to open a new area of chemistry on boronyl compounds.

Acknowledgements

Appendix A. Supplementary data

Detailed DFT structural parameters of cyanocarbons and BO-substituted ethylenes and acetylenes and the valence MO pictures of $C_n(BO)_m^-$ and $C_n(CN)_m^-$ anions are available free of charge. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.theochem.2007.07.006.

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