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Molecular wheel to monocyclic ring transition in boron–carbon mixed clusters $C_2B_6^{-}$ and $C_3B_5^{-} \ddagger$

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In this joint experimental and theoretical work we present a novel type of structural transition occurring in the series of $C_x B_{8-x^-}$ (x = 1-8) mixed clusters upon increase of the carbon content from x = 2 to x = 3. The wheel to ring transition is surprising because it is rather planar-to-linear type of transition to be expected in the series since B_8 , B_8^- , B_8^{2-} and CB_7^- are known to possess wheel-type global minimum structures while C_8 is linear.

Carbon and boron being neighbours in the Periodic Table have very different geometric structures of their small clusters. Small carbon clusters are either linear or cyclic,¹ whereas, those of boron are either planar or quasi-planar.² Thus, one can expect peculiar transitions from planar to linear structures upon increasing the number of carbon atoms in mixed boron-carbon clusters. An example of such planar-to-linear structural transition as a function of the number of carbon atoms has been found to occur in the mixed boron-carbon clusters, $C_x B_{5-x}$ (x = 1-5) between x = 2 and 3.³ Larger boron-carbon mixed clusters have been computationally proposed to exemplify unusual hexa-, hepta and octacoordinated planar carbon species ($CB_6^{2-,4}$ $CB_7^{-,5}$ and CB_8^{6}). However, it was shown later in joint experimental and theoretical works⁷⁻⁹ that carbon avoids the central position in those wheel-type global minimum geometries and occupies the peripheral position instead. It is known that the B_8 , $B_8^$ and B_8^{2-} clusters¹⁰⁻¹⁴ and the CB_7^{-} cluster⁸ have wheel-type heptagon structures with one boron atom in the center. The C₈ cluster has a linear global minimum structure with the cyclic isomer being about 10 kcal mol⁻¹ higher.^{1,15,16} Therefore, a

planar-to-linear transition could be expected in the $C_x B_{8-x}^{-1}$ (x = 1-8) series upon increasing the carbon content in the clusters. Surprisingly, we found a novel structural transition that has never been observed before—wheel-to-ring transition between $C_2 B_6^{-1}$ and $C_3 B_5^{-1}$ structures of the series. We would like to point out that ring-like structures have been previously reported in a theoretical study by Shao *et al.*¹⁷ for the neutral $C_n B_3$ (n = 4-8) clusters.

The $C_2B_6^-$ and $C_3B_5^-$ clusters were investigated by photoelectron spectroscopy (PES) and *ab initio* calculations. The experiment was performed with a laser-vaporization cluster source and a magnetic-bottle photoelectron spectrometer (see Experimental section).¹⁸

The photoelectron spectra of the $C_2B_6^-$ cluster are presented in Fig. 1 and the photoelectron spectra of $C_3B_5^$ are shown in Fig. 2. The experimentally observed vertical detachment energies (VDEs) for the clusters are given in Tables 1 and 2 and are compared to the theoretically calculated data.

Fig. 1 shows the PES spectra of $C_2B_6^-$ at three photon energies. The 193 nm spectrum of $C_2B_6^-$ reveals six wellresolved features labelled A–F (Fig. 1b). At the low binding energy side, we observe a very broad feature (X, X') corresponding to photodetachment from the two lowest lying isomers of $C_2B_6^-$. The ninth band (G) can be tentatively identified, but the signal-to-noise ratios are poor at the high binding energy side. The spectra recorded at 266 nm (Fig. 1a) reveal fine vibrational features for the A and B electronic bands. For the A band we measured a vibrational spacing of 330 ± 30 cm⁻¹ using the PES measured at 355 nm (see the inset of Fig. 1a). The B band shows a fine structure both at 193 nm and 266 nm, however, the measurement of the vibrational spacing is complicated by the existence of two nearly isoenergetic photodetachment channels.

The spectra of $C_3B_5^-$ are shown in Fig. 2. The VDE of the X band was measured to be 3.94 ± 0.03 eV. The intensity change between the X and the A bands confirms that there are two features rather than a vibrational progression. The X band shows a short vibrational progression with a spacing of 380 ± 30 cm⁻¹.

Computationally, we first performed the global minimum structure search for the $C_2B_6^-$ ion using the Coalescence Kick (CK)^{19–21} program written by Averkiev. The CK method

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[†] Electronic supplementary information (ESI) available: Adiabatic detachment energies of the $C_2B_6^-$ and $C_3B_5^-$ clusters, valence canonical molecular orbitals and AdNDP revealed chemical bonding patterns for the wheel-type and ring isomers of both clusters. See DOI: 10.1039/c1cp20359b



Fig. 1 Photoelectron spectra of $C_2B_6^-$ at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV). The inset shows a partial PES at 355 nm (3.496 eV). The short vertical lines represent the TD-B3LYP values of VDE for structures I.1 (bottom) and I.2 (top).

subjects large populations of randomly generated structures to a coalescence procedure in which all atoms are pushed gradually to the molecular center of mass to avoid generation of fragmented structures and then optimized to the nearest local minima. The CK calculations were performed at the B3LYP/ 3-21G level of theory. All the low-lying ($\Delta E < 25$ kcal mol⁻¹) isomers revealed were reoptimized with follow up frequency calculations at the B3LYP/6-311+G* level of theory. Single point calculations for the lowest energy structures were performed at the RCCSD(T)/6-311+G(2df) level of theory using the B3LYP/6-311+G* optimized geometries. The relative energies of a series of representative isomers are given in Fig. 3.

The CK search revealed that the cyclic structure I.6 is the lowest isomer with the structures I.1–I.5 being 12-25 kcal mol⁻¹ higher at the B3LYP/3-21G level of theory. However, when we reoptimized all the low-lying structures at the B3LYP/6-311+G* level of theory we found a significantly different order of the isomers with the wheel-type structure I.1 being the lowest isomer and the cyclic structure I.6 lying 9.1 kcal mol⁻¹ higher (Fig. 3). Therefore, the set of isomers for subsequent investigation should be formed of all the structures lying in the range of about 20 kcal mol⁻¹ relative energies at this level of theory as it was done in the current work. Moreover, the B3LYP/6-311+G* calculated results were further corrected by the single point calculations at the



Fig. 2 Photoelectron spectra of $C_3B_5^-$ at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV).

RCCSD(T)/ $6-311+G(2df)//B3LYP/6-311+G^*$ level of theory (Fig. 3). Thus, according to our most accurate calculations the wheel-type structure I.1 is the global minimum for the $C_2B_6^-$ cluster. In order to verify this theoretical prediction we calculated theoretical VDEs for the global minimum structure I.1 at three levels of theory: TD-B3LYP/6-311+G(2df), UOVGF/ 6-311+G(2df) and R(U)CCSD(T)/6-311+G(2df) all at the B3LYP/6-311+G^* optimized geometries. We also calculated VDEs for the second lowest structure I.2 at the same three levels of theory and found out that it also contributes to the experimental PES of $C_2B_6^-$. Results of the VDEs calculations are summarized in Table 1.

The broad feature X(X') in the experimental spectrum of $C_2B_6^-$ (Fig. 1) can be assigned to the electron detachment from the singly-occupied HOMO 7a1 of the global minimum structure I.1. The broad shape of the peak is an indication of a large geometry change upon the electron detachment, which was confirmed by geometry optimization of the neutral C_2B_6 cluster (see Fig. S1, ESI[†]). The electron detachment from the singly occupied HOMO 11a' of the I.2 isomer can also contribute to this peak since the first VDE is very close to that of I.1. None of the calculated VDEs of I.1 could be assigned to the experimental feature at ~ 3.2 eV. This peak confirms the presence of the second-lowest isomer I.2 of C_2B_6 in the molecular beam since it can be clearly explained by the electron detachment from 3a'' of I.2 leading to the final ${}^{3}A''$ state. Electron detachment processes with final triplet states are expected to be more prominent in the experimental

| Feature | VDE $(exp)^a$ | Final state and electronic configuration | VDE (theor.) | | |
|--------------------------------|---------------|---|-----------------------|--------------------|-----------------|
| | | | TD-B3LYP ^b | UOVGF^c | $R(U)CCSD(T)^d$ |
| $I.1 C_{2y} (^2A_1)$ | | | | | |
| X' | 2.3(1) | ${}^{1}A_{1}, \{\ldots 5a_{1}{}^{(2)}4b_{2}{}^{(2)}6a_{1}{}^{(2)}1a_{2}{}^{(2)}2b_{1}{}^{(2)}7a_{1}{}^{(0)}\}$ | 2.26 | 2.59 (0.89) | 2.17 |
| В | 3.54(3) | ${}^{3}B_{1}, \{\ldots 5a_{1}^{(2)}4b_{2}^{(2)}6a_{1}^{(2)}1a_{2}^{(2)}2b_{1}^{(1)}7a_{1}^{(1)}\}$ | 3.51 | 3.54 (0.89) | 3.64 |
| | | ${}^{1}B_{1}, \{\dots, 5a_{1}^{(2)}4b_{2}^{(2)}6a_{1}^{(2)}1a_{2}^{(2)}2b_{1}^{(1)}7a_{1}^{(1)}\}$ | 3.91 | e | e |
| С | 4.35(5) | ${}^{3}A_{2}, \{\dots 5a_{1}{}^{(2)}4b_{2}{}^{(2)}6a_{1}{}^{(2)}1a_{2}{}^{(1)}2b_{1}{}^{(2)}7a_{1}{}^{(1)}\}$ | 4.25 | 4.25 (0.88) | 4.41 |
| | | $^{1}A_{2}, \{\dots 5a_{1}^{(2)}4b_{2}^{(2)}6a_{1}^{(2)}1a_{2}^{(1)}2b_{1}^{(2)}7a_{1}^{(1)}\}$ | 4.46 | e | e |
| F | 4.96(5) | ${}^{3}A_{1}, \{\ldots 5a_{1}{}^{(2)}4b_{2}{}^{(2)}6a_{1}{}^{(1)}1a_{2}{}^{(2)}2b_{1}{}^{(2)}7a_{1}{}^{(1)}\}$ | 4.93 | 4.88 (0.89) | 5.06 |
| G | 5.7(2) | ${}^{3}B_{2}, \{\ldots 5a_{1}^{(2)}4b_{2}^{(1)}6a_{1}^{(2)}1a_{2}^{(2)}2b_{1}^{(2)}7a_{1}^{(1)}\}$ | 5.58 | 5.72 (0.89) | 5.79 |
| | | ${}^{1}A_{1}, \{\dots 5a_{1}^{(2)}4b_{2}^{(2)}6a_{1}^{(1)}1a_{2}^{(2)}2b_{1}^{(2)}7a_{1}^{(1)}\}$ | 5.66 | e | e |
| | | ${}^{1}B_{2}, \{\dots 5a_{1}^{(2)}4b_{2}^{(1)}6a_{1}^{(2)}1a_{2}^{(2)}2b_{1}^{(2)}7a_{1}^{(1)}\}$ | 5.93 | e | e |
| I.2 C_{s} (² A') | | / | | | |
| X | 2.2(1) | ${}^{1}A', \{\ldots 9a'^{(2)}10a'^{(2)}2a''^{(2)}3a''^{(2)}11a'^{(0)}\}$ | 2.19 | f | 2.09 |
| А | 3.23(2) | ${}^{3}A'', \{\ldots 9a'^{(2)}10a'^{(2)}2a''^{(2)}3a''^{(1)}11a'^{(1)}\}$ | 3.12 | f | 3.28 |
| | | $^{1}A''$, {9a' ⁽²⁾ 10a' ⁽²⁾ 2a'' ⁽²⁾ 3a'' ⁽¹⁾ 11a' ⁽¹⁾ } | 3.52 | f | e |
| D | 4.68(5) | ${}^{3}A', \{\ldots,9a'^{(2)}10a'^{(1)}2a''^{(2)}3a''^{(2)}11a'^{(1)}\}$ | 4.62 | f | 4.81 |
| Е | 4.77(5) | ${}^{3}A''$, {9a' ⁽²⁾ 10a' ⁽²⁾ 2a'' ⁽¹⁾ 3a'' ⁽²⁾ 11a' ⁽¹⁾ } | 4.69 | f | e |
| | | ${}^{1}A'', \{\ldots,9a'^{(2)}10a'^{(2)}2a''^{(1)}3a''^{(2)}11a'^{(1)}\}$ | 4.91 | f | e |
| | | $^{1}A', \{\ldots, 9a'^{(2)}10a'^{(1)}2a''^{(2)}3a''^{(2)}11a'^{(1)}\}$ | 5.31 | f | e |
| G | 5.7(2) | ${}^{3}A', \{\ldots,9a'^{(1)}10a'^{(2)}2a''^{(2)}3a''^{(2)}11a'^{(1)}\}$ | 5.90 | f | e |

Table 1 Comparison of the experimental VDEs with calculated values for the structures I.1 C_{2v} (²A₁) and I.2 C_s (²A') of the C₂B₆⁻ cluster. All energies are in eV

^{*a*} Numbers in parentheses represent the uncertainty in the last digit. ^{*b*} VDEs were calculated at the TD-B3LYP/6-311+G(2df)//B3LYP/6-311+G* level of theory. ^{*c*} VDEs were calculated at the UOVGF/6-311+G(2df)//B3LYP/6-311+G* level of theory. Values in parentheses represent the pole strength of the OVGF calculation. ^{*d*} VDEs were calculated at the R(U)CCSD(T)/6-311+G(2df)//B3LYP/6-311+G* level of theory. ^{*e*} VDE value cannot be calculated at this level of theory. ^{*f*} These VDEs are not presented because of large spin contamination at the UHF/6-311+G(2df) level of theory.

Table 2 Comparison of the experimental VDEs with calculated values for the structure II.1 C_{2v} (¹A₁) of the C₃B₅⁻ cluster. All energies are in eV

| Feature | VDE $(exp)^a$ | Final state and electronic configuration | VDE (theor.) | | |
|---------|---------------|---|-----------------------|----------------------|--------------|
| | | | TD-B3LYP ^b | \mathbf{ROVGF}^{c} | $RCCSD(T)^d$ |
| X | 3.94(3) | ${}^{2}\mathbf{B}_{2} \{ \dots 5a_{1}{}^{(2)}1b_{1}{}^{(2)}6a_{1}{}^{(2)}2b_{1}{}^{(2)}1a_{2}{}^{(2)}5b_{2}{}^{(1)} \}$ | 3.82 | 3.99 (0.87) | 3.94 |
| А | 4.04(3) | ${}^{2}A_{2} \left\{ \dots 5a_{1}^{(2)} 1b_{1}^{(2)} 6a_{1}^{(2)} 2b_{1}^{(2)} 1a_{2}^{(1)} 5b_{2}^{(2)} \right\}$ | 4.03 | 4.09 (0.88) | 4.11 |
| В | 5.26(5) | ${}^{2}B_{1} \left\{ \dots 5a_{1}^{(2)} 1b_{1}^{(2)} 6a_{1}^{(2)} 2b_{1}^{(1)} 1a_{2}^{(2)} 5b_{2}^{(2)} \right\}$ | 5.06 | 5.26 (0.87) | 5.38 |
| С | 5.47(5) | ${}^{2}A_{1} \left\{ \dots 5a_{1}^{(2)} 1b_{1}^{(2)} 6a_{1}^{(1)} 2b_{1}^{(2)} 1a_{2}^{(2)} 5b_{2}^{(2)} \right\}$ | 5.41 | 5.55 (0.85) | 5.53 |
| | | | | | |

^{*a*} Numbers in parentheses represent the uncertainty in the last digit. ^{*b*} VDEs were calculated at the TD-B3LYP/6-311+G(2df)//B3LYP/6-311+G* level of theory. ^{*c*} VDEs were calculated at the ROVGF/6-311+G(2df)//B3LYP/6-311+G* level of theory. Values in parentheses represent the pole strength of the OVGF calculation. ^{*d*} VDEs were calculated at the RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G* level of theory.

spectra, therefore, we discuss only the transitions leading to the final triplet states. The feature at 3.54 eV in the experimental PES is due to the electron detachment from HOMO -1 2b₁ with the final state ³B₁. The next feature (4.35 eV) corresponds to the electron detachment from HOMO $- 2 1a_2$ to the final ${}^{3}A_2$ state. Both of these detachment channels are of isomer I.1. The features at 4.68 and 4.77 eV can be explained only by the electron detachment from 2a" and 10a' of I.2 corresponding to two final states: ³A' and ${}^{3}A''$. The sharp peak at 4.96 eV is due to the detachment from HOMO -3 6a₁ leading to the ³A₁ state of I.1. The broad feature at about 6 eV can be assigned to two detachments of electrons from HOMO $-44b_2$ of I.1 and from HOMO -49a'of I.2 with the final states ${}^{3}B_{2}$ and ${}^{3}A'$, respectively. The excellent agreement between the experimentally observed and the theoretically calculated VDEs confirms the predicted structures of the two lowest-lying isomers I.1 and I.2 contributing to the experimental PES of $C_2B_6^-$.

According to the CK search the global minimum structure of the $C_3B_5^-$ cluster is a cyclic isomer II.1 with the lowest

wheel-type structure II.5 being 62.1 kcal mol^{-1} higher at the B3LYP/3-21G level of theory (Fig. 4).

Geometry optimization for the low-lying isomers ($\Delta E < 25$ kcal mol⁻¹) and the lowest-found wheel-type structure II.5 at the B3LYP/6-311+G* level of theory with subsequent single point calculations at the RCCSD(T)/ 6-311+G(2df)//B3LYP/6-311+G* level revealed the presented (Fig. 4) order. Thus, according to our calculations the global minimum is the cyclic isomer II.1 and the structural transition from the wheel-type structure to the monocyclic ring occurs between C₂B₆⁻ and C₃B₅⁻. The lowest wheel-type structure II.5 is 28.8 kcal mol⁻¹ higher than the global minimum (RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G*).

Again, we calculated VDEs of the proposed structure II.1 to compare those with the experimental PES. Only the isomer II.1 is expected to contribute to the experimental PES of the $C_3B_5^-$ cluster, since the lowest alternative isomer II.2 is 13 kcal mol⁻¹ higher than II.1. The VDE calculations were performed at the same three levels of theory: TD-B3LYP/6-311+G(2df), ROVGF/6-311+G(2df) and RCCSD(T)/6-311+G(2df) all at



Fig. 3 Representative optimized isomers of the $C_2B_6^-$ cluster, their point group symmetries, spectroscopic states and relative energies. The ZPE corrected energies are given at the RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G*, B3LYP/6-311+G* (in square brackets), and B3LYP/3-21G (in curly brackets) levels of theory.



Fig. 4 Optimized isomers of the $C_3B_5^-$ cluster, their point group symmetries, spectroscopic states and relative energies. The ZPE corrected energies are given at the RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G*, B3LYP/6-311+G* (in square brackets), and B3LYP/3-21G (in curly brackets) levels of theory.

the B3LYP/6-311+G* optimized geometry. The VDEs calculated are summarized in Table 2. Our calculations revealed two very close transitions corresponding to the electron detachments from HOMO ($5b_2$) and HOMO - 1 ($1a_2$). The first VDE is 0.1–0.2 eV lower than that assigned to the

detachment from HOMO - 1 according to all the three theory levels. These two transitions are responsible for the features X and A in the experimental spectra of the $C_3B_5^-$ cluster (Fig. 2). There is a big gap between these two transitions and the transition corresponding to electron detachment from HOMO $- 2 (2b_1)$ which varies from 1.0 eV (TD-DFT) to 1.3 eV (RCCSD(T)). This computational prediction is confirmed by the experimental spectra, showing the gap of 1.2 eV between feature A and feature B. The fourth electron detachment occurs from HOMO $- 3 (6a_1)$ and the calculated VDE agrees well with the experimental value (5.47 eV). The sharp shape of the first peak in the PES spectra of the $C_3B_5^$ cluster is consistent with the calculated small geometry change upon the electron detachment (see Fig. S1, ESI[†]). The perfect agreement between the experimental and the theoretical VDEs confirms the global minimum structure II.1 for the C₃B₅⁻ cluster.

In order to trace structural change from the wheel-type structure to the monocyclic ring structure we calculated the monocyclic structure for the cluster CB_7^- . The calculated relative energy of the wheel-type global minimum structure with respect to the monocyclic ring structure is presented in Fig. 5 as well as the corresponding relative energies of the monocyclic ring and wheel-type structures for the $C_2B_6^-$ and $C_3B_5^-$ clusters.

One can see that the energy difference between the wheeltype and monocyclic ring isomers dropped from 79.0 to 20.5 kcal mol⁻¹ (at RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G*) upon transition from CB_7^- to $C_2B_6^-$. The substitution of another boron by a carbon atom in $C_3B_5^-$ leads to the inversion of the wheel-type and monocyclic structures with the monocyclic structure being now the global minimum. It was proposed by Zubarev and Boldyrev²² that the wheel-type structures appear in boron clusters beginning from B₈ since the dangling electron density at the center of the monocyclic cluster cannot be supported by the valence charge of the boron atoms. Migration of one of the boron atoms into the center of the ring provides the necessary electrostatic field stabilization in the wheel-type structures and that is the reason why those structures are the global minima. The substitution of boron atoms in the peripheral ring by carbon atoms provided additional electrostatic field stabilization at the center of the ring due to the higher valence charge of carbon, which eventually leads to the higher stability of the monocyclic structures over the wheel-type structures in the mixed carbon-boron clusters.

It was previously shown⁷ that the global minimum wheeltype structure of CB_7^- is doubly aromatic. The CB_7^- monocyclic structure has a conflicting aromaticity. The chemical bonding is consistent with the higher stability of the doubly aromatic wheel-type structure relative to the monocyclic structure with the conflicting aromaticity.

We performed chemical analysis in the studied clusters using the Adaptive Natural Partitioning method (AdNDP) developed by Zubarev and Boldyrev.²³ Results of the AdNDP analysis are summarized in the ESI.† According to our AdNDP analysis, chemical bonding in the wheel-type structure of the $C_2B_6^-$ cluster (Fig. S2, ESI†) can be described as a combination of three 2c–2e σ B–B bonds, four 2c–2e σ C–B bonds, three delocalized π -bonds (responsible for π -aromaticity), three delocalized doubly-occupied σ -bonds and one delocalized singly-occupied σ -bond. Here and elsewhere the terms delocalized σ -bonds and delocalized π -bonds mean that those bonds cannot be reduced to 2c-2e bonds by the AdNDP method. It was previously proposed²⁴ to name cases like the one we have here with an odd number of electrons for σ -delocalized bonds as $\frac{1}{2}$ - σ -antiaromatic. " $\frac{1}{2}$ " is used as a label and means that the σ -system with singly occupied delocalized bond is half way down to being σ -antiaromatic in the wheel-type structure of the doubly-charged $C_2B_6^{2-}$ ion. The $\frac{1}{2}$ - σ -antiaromatic nature of the global minimum structure I.1 of the $C_2B_6^-$ cluster is consistent with relatively low first VDE of the cluster. When the extra electron in the $C_2B_6^-$ cluster is removed from the singly-occupied orbital the resulting neutral C_2B_6 species becomes a doubly-aromatic system which is consistent with the round structure of the neutral species (Fig. S1, ESI[†]).

The chemical bonding in the monocyclic structure I.6 of the $C_2B_6^-$ cluster can be described as follows. There are four 2c–2e σ B–B bonds, four 2c–2e σ C–B bonds, three delocalized π -bonds (responsible for π -aromaticity), two delocalized doubly-occupied σ -bonds and one delocalized singly-occupied σ -bond. Thus, the structure I.6 is $\frac{1}{2}\sigma$ -aromatic since the singly occupied delocalized bond is half way down to being σ -aromatic in the monocyclic ring-type structure of the doubly-charged $C_2B_6^{2-}$ ion (see Fig. S2, ESI†). The presence of $\frac{1}{2}\sigma$ -aromaticity in the wheel-type structure and of the $\frac{1}{2}\sigma$ -aromaticity in the monocyclic structure explains the relatively low energy difference compared to that of the CB₇⁻ structures (Fig. 5).

The global minimum monocyclic structure II.1 of the $C_3B_5^$ cluster (Fig. S3, ESI[†]) is doubly-aromatic with two 2c–2e σ B–B bonds, six 2c–2e σ C–B bonds, three delocalized π -bonds (responsible for π -aromaticity), three delocalized σ -bonds (responsible for σ -aromaticity). The doubly-aromatic nature of the global minimum structure $C_3B_5^-$ is consistent with the rather high first VDE of this cluster.



Fig. 5 Wheel-type to monocyclic ring structural transition in the series of the $C_x B_{8-x}^{-}$ (x = 1-3) clusters. Relative energies are given at RCCSD(T)/6-311+G(2df)//B3LYP/6-311+G*.

Chemical bonding analysis of the lowest-lying wheel-type isomer II.5 (Fig. S3, ESI[†]) revealed one 2c–2e σ B–B bond, six 2c–2e σ C–B bonds, three delocalized π -bonds (responsible for π -aromaticity) and four delocalized σ -bonds (responsible for σ -antiaromaticity). The σ -antiaromaticity leads to deformation of the heptagon structure into the hexagon structure with one carbon atom coordinated to the edge of the hexagon. As a result of that we have three σ -bonds delocalized over the hexagon and one 3c–2e σ -bond delocalized over the external carbon atom and the two edge boron atoms (see Fig. S3, ESI[†]). The structure II.5 possessing conflicting aromaticity is higher in energy than the doubly-aromatic global minimum structure II.1.

In the above discussion we presented chemical bonding explanation for different stabilities of the wheel-type and monocyclic ring-type structures. With the chemical bonding analysis we can explain why the $C_2B_6^-$ cluster has relatively low first VDE compared to that of the $C_3B_5^-$ cluster. However we would like to stress that we believe that the transition from the wheel-type to the ring-type structures in the series occurs due to the increase of the stabilizing electrostatic field at the center of the cluster as a result of the increased number of carbon atoms in $C_3B_5^-$, which makes the presence of the central boron atom unnecessary.

Experimental section

The experiment was performed using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been published elsewhere.^{25,26} Briefly, the carbon-doped boron clusters were produced by laser vaporization of a disk target made of isotopically enriched 10 B (~6% wt), C (~0.6% wt), and Bi. The clusters were entrained by the helium carrier gas supplied by two pulsed Jordan valves and underwent a supersonic expansion to form a collimated molecular beam. The cluster composition and the cooling were controlled by the time delay between the pulsed beam valves and the vaporization laser. The negatively charged clusters were extracted from the cluster beam and analyzed with a time-of-flight mass spectrometer. The clusters of interest were mass selected and decelerated before being intercepted by the probe photodetachment laser beam: 193 nm (6.424 eV) from an ArF excimer laser and 355 nm (3.496 eV) or 266 nm (4.661 eV) from a Nd:YAG laser. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5 m long electron flight tube. The cluster PE spectra were calibrated using the known spectra of Bi⁻. The kinetic energy resolution of the magnetic bottle apparatus, $\Delta E/E$, was typically better than 2.5%, *i.e.* ~25 meV for 1 eV electrons.

Theoretical section

We searched for the global minimum of the $C_2B_6^-$ and $C_3B_5^-$ clusters using the Coalescence Kick (CK) program^{19–21} with the B3LYP/3-21G method for energy and gradient calculations. Then we reoptimized the geometries and performed frequency calculations for the lowest isomers (E < 25 kcal mol⁻¹) at the B3LYP/6-311+G* level of theory and recalculated total

energies of the isomers at the RCCSD(T)/6-311+G(2df)//B3LYP/ $6-311+G^*$ level of theory. The VDEs for the global minima I.1 and II.1 and the low-lying isomer I.2 were calculated using the R(U)CCSD(T)/6-311+G(2df) method, the outer-valence Green Function method (R(U)OVGF/6-311+G(2df)) and the time-dependent DFT method (TD B3LYP/6-311+G(2df)) at the B3LYP/ $6-311+G^*$ geometries. The calculations were performed with the Gaussian 03^{27} and Molpro²⁸ software. Molecular orbitals were visualized with the MOLDEN 3.4^{29} and Molekel $5.4.0.8^{30}$ programs.

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