

CB₇⁻: Experimental and Theoretical Evidence against Hypercoordinate Planar Carbon**

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In organic chemistry, saturated carbon is known to bond to four ligands tetrahedrally, as first recognized independently by J. H. van't Hoff and J. A. Le Bel in 1874. However, after the proposal by Hoffmann and co-workers of tetracoordinate planar carbon in 1970,^[1] extensive experimental and theoretical efforts were made to search for so-called anti-van't Hoff/anti-Le Bel molecules (for recent reviews, see references [2–4]). In particular, the first experimental and theoretical realization of pentaatomic planar-coordinated carbon species in 1999 and 2000,^[5–8] which confirmed earlier theoretical predictions,^[9,10] has stimulated renewed interest in designing new tetracoordinate^[11,12] and even hypercoordinate planar carbon molecules.^[13–16]

Notably, a series of hypercoordinate planar carbon species with boron ligands have been proposed.^[13–15,16a,c,e] Although none of these species is the global minimum on the potential-energy surfaces, it has been suggested that they may be viable experimentally. The two proposed hexa- and heptacoordinate carbon species are D_{6h} CB₆²⁻^[13a,b,d,14c,15] and D_{7h} CB₇⁻,^[13b,14c] respectively. The CB₇⁻ species is isoelectronic to B₈²⁻, which we have shown previously to have a global-minimum D_{7h} structure with a heptacoordinate boron atom.^[17–20] The D_{7h} CB₇⁻ can be viewed as replacing the central B⁻ ion in B₈²⁻ by a C atom. Herein we report serendipitous experimental observation of CB₇⁻. It was investigated by photoelectron spectroscopy (PES) and ab initio calculations, which showed that the observed species is a C_{2v} CB₇⁻ ion in which

the C atom replaces a B⁻ ion at the rim of the D_{7h} B₈²⁻ molecular wheel.

The experiment was performed with a laser-vaporization cluster source and a magnetic-bottle photoelectron spectrometer (see Experimental Section).^[21] We recently modified our cluster source by adding a 10-cm-long and 0.3-cm-diameter stainless steel tube to enhance cluster cooling.^[22] We were using boron clusters, which we have previously investigated extensively,^[17–20,23–28] to test the new cluster-source conditions. A ¹⁰B-enriched disk target containing a small amount of Au was used as the laser-vaporization target.^[23] Under certain conditions, when the vaporization laser was not perfectly aligned, we noted that in addition to the pure boron clusters we were also able to produce clusters containing one or two carbon atoms, as shown in Figure 1. The carbon most likely

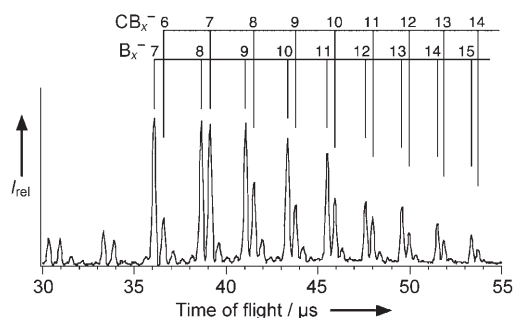


Figure 1. Mass spectrum of B_x⁻ and C_yB_x⁻ clusters from a ¹⁰B-enriched boron target. The B_x⁻ and C_yB_x⁻ series are marked. Lower mass intensities for the C₂B_x⁻ and C₃B_x⁻ series can also be seen.

originated from impingement of the slightly misaligned vaporization laser beam on the stainless steel tubing. The trace amount of carbon contamination was ideal to produce boron clusters doped with only one or two carbon atoms, and the beam condition was stable and reproducible.

The peak of the CB₇⁻ cluster is particularly intense with abundance as strong as those of the nearby pure B_x⁻ clusters (Figure 1). Its photoelectron spectra at two detachment laser wavelengths are shown in Figure 2. The 193-nm spectrum reveals five well-separated bands (X, A–D), and the B band exhibits a short vibrational progression with a frequency of (1050 ± 60) cm⁻¹. The 355-nm spectrum shows a much better resolved X band, which seems to also display a short vibrational progression. However, the broad line width suggests that more than one low-frequency mode may also be involved in the X band. The onset of the X band yields an adiabatic detachment energy or electron affinity for CB₇⁻ of (2.99 ± 0.03) eV. The vertical detachment energies (VDEs)

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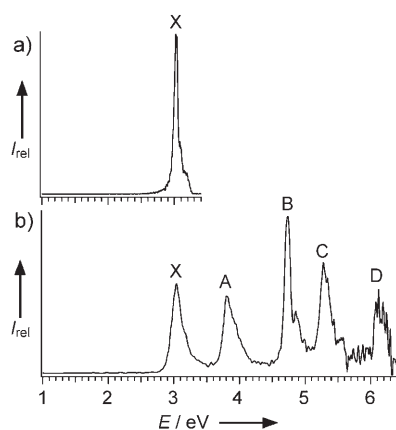


Figure 2. Photoelectron spectra of CB_7^- at a) 355 nm (3.496 eV) and b) 193 nm (6.424 eV).

are given in Table 1, in comparison with theoretical results at several levels of theory.

Table 1: Comparison of the experimental VDEs of CB_7^- to the calculated values for the global-minimum C_{2v} structure and the high-lying D_{7h} isomer. All energies are in eV.

Feature	VDE (exp) ^[a]	Final state and electronic configuration	VDE (theor)		
			TD-B3LYP	OVGF ^[b]	$\Delta\text{CCSD(T)}$ ^[c]
$\text{CB}_7^- (C_{2v}, {}^1A_1)$					
X ^[d]	3.03 (2)	${}^2A_2, 4a_1^2 1b_1^2 5a_1^2 6a_1^2 4b_2^2 2b_1^2 1a_2^1$	2.90	2.94 (0.89)	3.04
A	3.80 (3)	${}^2B_1, 4a_1^2 1b_1^2 5a_1^2 6a_1^2 4b_2^2 2b_1^2 1a_2^2$	3.79	3.81 (0.88)	3.86
B ^[e]	4.73 (3)	${}^2B_2, 4a_1^2 1b_1^2 5a_1^2 6a_1^2 4b_2^2 2b_1^2 1a_2^2$	4.66	4.80 (0.89)	4.78
C	5.28 (3)	${}^2A_1, 4a_1^2 1b_1^2 5a_1^2 6a_1^2 4b_2^2 2b_1^2 1a_2^2$	5.17	5.24 (0.88)	5.35
D	6.2 (1)	${}^2A_1, 4a_1^2 1b_1^2 5a_1^2 6a_1^2 4b_2^2 2b_1^2 1a_2^2$	6.10	6.29 (0.87)	
$\text{CB}_7^- (D_{7h}, {}^1A_1)$					
		${}^2E_1'', 2a_1^2 1a_2^2 1e_3^2 2e_1^4 1e_1^3$	2.86	2.86 (0.89)	2.98
		${}^2E_1', 2a_1^2 1a_2^2 1e_3^2 2e_1^4 1e_1^3$	5.40	5.29 (0.89)	5.51
		${}^2E_3', 2a_1^2 1a_2^2 1e_3^2 2e_1^4 1e_1^3$	6.18	6.34 (0.87)	
		${}^2A_2'', 2a_1^2 1a_2^2 1e_3^2 2e_1^4 1e_1^3$	7.04	6.77 (0.65)	

[a] Numbers in parentheses represent the uncertainty in the last digit. [b] VDEs were calculated at the ROVGF/6-311 + G(2df)//RCCSD(T)/6-311 + G* level of theory. Values in parentheses represent the pole strength of the OVGF calculation. [c] VDEs were calculated at the UCCSD(T)/6-311 + G(2df)//RCCSD(T)/6-311 + G* level of theory. [d] The adiabatic detachment energy of the X band or the electron affinity of CB_7^- is (2.99 ± 0.03) eV. [e] The vibrational frequency observed for this band is (1050 ± 60) cm^{-1} .

In our calculations (see Theoretical Section), we first tested the two planar wheel structures of CB_7^- in which the C atom substitutes either the central B atom (D_{7h}) or a rim B atom (C_{2v}) in the B_8^{2-} molecular wheel. We found that the C_{2v} structure is overwhelmingly favored and is more stable than the D_{7h} structure with heptacoordinate carbon by 63.9 kcal mol^{-1} at the B3LYP/6-311 + G* level and 63.1 kcal mol^{-1} at the CCSD(T)/6-311 + G(2df)//CCSD(T)/6-311 + G* level. We further searched the potential-energy surface for the global minimum and other low-lying structures using the GEGA method,^[29,30] and the twelve low-lying isomers are shown in Figure 3 (the genetic algorithm is known to be a reliable tool for finding global-minimum structures). The C_{2v} wheel structure (no. 1) was found to be the global minimum, and the closest-lying isomer (no. 2, C_s) is 37.6 kcal mol^{-1}

(CCSD(T)/6-311 + G(2df)//B3LYP/6-311 + G*) higher in energy.

The VDEs from the C_{2v} structure and the D_{7h} isomer were calculated by three theoretical methods (Table 1), which are consistent with each other. We found that the calculated VDEs for the first five detachment channels from the C_{2v} structure are in excellent agreement with the experimental PES data, whereas those from the D_{7h} isomer totally disagree with the experiment. The excellent agreement between experiment and theory confirmed unequivocally the C_{2v} molecular wheel global minimum for CB_7^- .

To understand the difference in stability and chemical bonding in the two different molecular-wheel structures of CB_7^- , we analyzed their valence molecular orbitals (Figure 4). The MOs of D_{7h} CB_7^- (Figure 4b) are identical to those of the B_8^{2-} molecular wheel,^[17–19] that is, the ion is doubly aromatic with six totally delocalized π electrons (HOMO, $1e_1'$ and HOMO–3, $1a_1''$) and six totally delocalized σ electrons (HOMO–1, $2e_1'$ and HOMO–4, $2a_1'$), as well as seven MOs (HOMO–2, $1e_3'$, HOMO–5, $1e_2'$, HOMO–6,

$1e_1'$, and HOMO–7, $1a_1'$) which can be localized into seven two-center, two-electron (2c–2e) B–B peripheral bonds. The MOs of the C_{2v} structure (Figure 4a) are rather similar to those of the D_{7h} isomer; this ion is also π -aromatic with six totally delocalized π electrons (HOMO, $1a_2$, HOMO–1, $2b_1$, and HOMO–5, $1b_1$). There are also seven MOs (HOMO–4, $5a_1$, HOMO–7, $3b_2$, HOMO–8, $3a_1$, HOMO–9, $2b_2$, HOMO–10, $1b_2$, HOMO–11, $2a_1$, and HOMO–12, $1a_1$) that can be localized into five 2c–2e peripheral B–B and two 2c–2e C–B peripheral bonds, similar to those in the D_{7h} isomer. The only major difference from the MOs of the D_{7h} isomer is shown by the HOMO–6, $4a_1$ of the C_{2v} isomer, in which the peripheral electron delocalization is broken between the two boron atoms located on

the opposite side to the carbon atom; the corresponding HOMO–4, $2a_1'$ in the D_{7h} isomer is a completely delocalized σ -bonding orbital. An enhancement is also evident in the area between these two boron atoms in HOMO–3 $6a_1$ (Figure 4a).

Hence, the σ aromaticity in the C_{2v} isomer of CB_7^- is less pronounced, though we think that this structure is still σ -aromatic from HOMO–2, $4b_2$, HOMO–3, $6a_1$, and HOMO–6, $4a_1$. In the D_{7h} isomer the bonding between the central carbon atom and the peripheral boron ring is completely delocalized (doubly σ - and π -aromatic), while in the C_{2v} structure, the carbon atom is involved in the two 2c–2e B–C peripheral bonds, in addition to participation in the delocalized σ and π bonding. Carbon is known to form strong 2c–2e σ bonds because of its high valence charge that makes its peripheral position significantly more favorable than the

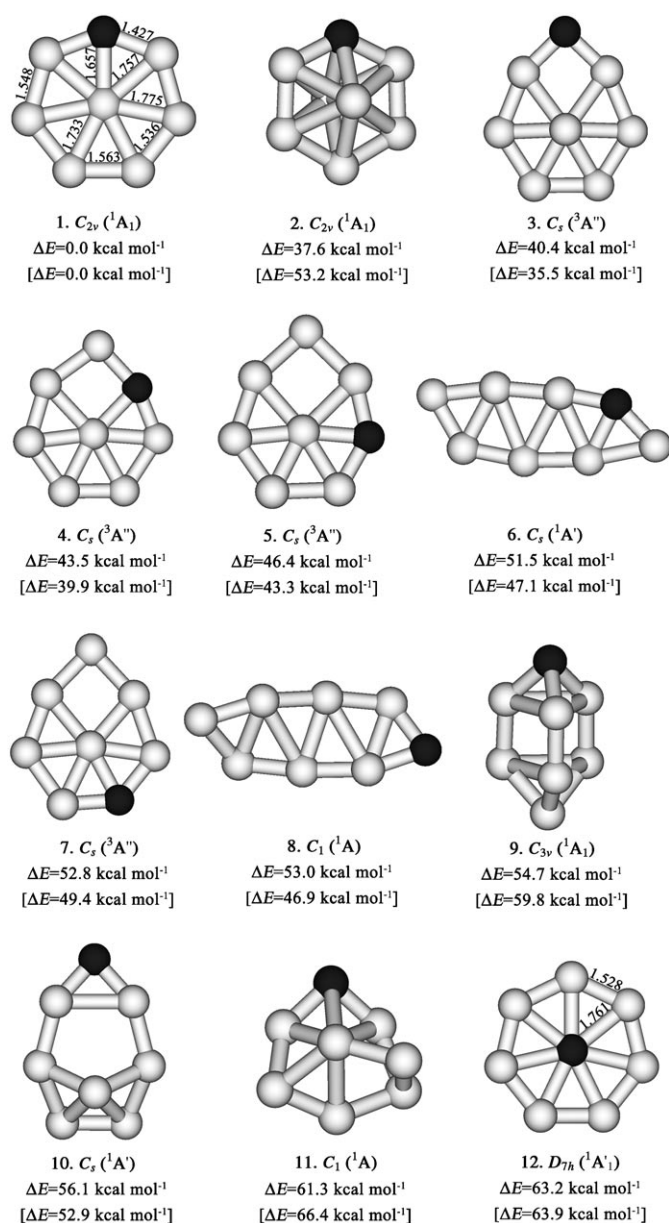


Figure 3. Optimized isomers (B3LYP/6-311 + G*) and relative energies of CB_7^- (CCSD(T)/6-311 + G(2df)//B3LYP/6-311 + G*). The relative energies in brackets are at the B3LYP/6-311 + G* level.

central position. On the other hand, boron is known to participate in delocalized σ bonding because of its relatively low valence charge, which makes the doubly aromatic C_{2v} structure (no. 1 in Figure 3) the most stable. The current experimental and theoretical study shows that heptacoordinate carbon in the C–B system is extremely unfavorable.

The low symmetry of the global-minimum structure of CB_7^- leads to a dipole moment (1.4 D at the B3LYP/6-311 + G* level), and this makes it possible to use the CB_7^- cluster for rotary motion, similar to that experimentally observed in metallocarboranes^[33] by Hawthorne and co-workers, if the CB_7^- anion is incorporated into a sandwichlike structure.

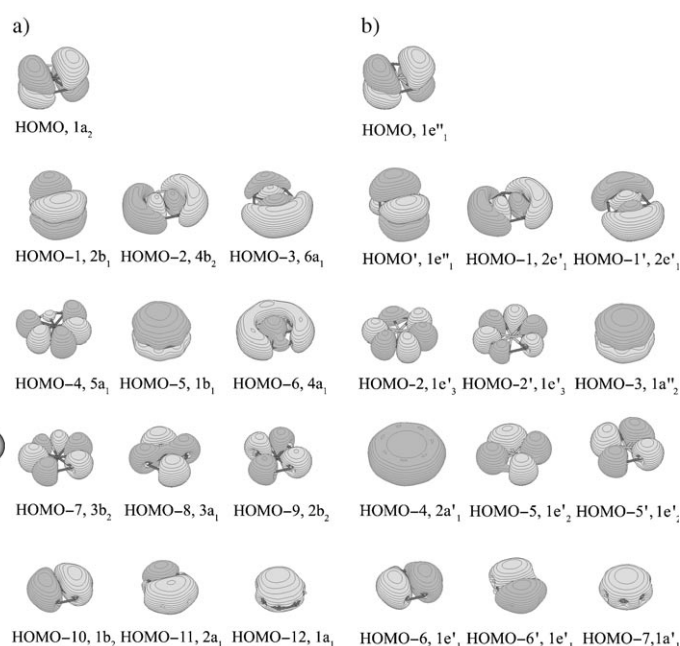


Figure 4. Comparison of the valence molecular orbitals of a) the C_{2v} structure and b) the high-lying D_{7h} isomer of CB_7^- .

Experimental Section

Photoelectron spectroscopy: The $C_nB_x^-$ clusters were produced by laser vaporization of a ^{10}B -enriched disk target containing 60% ^{10}B and 40% Au by atom for mass calibration. The carbon originated from the long stainless steel tubing in the source due to a slight misalignment. Subsequently we also prepared a $^{10}B/C$ mixed target containing 5% C and produced $C_nB_x^-$ clusters similar to those shown in Figure 1. Negatively charged clusters were extracted from the cluster beam and were analyzed with a time-of-flight mass spectrometer (Figure 1).^[21] The CB_7^- clusters of interest were mass-selected and decelerated before being intercepted by a 193-nm laser beam from an ArF excimer laser or a 355-nm laser beam from an Nd:YAG laser for photodetachment. Photoelectron time-of-flight spectra were calibrated by using the known spectra of Au^- and Rh^- and converted to binding-energy spectra by subtracting the kinetic-energy spectra from the photon energies. The resolution of the magnetic-bottle PES spectrometer was $\Delta E/E \approx 2.5\%$, that is, about 25 meV for 1-eV electrons.

Theoretical Section

Calculations: We searched for the global minimum of CB_7^- using a gradient-embedded genetic algorithm (GEGA) program,^[29,30] with the B3LYP/3-21G method for energy, gradient, and force calculations. We reoptimized geometries and calculated frequencies for the lowest twelve isomers at the B3LYP/6-311 + G* level of theory. We also recalculated geometries of the C_{2v} 1A_1 and D_{7h} 1A_1 structures of CB_7^- using the CCSD(T)/6-311 + G* method. Total energies of the twelve local minimum structures were also recalculated at the CCSD(T)/6-311 + G(2df)//B3LYP/6-311 + G* level of theory.

The CB_7^- VDEs were calculated by using the R(U)CCSD(T)/6-311 + G(2df) method, the outer-valence Green Function method (ROVGF/6-311 + G(2df)) at the RCCSD(T)/6-311 + G* geometries, and the time-dependent DFT method (TD B3LYP/6-311 + G(2df)) at the B3LYP/6-311 + G* geometries. All calculations were performed with the Gaussian03 program.^[31] Molecular orbitals were visualized with the MOLDEN3.4 program.^[32]

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