Supporting Information:

Boronyls as Key Structural Units in Boron Oxide Clusters:

B(BO)_2^- and B(BO)_3^-

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Experimental and Computational Methods.

Table S1. Calculated Ground State Molecular Properties of B(BO)_2^- and B(BO)_3^- and Their Neutrals.

Table S2. Calculated Vertical Electron Detachment Energies of B(BO)_2^- ($D_{\infty h}$, $^3\Sigma_g$) and B(BO)_3^- (D_{3h} , $^2A_2''$) via TDDFT.

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Experimental and Computational Methods.

Photoelectron Spectroscopy. The experiments were carried out using a magnetic-bottle-type PES apparatus equipped with a laser vaporization supersonic cluster source, details of which have been described previously.^{S1} Briefly, the boron oxide cluster anions were produced by laser vaporization of a pure disk target made of enriched ^{10}B isotope (99.75%) in the presence of either a pure helium carrier gas or that seeded with 0.01% O_2 . The B_mO_n^- cluster distribution was analyzed using a time-of-flight mass spectrometer. The B_3O_2^- and B_4O_3^- species of current interest were each mass-selected and decelerated before being photodetached. Three detachment photon energies were used in the current study: 355 nm (3.496 eV), 266 nm (4.661 eV), and 193 nm (6.424 eV). Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 meter long electron flight tube. The PES spectra were calibrated using the known spectrum of Rh^- and Au^- , and the resolution of the apparatus was $\Delta E_k/E_k \sim 2.5\%$, that is, ~ 25 meV for 1 eV electrons.

Computational Methods. DFT structural optimizations and frequency analyses were performed using the hybrid B3LYP procedure^{S2} with the augmented Dunning's all-electron basis set (aug-cc-pVTZ)^{S3} implemented in Gaussian 03.^{S4} Frequency calculations were done to confirm that all obtained ground state structures are true minima. Excitation energies of the neutrals were calculated with the time-dependent DFT (TDDFT) method^{S5} at the ground state structures of the anions. All calculations were carried out using Gaussian 03.^{S4}

References:

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Table S1. Calculated Ground State Molecular Properties of B(BO)_2^- and B(BO)_3^- and Their Neutrals.

	B(BO)_2 ($D_{\infty h}$, $^2\Pi_u$)	B(BO)_2^- ($D_{\infty h}$, $^3\Sigma_g$)	B(BO)_3 (D_{3h} , $^1A_1'$)	B(BO)_3^- (D_{3h} , $^2A_2''$)
$E_{\text{total}}/\text{Hartree}$	-225.0973586	-225.2080259	-325.3219391	-325.4597289
$R_{\text{B-B}}/\text{\AA}$	1.604	1.577	1.660	1.631
$R_{\text{B=O}}/\text{\AA}$	1.209 ^a	1.233 ^a	1.203 ^a	1.221 ^a
ω_1	58 (π_u) 119 (π_u)	84 (π_u)	89 (e')	90 (e')
ω_2	313 (π_g) 371 (π_g)	423 (π_g)	128 (a_2'')	128 (a_2'')
ω_3	379 (π_u) 534 (π_u)	444 (π_u)	293 (e'')	392 (e'')
ω_4	471 (σ_g) ^b	491 (σ_g)	328 (a_2')	379 (a_2')
ω_5	1110 (σ_u)	1139 (σ_u)	425 (a_1') ^c	436 (a_1')
ω_6	1971 (σ_u)	1831 (σ_u)	484 (e')	517 (e')
ω_7	1969 (σ_g) ^b	1849 (σ_g)	595 (a_2'')	535 (a_2'')
ω_8			931 (e')	951 (e')
ω_9			1992 (a_1') ^c	1902 (a_1')
ω_{10}			2001 (e')	1880 (e')

^a For comparison, the bond distances in free BO ($^2\Sigma^+$) and BO^- ($^1\Sigma^+$) species are 1.203 and 1.234 $\text{\AA}$, respectively, at the same level of theory.

^b 471(σ_g) and 1969(σ_g) are symmetric vibrational frequencies of B(BO)_2 .

^c 425(a_1') and 1992(a_1') are symmetric vibrational frequencies of B(BO)_3 .

Table S2. Calculated Vertical Electron Detachment Energies of B(BO)_2^- ($D_{\infty h}$, $^3\Sigma_g$) and B(BO)_3^- (D_{3h} , $^2A_2''$) via TDDFT.

anion	MO	transition	theo ADE (eV)	theo VDE (eV)
B(BO)_2^- ($D_{\infty h}$, $^3\Sigma_g$)	HOMO (π_u)	$^3\Sigma_g \rightarrow ^2\Pi_u$	3.012	3.074
	HOMO-1 (π_g)	$^3\Sigma_g \rightarrow ^2\Pi_g$		6.423 ^a
	HOMO-2 (π_u)	$^3\Sigma_g \rightarrow ^2\Pi_u$		6.538 ^a
B(BO)_3^- (D_{3h} , $^2A_2''$)	HOMO (a_2'')	$^2A_2'' \rightarrow ^1A_1'$	3.749	3.815
	HOMO-1 (e')	$^2A_2'' \rightarrow ^3E''$		6.947
	HOMO-3 (e'')	$^2A_2'' \rightarrow ^3E'$		6.983
	HOMO-2 (a_2')	$^2A_2'' \rightarrow ^3A_1''$		7.201
	HOMO-4 (a_2'')	$^2A_2'' \rightarrow ^3A_1'$		7.213

^a Quartet final states can not be calculated using TDDFT, but the quartet-doublet splitting is expected to be small. For example, the first quartet final state of B(BO)_2 corresponds to a VDE of 6.78 eV, according to B3LYP calculations.

Figure S1. Alternative optimized structures of the B_3O_2^- anion. Bond distances are given in Å. Also labeled are symmetry and state, relative total energy in eV (***bold italic***), minimum frequency ($\nu_{\min}$) in cm^{-1} , and number of imaginary frequencies (N_{imag}).

$D_{\infty h} (^3\Sigma_g) \textbf{0.00} +83 (N_{\text{imag}}=0)$

$C_{2v} (^1A_1) +\textbf{0.75} +70 (N_{\text{imag}}=0)$

$C_{2v} (^3A_2) +\textbf{1.40} +242 (N_{\text{imag}}=0)$

$C_{2v} (^1A_1) +\textbf{1.97} +225 (N_{\text{imag}}=0)$

$D_{3h} (^1A_1') +\textbf{7.06} -322 (N_{\text{imag}}=2)$

Figure S2. Same as Figure S1 but for the B₃O₂ neutral.

$D_{\infty h} (^2\Pi_u)$ **0.00** +58 ($N_{\text{imag}}=0$)

$C_{2v} (^2B_2)$ **+3.11** -282 ($N_{\text{imag}}=1$)

$C_{2v} (^2B_1)$ **+3.28** -298 ($N_{\text{imag}}=1$)

$C_{2v} (^2A_1)$ **+1.52** +210 ($N_{\text{imag}}=0$)

Figure S3. Same as Figure S1 but for the B_4O_3^- anion.

$D_{3h} (^2A_2'')$ **0.00** +90 ($N_{\text{imag}}=0$)

$C_{2v} (^2B_1)$ **+3.79** -69 ($N_{\text{imag}}=2$)

$C_{2v} (^2A_2)$ **+4.26** +138 ($N_{\text{imag}}=0$)

$C_{2v} (^2B_1)$ **+5.13** -15 ($N_{\text{imag}}=1$)

$C_{2v} (^2B_2)$ **+5.21** -871 ($N_{\text{imag}}=3$)

Figure S4. Same as Figure S1 but for the B₄O₃ neutral.

$D_{3h} (^1A_1')$ **0.00** +89 (N_{imag}=0)

$C_{2v} (^1A_1)$ **+2.70** -80 (N_{imag}=1)

$C_{2v} (^3B_1)$ **+3.46** +132 (N_{imag}=0)

$C_{2v} (^1A_1)$ **+3.74** +90 (N_{imag}=0)

$C_{2v} (^1A_1)$ **+5.18** -482 (N_{imag}=2)

Figure S5. Molecular Orbital Pictures of $\text{B}(\text{BO})_2^-$ ($D_{\infty h}$, $^3\Sigma_g$) and $\text{B}(\text{BO})_3^-$ (D_{3h} , $^2A_2''$) as Compared with Those of the BO^- Radical.

BO^-	$\text{B}(\text{BO})_2^-$	$\text{B}(\text{BO})_3^-$
	HOMO (π_u)	HOMO (a_2'')
HOMO-1 (1π)	HOMO-1 (π_g)	HOMO-1 (e')
	HOMO-2 (π_u)	HOMO-2 (a_2')
HOMO-2 (2σ)	HOMO-3 (σ_u)	HOMO-3 (e'')
	HOMO-4 (σ_g)	HOMO-4 (a_2'')
HOMO (3σ)	HOMO-5 (σ_u)	HOMO-5 (e')
	HOMO-6 (σ_g)	HOMO-6 (a_1')
HOMO-3 (1σ)	HOMO-7 (σ_u)	HOMO-7 (e')
	HOMO-8 (σ_g)	HOMO-8 (a_1'')
		HOMO-9 (e')
		HOMO-10 (a_1')