## Supplementary Information

# Chemical bonding in electron-deficient boron oxide clusters: core boronyl group, dual 3c-4e hypervalent bond, and rhombic $4 \mathrm{c}-4 \mathrm{e}$ bond $\dagger$ 

Qiang Chen, Haigang Lu, Hua-Jin Zhai,* and Si-Dian Li*<br>Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China<br>E-mail: hj.zhai@sxu.edu.cn; lisidian@sxu.edu.cn

## Full citation of ref 22.

Tables S1-S7 Natural charges, natural resonance theory (NRT) bond orders and atomic valencies for the global-minimum structures 3-9 of $\mathrm{B}_{3} \mathrm{O}_{2}^{+}, \mathrm{B}_{3} \mathrm{O}_{3}{ }^{-/ 0 /+}$, and $\mathrm{B}_{3} \mathrm{O}_{4}{ }^{-10 /+}$.

Table S8 Calculated vertical electron detachment energies (VDEs) at the TD-B3LYP level based on the global minimum structures $\mathrm{D}_{\infty \mathrm{h}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{-}\left(1,{ }^{3} \Sigma_{\mathrm{g}}\right), \mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}{ }^{-}\left(4,{ }^{1} \mathrm{~A}_{1}\right)$, and $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}^{-}\left(7,{ }^{1} \mathrm{~A}_{1}\right)$.

Figs. S1-S7 Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}, \mathrm{B}_{3} \mathrm{O}_{3}{ }^{-10 / 4}$, and $\mathrm{B}_{3} \mathrm{O}_{4}^{-/ 0 /+}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and $\operatorname{CCSD}(\mathrm{T}) / / \mathrm{B} 3 \mathrm{LYP} /$ aug-cc-pVTZ (in curly brackets). The structures were obtained initially using the Coalescence Kick and Basin Hopping global-minimum search programs at B3LYP/3-21G.

Figs. S8-S15 AdNDP bonding patterns and canonical molecular orbitals (CMOs) for the global-minimum structures 3-9 of $\mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}, \mathrm{B}_{3} \mathrm{O}_{3}^{-/ 0 /+}$, and $\mathrm{B}_{3} \mathrm{O}_{4}{ }^{-/ 0 /+}$. A low-lying $\mathrm{D}_{\infty \mathrm{h}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \Sigma_{\mathrm{g}}\right)$ structure is also analyzed.

## Full citation of ref 22.

22 Gaussian 09, Revision A.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R.

Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A.
Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B.
Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Table S1. Natural resonance theory (NRT) bond orders and atomic valencies of $\mathrm{C}_{\infty \mathrm{ov}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left(\mathbf{3},{ }^{1} \Sigma\right)$ at B3LYP/aug-cc- pVTZ. The bond lengths (in $\AA$ ) and natural atomic charges (in lel) are also labeled.


|  |  | Natural Bond Order |  |  |  | Natural Atomic Valency |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{B}_{1}-\mathrm{O}_{4}$ | $\mathrm{~B}_{2}-\mathrm{B}_{3}$ | $\mathrm{~B}_{2}-\mathrm{O}_{4}$ | $\mathrm{~B}_{3}-\mathrm{O}_{5}$ | $\mathrm{O}_{5}$ | $\mathrm{~B}_{3}$ | $\mathrm{~B}_{2}$ | $\mathrm{O}_{4}$ | $\mathrm{~B}_{1}$ |
| NRT | $\mathrm{t}^{\mathrm{a}}$ | 1.03 | 1.03 | 2.93 | 2.97 | 2.97 | 3.99 | 3.95 | 3.97 | 1.03 |
|  | c | 0.17 | 0.93 | 0.72 | 1.39 | 1.39 | 2.32 | 1.65 | 0.89 | 0.17 |
|  | i | 0.86 | 0.10 | 2.21 | 1.58 | 1.58 | 1.67 | 2.30 | 3.08 | 0.86 |

${ }^{a} t$, the total bond orders; $c$, the covalent bond orders of NRT; $i$, the ionic bond orders of NRT.

Table S2. Natural resonance theory (NRT) bond orders and atomic valencies of $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}{ }^{-}\left(\mathbf{4},{ }^{1} \mathrm{~A}_{1}\right)$ at B3LYP/aug-cc- pVTZ. The bond lengths (in $\AA$ ) and natural atomic charges (in lel) are also labeled.


|  |  | Natural Bond Order |  |  |  |  |  | Natural Atomic Valencies |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{B}_{1}-\mathrm{B}_{2}$ | $\mathrm{~B}_{2}-\mathrm{B}_{3}$ | $\mathrm{~B}_{1}-\mathrm{O}_{4}$ | $\mathrm{~B}_{2}-\mathrm{O}_{5}$ | $\mathrm{O}_{3}-\mathrm{O}_{6}$ | $\mathrm{O}_{6}$ | $\mathrm{~B}_{3}$ | $\mathrm{~B}_{2}$ | $\mathrm{O}_{5}$ |  |
| NRT | $\mathrm{t}^{\mathrm{a}}$ | 0.98 | 0.98 | 2.98 | 2.04 | 2.98 | 2.98 | 3.96 | 4.00 | 2.04 |  |
|  | c | 0.90 | 0.90 | 1.08 | 0.95 | 1.08 | 1.08 | 1.98 | 2.75 | 0.95 |  |
|  | i | 0.08 | 0.08 | 1.90 | 1.09 | 1.90 | 1.90 | 1.98 | 1.25 | 1.09 |  |

[^0]Table S3. Natural resonance theory (NRT) bond orders and atomic valencies of $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}\left(\mathbf{5},{ }^{2} \mathrm{~A}_{1}\right)$ at B3LYP/aug-cc- pVTZ. The bond lengths (in $\AA$ ) and natural atomic charges (in lel) are also labeled.


$$
\mathbf{C}_{2 \mathrm{v}} \mathbf{B}_{3} \mathrm{O}_{3}\left({ }^{2} \mathbf{A}_{1}\right)
$$

|  |  | Natural Bond Order |  |  |  |  |  | Natural Atomic Valency |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{B}_{1}-\mathrm{B}_{3}$ | $\mathrm{~B}_{1}-\mathrm{O}_{4}$ | $\mathrm{~B}_{1}-\mathrm{O}_{5}$ | $\mathrm{~B}_{2}-\mathrm{O}_{4}$ | $\mathrm{~B}_{2}-\mathrm{O}_{5}$ | $\mathrm{~B}_{3}-\mathrm{O}_{6}$ | $\mathrm{O}_{6}$ | $\mathrm{~B}_{3}$ | $\mathrm{~B}_{1}$ | $\mathrm{O}_{4}$ | $\mathrm{O}_{5}$ | $\mathrm{~B}_{2}$ |  |
| $\mathrm{NRT}^{\mathrm{a}}$ | t | 0.99 | 1.45 | 1.45 | 1.46 | 1.46 | 3.00 | 3.00 | 3.98 | 3.88 | 2.91 | 2.91 | 2.92 |
|  | c | 0.95 | 0.49 | 0.49 | 0.42 | 0.42 | 1.23 | 1.23 | 2.18 | 1.93 | 0.91 | 0.91 | 0.84 |
|  | i | 0.04 | 0.96 | 0.96 | 1.04 | 1.04 | 1.77 | 1.77 | 1.80 | 1.95 | 2.00 | 2.00 | 2.08 |

${ }^{\mathrm{a}} \mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}\left({ }^{2} \mathrm{~A}_{1}\right)$ possesses two leading NRT reference structures: $\mathrm{NRT}_{1}$ and $\mathrm{NRT}_{2}$.

$\mathrm{NRT}_{1} \quad 40 \%$
$\mathrm{NRT}_{2}$ 40\%

Table S4. Natural resonance theory (NRT) bond orders and atomic valencies of $\mathrm{C}_{\infty \mathrm{ov}} \mathrm{B}_{3} \mathrm{O}_{3}{ }^{+}\left(\mathbf{6},{ }^{1} \Sigma\right)$ at B3LYP/aug-cc- pVTZ. The bond lengths (in $\AA$ ) and natural atomic charges (in lel) are also labeled.


|  |  | Natural Bond Order |  |  |  |  | Natural Atomic Valencies |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{B}_{1}-\mathrm{B}_{2}$ | $\mathrm{~B}_{2}-\mathrm{B}_{3}$ | $\mathrm{~B}_{3}-\mathrm{O}_{4}$ | $\mathrm{~B}_{4}-\mathrm{O}_{5}$ | $\mathrm{~B}_{5}-\mathrm{O}_{6}$ | $\mathrm{O}_{1}$ | $\mathrm{~B}_{2}$ | $\mathrm{~B}_{3}$ | $\mathrm{O}_{4}$ | $\mathrm{~B}_{5}$ |
| NRT | $\mathrm{t}^{\mathrm{a}}$ | 2.97 | 1.02 | 2.91 | 1.04 | 2.95 | 2.97 | 3.99 | 3.93 | 3.95 | 4.00 | 2.95 |
|  | c | 1.40 | 0.93 | 0.72 | 0.34 | 1.31 | 1.40 | 2.32 | 1.65 | 1.06 | 1.65 | 1.31 |
|  | i | 1.57 | 0.09 | 2.19 | 0.70 | 1.64 | 1.57 | 1.67 | 2.28 | 2.89 | 2.35 | 1.64 |

${ }^{a} t$, the total bond orders; $c$, the covalent bond orders of NRT; $i$, the ionic bond orders of NRT.

Table S5. Natural resonance theory (NRT) bond orders and atomic valencies of $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}{ }^{-}\left(7,{ }^{1} \mathrm{~A}_{1}\right)$ at B3LYP/aug-cc- pVTZ. The bond lengths (in $\AA$ ) and natural atomic charges (in lel) are also labeled in the structure.


|  |  | Natural Bond Order |  |  |  |  |  | Natural Atomic Valency |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\mathrm{B}_{1}-\mathrm{B}_{2}$ | $\mathrm{~B}_{1}-\mathrm{O}_{5}$ | $\mathrm{~B}_{1}-\mathrm{O}_{7}$ | $\mathrm{~B}_{2}-\mathrm{O}_{6}$ | $\mathrm{~B}_{3}-\mathrm{O}_{4}$ | $\mathrm{~B}_{3}-\mathrm{O}_{5}$ | $\mathrm{~B}_{3}-\mathrm{O}_{7}$ | $\mathrm{O}_{6}$ | $\mathrm{~B}_{2}$ | $\mathrm{~B}_{1}$ | $\mathrm{O}_{5}$ | $\mathrm{O}_{7}$ | $\mathrm{~B}_{3}$ | $\mathrm{O}_{4}$ |
| $\mathrm{NRT}^{\mathrm{a}}$ | $\mathrm{t}^{\mathrm{b}}$ | 0.99 | 1.47 | 1.47 | 2.99 | 2.04 | 1.38 | 1.38 | 2.99 | 3.98 | 3.93 | 2.86 | 2.86 | 4.81 | 2.04 |  |
|  | c | 0.95 | 0.53 | 0.53 | 1.13 | 0.82 | 0.34 | 0.34 | 1.13 | 2.08 | 2.01 | 0.88 | 0.88 | 1.51 | 0.82 |  |
|  | i | 0.04 | 0.94 | 0.94 | 1.86 | 1.22 | 1.04 | 1.04 | 1.86 | 1.90 | 1.92 | 1.98 | 1.98 | 3.30 | 1.22 |  |

${ }^{\mathrm{a}} \mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}{ }^{-}\left({ }^{1} \mathrm{~A}_{1}\right)$ possesses two significant NRT reference structures: $\mathrm{NRT}_{1}$ and $\mathrm{NRT}_{2}$.

$\mathrm{NRT}_{1} \quad 32 \%$

$\mathrm{NRT}_{2} \quad 32 \%$
${ }^{\mathrm{b}} \mathrm{t}$, the total bond orders; c , the covalent bond orders of NRT; i , the ionic bond orders of NRT.

Table S6. Natural resonance theory (NRT) bond orders and atomic valencies of $\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left(\mathbf{8},{ }^{2} \mathrm{~A}^{\prime}\right)$ at B3LYP/aug-cc- pVTZ. The bond lengths (in $\AA$ ) and natural atomic charges (in lel) are also labeled.

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{\mathbf{2}} \mathrm{A}^{\prime}\right)$

|  |  | Natural Bond Order |  |  |  |  |  |  | Natural Atomic Valencies |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{B}_{1}-\mathrm{O}_{4}$ | $\mathrm{B}_{1}-\mathrm{O}_{5}$ | $\mathrm{B}_{2}-\mathrm{O}_{6}$ | $\mathrm{B}_{2}-\mathrm{O}_{7}$ | $\mathrm{B}_{3}-\mathrm{O}_{4}$ | $\mathrm{B}_{3}-\mathrm{O}_{5}$ | $\mathrm{B}_{3}-\mathrm{O}_{6}$ | $\mathrm{O}_{7}$ | $\mathrm{B}_{2}$ | $\mathrm{O}_{6}$ | $\mathrm{B}_{3}$ | $\mathrm{O}_{4}$ | $\mathrm{O}_{5}$ | $\mathrm{B}_{1}$ |
| $\mathrm{NRT}^{\text {a }}$ | t | 1.47 | 1.47 | 1.08 | 2.91 | 1.42 | 1.42 | 1.04 | 2.91 | 3.99 | 2.12 | 3.88 | 2.89 | 2.89 | 2.93 |
|  | c | 0.43 | 0.43 | 0.39 | 1.16 | 0.48 | 0.48 | 0.40 | 1.16 | 1.56 | 0.79 | 1.36 | 0.91 | 0.90 | 0.85 |
|  | i | 1.04 | 1.04 | 0.69 | 1.75 | 0.94 | 0.94 | 0.64 | 1.75 | 2.43 | 1.33 | 2.52 | 1.98 | 1.98 | 2.08 |

${ }^{\mathrm{a}} \mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$ possesses two leading NRT reference structures: $\mathrm{NRT}_{1}$ and $\mathrm{NRT}_{2}$.


Table S7. Natural resonance theory (NRT) bond orders and atomic valencies of $\mathrm{D}_{\infty \mathrm{h}} \mathrm{B}_{3} \mathrm{O}_{4}{ }^{+}\left(9,{ }^{1} \Sigma_{\mathrm{g}}\right)$ at B3LYP/aug-cc- pVTZ. The bond lengths (in $\AA$ ) and natural atomic charges (in lel) are also labeled.


|  |  | Natural Bond Order |  |  |  |  | Natural Atomic Valencies |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{O}_{1}-\mathrm{B}_{2}$ | $\mathrm{B}_{2}-\mathrm{O}_{7}$ | $\mathrm{B}_{3}-\mathrm{O}_{7}$ | $\mathrm{B}_{3}-\mathrm{O}_{4}$ | $\mathrm{O}_{4}-\mathrm{B}_{5}$ | $\mathrm{B}_{5}-\mathrm{O}_{6}$ | $\mathrm{O}_{1}$ | $\mathrm{B}_{2}$ | $\mathrm{O}_{7}$ | $\mathrm{B}_{3}$ |
| NRT ${ }^{\text {a }}$ | $\mathrm{T}^{\text {b }}$ | 2.96 | 1.04 | 1.97 | 1.97 | 1.04 | 2.95 | 2.96 | 3.99 | 3.00 | 3.93 |
|  | c | 1.30 | 0.34 | 0.55 | 0.55 | 0.34 | 1.30 | 1.30 | 1.64 | 0.89 | 1.10 |
|  | i | 1.66 | 0.70 | 1.42 | 1.42 | 0.70 | 1.65 | 1.66 | 2.35 | 2.11 | 2.83 |

${ }^{\mathrm{a}} \mathrm{D}_{\infty \mathrm{h}} \mathrm{B}_{3} \mathrm{O}_{4}{ }^{+}\left({ }^{1} \Sigma_{\mathrm{g}}\right)$ possesses three significant NRT reference structures: $\mathrm{NRT}_{1}, \mathrm{NRT}_{2}$ and $\mathrm{NRT}_{3}$.

${ }^{\mathrm{b}} \mathrm{t}$, the total bond orders; c , the covalent bond orders of NRT; i, the ionic bond orders of NRT.

Table S8. Calculated vertical electron detachment energies (VDEs) at the TD-B3LYP level based on the global minimum structures $\mathrm{D}_{\infty \mathrm{h}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{-}\left(\mathbf{1},{ }^{3} \Sigma_{\mathrm{g}}\right), \mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}{ }^{-}\left(\mathbf{4},{ }^{1} \mathrm{~A}_{1}\right)$, and $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}{ }^{-}\left(7,{ }^{1} \mathrm{~A}_{1}\right)$.

| Species | Feature | Final State | VDE $(\mathrm{eV})$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{B}_{3} \mathrm{O}_{2}{ }^{-} \mathrm{D}_{\boldsymbol{\infty}}\left(\mathbf{1},{ }^{3} \Sigma_{\mathrm{g}}\right)$ | X | ${ }^{2} \Pi_{\mathrm{u}}$ | 3.07 |
| $\mathrm{~B}_{3} \mathrm{O}_{3}{ }^{-} \mathrm{C}_{2 \mathrm{v}}\left(\mathbf{4},{ }^{1} \mathrm{~A}_{1}\right)$ | A | ${ }^{2} \Pi_{\mathrm{u}}$ | 6.43 |
| $\mathrm{~B}_{3} \mathrm{O}_{4}{ }^{-} \mathrm{C}_{2 \mathrm{v}}\left(\mathbf{7},{ }^{1} \mathrm{~A}_{1}\right)$ | X | ${ }^{2} \mathrm{~B}_{2}$ | 4.06 |
|  | X | ${ }^{2} \mathrm{~B}_{2}$ | 6.40 |

Figure S1. Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and CCSD(T)//B3LYP/aug-cc-pVTZ (in curly brackets).

The structures were obtained initially using the Coalescence Kick and Basin Hopping global-minimum search programs at B3LYP/3-21G.


$$
\begin{gathered}
\left.\mathrm{C}_{\infty \mathrm{ov}} \mathrm{~B}_{3} \mathrm{O}_{2}^{+}{ }^{1} \Sigma\right) \\
+5 \mathrm{~cm}^{-1} \\
0.00 \mathrm{kcal} / \mathrm{mol} \\
\{0.00 \mathrm{kcal} / \mathrm{mol}\}
\end{gathered}
$$


$\mathrm{C}_{5} \mathrm{~B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \mathrm{~A}^{\prime}\right)$ $+142 \mathrm{~cm}^{-1}$
$+16.82 \mathrm{kcal} / \mathrm{mol}$
$\{+20.12 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \mathrm{~A}_{1}\right)$
$+178 \mathrm{~cm}^{-1}$
$+56.52 \mathrm{kcal} / \mathrm{mol}$


$$
\mathrm{D}_{\mathrm{olh}} \mathrm{~B}_{3} \mathrm{O}_{2}^{+}\left(^{1} \Sigma_{\mathrm{g}}\right)
$$

$$
+97 \mathrm{~cm}^{-1}
$$

$+7.72 \mathrm{kcal} / \mathrm{mol}$
$\{+14.49 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{\infty \mathrm{ov}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \Sigma\right)$
$+61 \mathrm{~cm}^{-1}$
$+32.53 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \mathrm{~A}_{1}\right)$
$+125 \mathrm{~cm}^{-1}$
$+77.48 \mathrm{kcal} / \mathrm{mol}$


$$
\mathrm{C}_{2 \mathrm{~h}} \mathrm{~B}_{3} \mathrm{O}_{2}^{+}\left({ }^{1} \mathrm{~A}_{\mathrm{g}}\right)
$$

$$
+19 \mathrm{~cm}^{-1}
$$

$$
+16.10 \mathrm{kcal} / \mathrm{mol}
$$

$\{+13.01 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \mathrm{~A}_{1}\right)$ $+310 \mathrm{~cm}^{-1}$ $+45.80 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \mathrm{~A}_{1}\right)$ $+63 \mathrm{~cm}^{-1}$
$+85.22 \mathrm{kcal} / \mathrm{mol}$

Figure S2. Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{3}{ }^{-}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and CCSD(T)//B3LYP/aug-cc-pVTZ (in curly brackets).
The structures were obtained initially using the Coalescence Kick and Basin Hopping global-minimum search programs at B3LYP/3-21G.


Figure S3. Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{3}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and CCSD(T)//B3LYP/aug-cc-pVTZ (in curly brackets).

The structures were obtained initially using the Coalescence Kick and Basin Hopping global-minimum search programs at B3LYP/3-21G.


Figure S4. Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{3}{ }^{+}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and $\operatorname{CCSD}(\mathrm{T}) / / \mathrm{B} 3 \mathrm{LYP} /$ aug-cc-pVTZ (in curly brackets).

The structures were obtained initially using the Coalescence Kick and Basin Hopping global-minimum search programs at B3LYP/3-21G.


Figure S5. Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{4}{ }^{-}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and CCSD(T)//B3LYP/aug-cc-pVTZ (in curly brackets).

The structures were obtained initially using the Coalescence Kick and Basin Hopping global-minimum search programs at B3LYP/3-21G.

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}^{-}\left({ }^{1} \mathrm{~A}_{1}\right)$
$+87 \mathrm{~cm}^{-1}$
$0.00 \mathrm{kcal} / \mathrm{mol}$
$\{0.00 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}^{-}\left({ }^{1} \mathrm{~A}^{\prime}\right)$
$+60 \mathrm{~cm}^{-1}$
$+19.66 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}^{-}\left({ }^{1} \mathrm{~A}^{\prime}\right)$
$+65 \mathrm{~cm}^{-1}$
$+34.76 \mathrm{kcal} / \mathrm{mol}$


$$
\begin{gathered}
\mathrm{C}_{2 \mathrm{v}} \mathrm{~B}_{3} \mathrm{O}_{4}^{-}\left({ }^{1} \mathrm{~A}_{1}\right) \\
+87 \mathrm{~cm}^{-1} \\
+114.75 \mathrm{kcal} / \mathrm{mol}
\end{gathered}
$$


$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}-\left({ }^{1} \mathrm{~A}^{\prime}\right)$
$+57 \mathrm{~cm}^{-1}$
$+0.09 \mathrm{kcal} / \mathrm{mol}$
$\{+3.90 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}^{-}\left({ }^{1} \mathrm{~A}_{1}\right)$
$+58 \mathrm{~cm}^{-1}$
$+20.10 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}-\left({ }^{1} \mathrm{~A}_{1}\right)$
$+95 \mathrm{~cm}^{-1}$
$+52.10 \mathrm{kcal} / \mathrm{mol}$


$$
\begin{gathered}
\mathrm{C}_{\mathrm{s}} \mathrm{~B}_{3} \mathrm{O}_{4}^{-}\left({ }^{1} \mathrm{~A}^{\prime}\right) \\
+111 \mathrm{~cm}^{-1} \\
+128.51 \mathrm{kcal} / \mathrm{mol}
\end{gathered}
$$


$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}{ }^{-}\left({ }^{1} \mathrm{~A}^{\prime}\right)$
$+43 \mathrm{~cm}^{-1}$
$+2.07 \mathrm{kcal} / \mathrm{mol}$
$\{+6.42 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}-\left({ }^{1} \mathrm{~A}^{\prime}\right)$
$+52 \mathrm{~cm}^{-1}$ $+21.61 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}^{-}\left({ }^{1} \mathrm{~A}_{1}\right)$
$+355 \mathrm{~cm}^{-1}$
$+82.03 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}{ }^{-}\left({ }^{1} \mathrm{~A}^{\prime}\right)$
$+80 \mathrm{~cm}^{-1}$
$+131.76 \mathrm{kcal} / \mathrm{mol}$

Figure S6. Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{4}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and CCSD(T)//B3LYP/aug-cc-pVTZ (in curly brackets).

The structures were obtained initially using the Coalescence Kick and Basin Hopping global-minimum search programs at B3LYP/3-21G.

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$
$+76 \mathrm{~cm}^{-1}$
$0.00 \mathrm{kcal} / \mathrm{mol}$
$\{0.00 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{5} \mathrm{~B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$
$+64 \mathrm{~cm}^{-1}$
$+30.46 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$
$+62 \mathrm{~cm}^{-1}$
$+46.98 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{5} \mathrm{~B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$
$+36 \mathrm{~cm}^{-1}$
$+121.95 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}_{1}\right)$
$+64 \mathrm{~cm}^{-1}$
$+4.78 \mathrm{kcal} / \mathrm{mol}$
$\{+9.83 \mathrm{kcal} / \mathrm{mol}\}$

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$ $+64 \mathrm{~cm}^{-1}$
$+30.58 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{5} \mathrm{~B}_{3} \mathrm{O}_{4}\left({ }^{( } \mathrm{A}^{\prime}\right)$
$+25 \mathrm{~cm}^{-1}$
$+64.88 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$ $+60 \mathrm{~cm}^{-1}$
$+127.71 \mathrm{kcal} / \mathrm{mol}$

$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}_{1}\right)$
$+73 \mathrm{~cm}^{-1}$ $+28.04 \mathrm{kcal} / \mathrm{mol}$


$\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~B}_{2}\right)$
$+6 \mathrm{~cm}^{-1}$
$+65.30 \mathrm{kcal} / \mathrm{mol}$

Figure S7. Alternative optimized structures for $\mathrm{B}_{3} \mathrm{O}_{4}{ }^{+}$, along with their point group symmetries, electronic states, and minimum vibrational frequencies. Relative energies are given at B3LYP/aug-cc-pVTZ and CCSD(T)//B3LYP/aug-cc-pVTZ (in curly brackets).
The structures were obtained initially using the Coalescence Kick and Basin
Hopping global-minimum search programs at B3LYP/3-21G.


Figure S8. (a) AdNDP bonding pattern for the $\mathrm{C}_{\infty} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left(\mathbf{3},{ }^{1} \Sigma\right)$ global-minimum structure and (b) its canonical molecular orbitals (CMOs).
(a)

(b)


Figure S9. (a) AdNDP bonding pattern for $\mathrm{D}_{\infty \mathrm{oh}} \mathrm{B}_{3} \mathrm{O}_{2}{ }^{+}\left({ }^{1} \Sigma_{\mathrm{g}}\right)$ and (b) its canonical molecular orbitals (CMOs).
(a)

(b)


Figure S10. (a) AdNDP bonding pattern for the $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}{ }^{-}\left(4,{ }^{1} \mathrm{~A}_{1}\right)$ global-minimum structure and (b) its canonical molecular orbitals (CMOs).
(a)


$4 \times 1 \mathrm{c}-2 \mathrm{e}$ O lone pairs $\mathrm{ON}=1.86-1.98 \mathrm{lel}$

$2 \times 2 \mathrm{c}-2 \mathrm{e}$ B-B $\sigma$ $\mathrm{ON}=1.99$ lel
4. $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}-\left({ }^{1} \mathrm{~A}_{1}\right)$

$3 \times 2 \mathrm{c}-2 \mathrm{e} \mathrm{B}-\mathrm{O} \sigma$ $\mathrm{ON}=1.99-2.00 \mathrm{lel}$

$5 \times 2 \mathrm{c}-2 \mathrm{e}$ B-O $\pi$
$\mathrm{ON}=1.95-2.00 \mathrm{lel}$
(b)


Figure S11. (a) AdNDP bonding pattern for the $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}\left(5,{ }^{2} \mathrm{~A}_{1}\right)$ global-minimum structure and (b) its canonical molecular orbitals (CMOs).
(a)

5. $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{3}\left({ }^{2} \mathrm{~A}_{1}\right)$

$3 \times 1 \mathrm{c}-2 \mathrm{e} \mathrm{O}$ lone pairs $\mathrm{ON}=1.99 \mathrm{le\mid}$

$1 \times 2 \mathrm{c}-2 \mathrm{e}$ B-O $\sigma$ $\mathrm{ON}=2.00 \mathrm{lel}$

$1 \times 1 \mathrm{c}-1 \mathrm{e}$ B lone electron
$\mathrm{ON}=0.96$ lel $1 \times 2 \mathrm{c}-2 \mathrm{e} \mathrm{O}-\mathrm{O} \pi$ $\mathrm{ON}=2.00 \mathrm{le} \mathrm{l}$

$\times 2 \mathrm{c}-2 \mathrm{e}$ B-O $\pi$ $\mathrm{ON}=1.99 \mathrm{lel}$

$4 \times 2 \mathrm{c}-2 \mathrm{e}$ B-O and $1 \times 2 \mathrm{c}-2 \mathrm{e}$ B-B $\sigma$ $\mathrm{ON}=1.95-1.99 \mathrm{lel}$

$1 \times 4 \mathrm{c}-2 \mathrm{e} \pi$ $\mathrm{ON}=1.99 \mathrm{lel}$
(b)


Figure S12. (a) AdNDP bonding pattern for the $\mathrm{C}_{\infty} \mathrm{B}_{3} \mathrm{O}_{3}{ }^{+}\left(6,{ }^{1} \Sigma\right)$ global-minimum structure and (b) its canonical molecular orbitals (CMOs).
(a)

(b)


HOMO-9 ( $\sigma$ )

Figure S13. Canonical molecular orbitals (CMOs) for the $\mathrm{C}_{2 \mathrm{v}} \mathrm{B}_{3} \mathrm{O}_{4}\left(7,{ }^{1} \mathrm{~A}_{1}\right)$ global-minimum structure. For its AdNDP bonding pattern, see Figure 4 in the text.


Figure S14. (a) AdNDP bonding pattern for the $\mathrm{C}_{5} \mathrm{~B}_{3} \mathrm{O}_{4}\left(8,{ }^{2} \mathrm{~A}^{\prime}\right)$ global-minimum structure and (b) its canonical molecular orbitals (CMOs).
(a)

$1 \times 2 \mathrm{c}-2 \mathrm{e} \mathrm{O}-\mathrm{O} \pi$ $\begin{aligned} 5 \times 1 \mathrm{c}-2 \mathrm{e} \text { O lone pairs } \mathrm{ON} & =1.97 \mathrm{lel} \\ 1 \times 1 \mathrm{c}-1 \mathrm{e} \mathrm{B} \text { lone electron } \mathrm{ON} & =0.89 \mathrm{lel}\end{aligned}$ $\mathrm{ON}=2.00 \mathrm{lel}$

$6 \times 2 \mathrm{c}-2 \mathrm{e} \mathrm{B-O} \sigma$
$\mathrm{ON}=1.94-1.99$ lel
8. $\mathrm{C}_{\mathrm{s}} \mathrm{B}_{3} \mathrm{O}_{4}\left({ }^{2} \mathrm{~A}^{\prime}\right)$

$1 \times 2 \mathrm{c}-2 \mathrm{e}$ B-O $\sigma$ $\mathrm{ON}=2.00 \mathrm{lel}$

$2 \times 2 \mathrm{c}-2 \mathrm{e}$ B-O $\pi$ $\mathrm{ON}=2.00 \mathrm{lel}$

$1 \times 4 \mathrm{c}-2 \mathrm{e} \pi$ $\mathrm{ON}=2.00 \mathrm{le} \mid$
(b)


Figure S15. (a) AdNDP bonding pattern for the $\mathrm{D}_{\infty h} \mathrm{~B}_{3} \mathrm{O}_{4}{ }^{+}\left(9,{ }^{1} \Sigma_{\mathrm{g}}\right)$ global-minimum structure and (b) its canonical molecular orbitals (CMOs).
(a)

$$
\begin{gathered}
0-0-0-0-0-0-\mathrm{D}_{\infty h} \mathrm{~B}_{3} \mathrm{O}_{4}^{+}\left({ }^{1} \Sigma_{\mathrm{g}}\right)
\end{gathered}
$$


(b)



[^0]:    ${ }^{a} t$, the total bond orders; $c$, the covalent bond orders of NRT; $i$, the ionic bond orders of NRT.

