Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

On the structure and bonding in $B_4O_4^+$ cluster: a boron oxide analogue of the 3,5-dehydrophenyl cation with π and σ double aromaticity†

Ting Ou,[a] Wen-Juan Tian,[a] Xue-Rui You,[a] Ying-Jin Wang,[ab] Kang Wang[a] and Hua-Jin Zhai*[ac]

[a]*Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China*

[b]*Department of Chemistry, Xinzhou Teachers University, Xinzhou 034000, China*

[c]*State Key Laboratory of Quantum Optics and Quantum Optics Devices, Shanxi University, Taiyuan 030006, China*

*E-mail: hj.zhai@sxu.edu.cn

Full citation of ref 40.

Table S1. Cartesian coordinates (x, y, z) in Å at the B3LYP/aug-cc-pVTZ level for C_s $B_4O_4^+$ (**1**), quasi-planar C_{2h} $B_4O_4^+$, D_{2h} $B_4O_4^+$ (**2**), and C_{2v} $B_4O_4^+$ (**3**).

Figure S1. Optimized structures at the B3LYP/ aug-cc-pVTZ level for (a) rhombic D_{2h} $B_4O_4^+$ (**2**), (b) Y-shaped C_{2v} $B_4O_4^+$ (**3**), and (c) quasi-linear C_{2h} B_4O_4 neutral cluster.

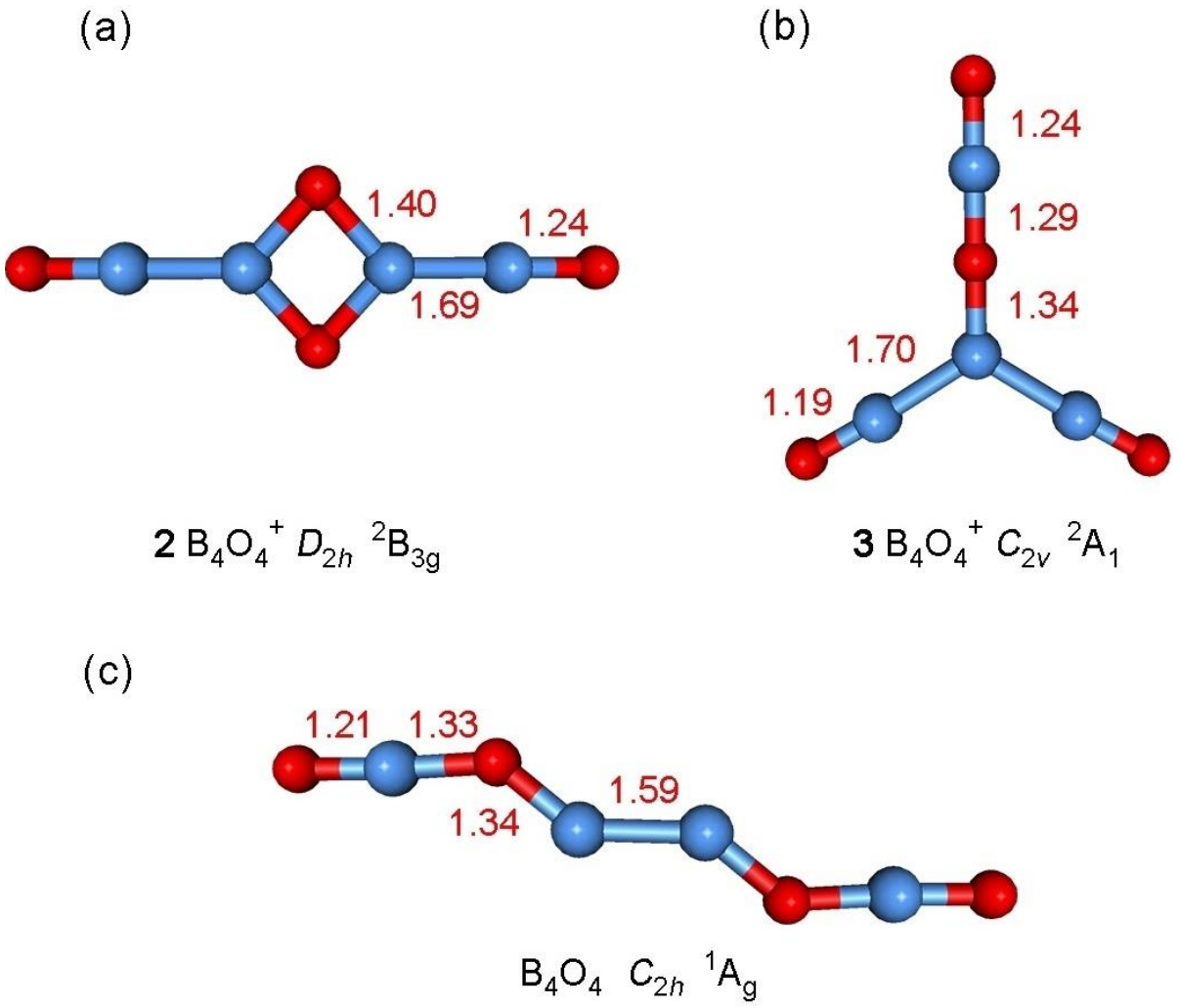
Figure S2. Canonical molecular orbitals (CMOs) of the quasi-linear C_{2h} isomer of $B_4O_4^+$.

Figure S3. Natural charge distributions of the global minimum and selected low-lying isomers of $B_4O_4^+$: (a) **1** (C_s, $^2A'$), (b) C_{2h} (^2B_u), (c) **2** (D_{2h}, $^2B_{3g}$), and (d) **3** (C_{2v}, $^2A_1$).

Full citation of ref 40.

40 GAUSSIAN 09, Revision D.01, 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.

Figure S1. Optimized structures at the B3LYP/ aug-cc-pVTZ level for (a) rhombic D_{2h} $B_4O_4^+$ (**2**), (b) Y-shaped C_{2v} $B_4O_4^+$ (**3**), and (c) quasi-linear C_{2h} B_4O_4 neutral cluster.



2 $B_4O_4^+$ D_{2h} $^2B_{3g}$

3 $B_4O_4^+$ C_{2v} $^2A_1$

B_4O_4 C_{2h} ^1A_g

Figure S2. Canonical molecular orbitals (CMOs) of the quasi-linear C_{2h} isomer of $B_4O_4^+$. SOMO stands for the single occupied molecular orbital.

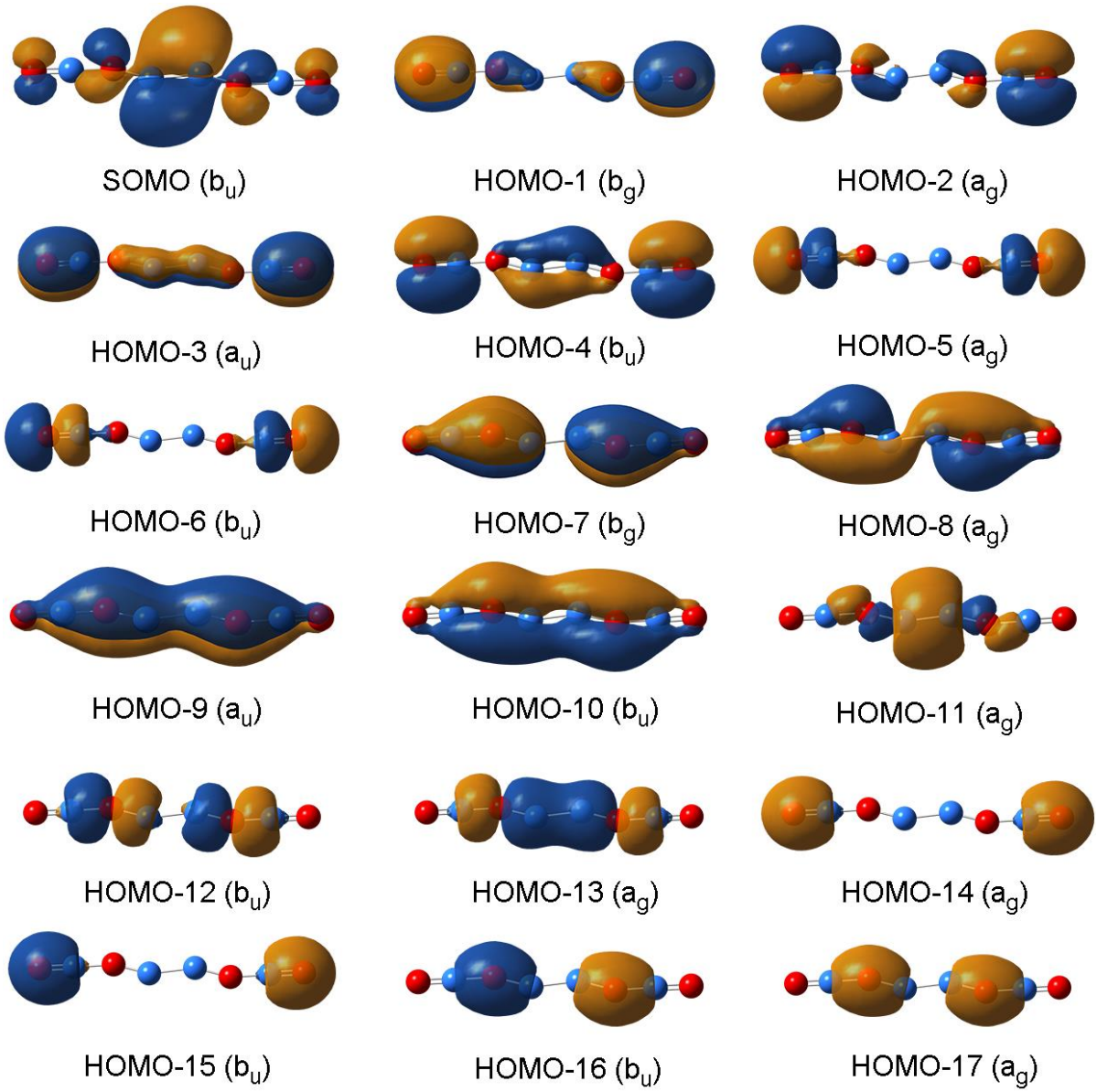


Figure S3. Natural charge distributions of the global minimum and selected low-lying isomers of $B_4O_4^+$: (a) **1** (C_s, $^2A'$), (b) C_{2h} (^2B_u), (c) **2** (D_{2h}, $^2B_{3g}$), and (d) **3** (C_{2v}, $^2A_1$).

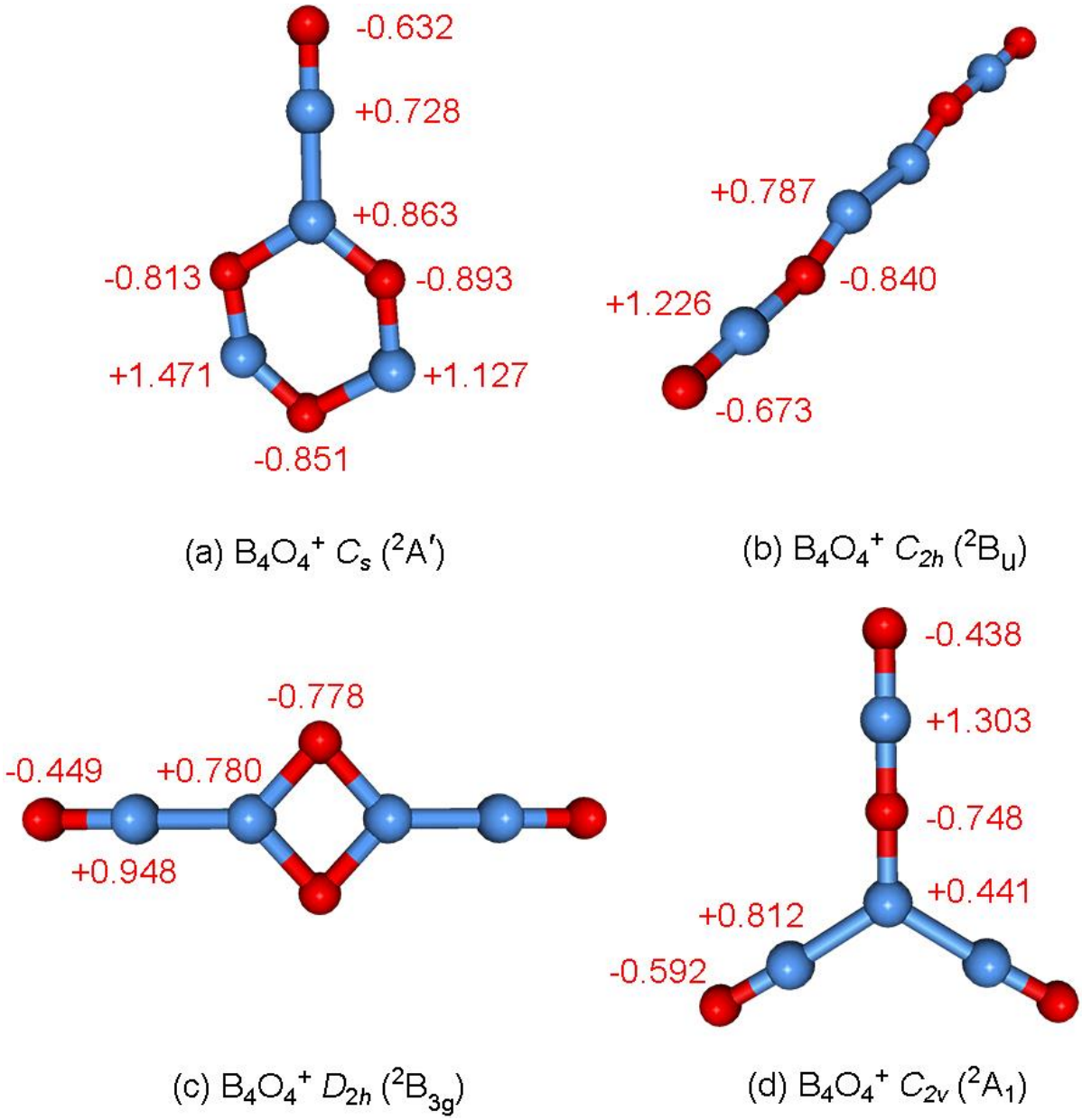


Table S1. Cartesian coordinates (x, y, z) in Å at the B3LYP/aug-cc-pVTZ level for C_s $B_4O_4^+$ (**1**), quasi-planar C_{2h} $B_4O_4^+$, D_{2h} $B_4O_4^+$ (**2**), and C_{2v} $B_4O_4^+$ (**3**).

$B_4O_4^+$ (**1**, C_s, $^2A'$)

B	0.00000000	0.48758600	0.00000000
B	-0.08098500	2.14940300	0.00000000
B	1.26971900	-1.61679100	0.00000000
B	-0.90536400	-1.55498400	0.00000000
O	-0.14494000	3.34329100	0.00000000
O	0.04765900	-2.41728100	0.00000000
O	1.14557400	-0.27589100	0.00000000
O	-1.22539800	-0.31587800	0.00000000

$B_4O_4^+$ (C_{2h}, ^2B_u)

B	0.34415600	-3.35247800	0.00000000
B	-0.34415600	3.35247800	0.00000000
B	0.04558000	0.79553100	0.00000000
B	-0.04558000	-0.79553100	0.00000000
O	-0.36051400	4.54947800	0.00000000
O	0.36051400	-4.54947800	0.00000000
O	-0.34415600	2.00214200	0.00000000
O	0.34415600	-2.00214200	0.00000000

$B_4O_4^+$ (**2**, D_{2h}, $^2B_{3g}$)

B	0.00000000	0.00000000	2.58438300
B	0.00000000	0.00000000	0.89385300
B	0.00000000	0.00000000	-0.89385300
B	0.00000000	0.00000000	-2.58438300
O	0.00000000	1.07551900	0.00000000
O	0.00000000	-1.07551900	0.00000000
O	0.00000000	0.00000000	3.82441300
O	0.00000000	0.00000000	-3.82441300

$B_4O_4^+$ (**3**, C_{2v}, $^2A_1$)

B	0.00000000	0.00000000	-0.41280600
B	0.00000000	1.43322400	-1.32648400
B	0.00000000	-1.43322400	-1.32648400
B	0.00000000	0.00000000	2.21727200
O	0.00000000	-2.47255300	-1.92408000
O	0.00000000	2.47255300	-1.92408000
O	0.00000000	0.00000000	0.92334400
O	0.00000000	0.00000000	3.45513000