

SUPPLEMENTARY INFORMATION

Boronyl as a terminal ligand in boron oxide clusters: Hexagonal ring C_{2v} B_6O_4 and ethylene-like D_{2h} $B_6O_4^{-/2-}\dagger$

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Figure S1. Representative isomeric structures of B_6O_4 with their relative energies (in kcal/mol) indicated at the B3LYP/aug-cc-pVTZ level. Shown in ***bold italic*** are the relative energies for the top two structures at PBE0/aug-cc-pVTZ level. The B atom is in gray, and O is in black.

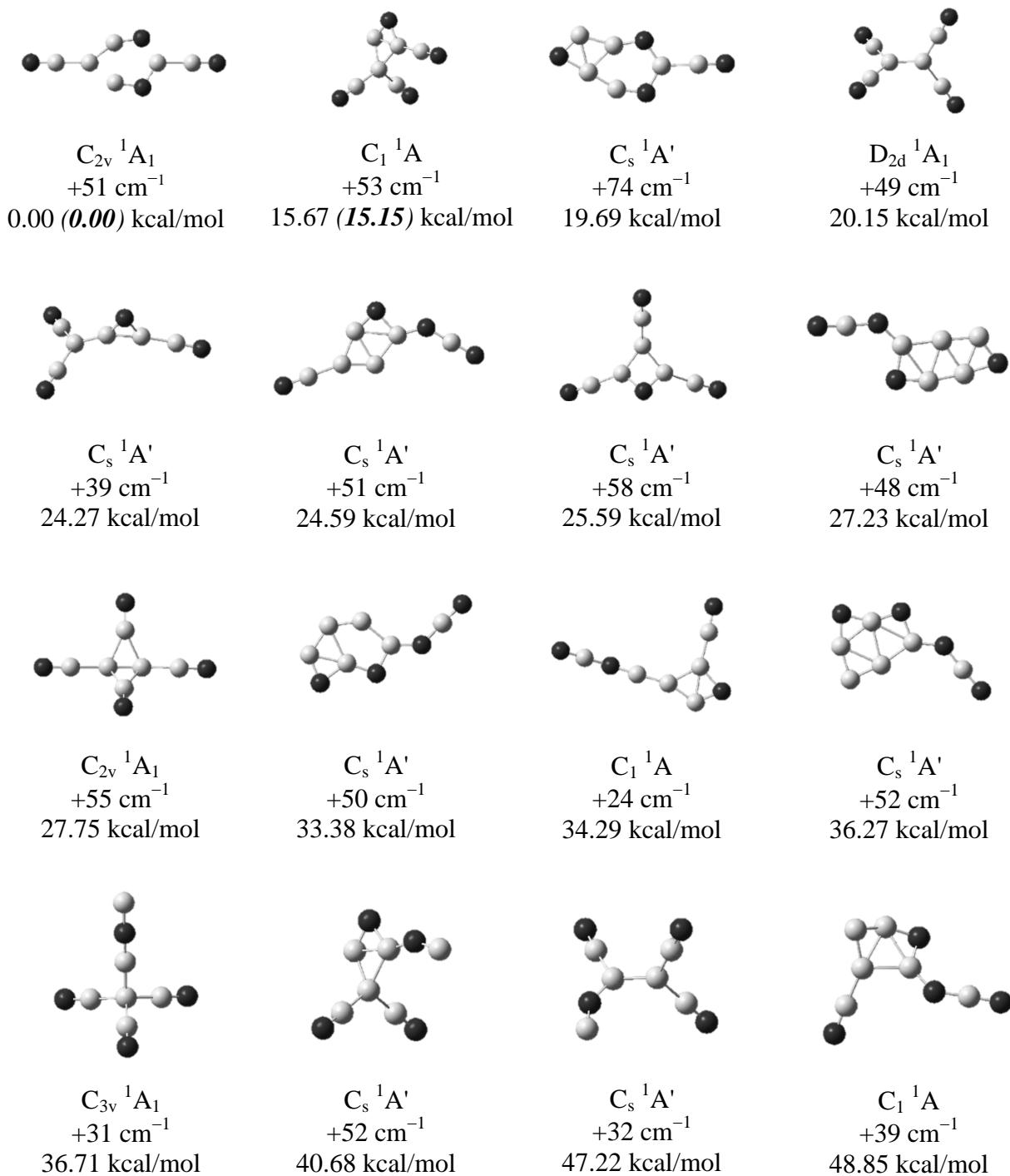
Figure S2. Representative isomeric structures of $B_6O_4^-$ with their relative energies (in kcal/mol) indicated at the B3LYP/aug-cc-pVTZ level. Shown in ***bold italic*** are the relative energies for the top three structures at PBE0/aug-cc-pVTZ level. The B atom is in gray, and O is in black.

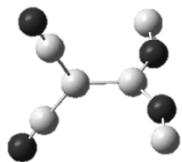
Figure S3. Representative isomeric structures of $B_6O_4^{2-}$ with their relative energies (in kcal/mol) indicated at the B3LYP/aug-cc-pVTZ level. Shown in ***bold italic*** are the relative energies for the top two structures at PBE0/aug-cc-pVTZ level. The B atom is in gray, and O is in black.

Figure S4. Selected canonical molecular orbitals (CMOs) of (a) C_{2v} B_6O_4 (**1**, 1A_1) and (b) D_{2h} $B_6O_4^-$ (**2**, $^2B_{3u}$).

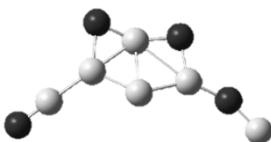
Figure S5. The Wiberg bond indices of C_{2v} B_6O_4 (**1**, 1A_1).

Figure S1. Representative isomeric structures of B_6O_4 with their relative energies (in kcal/mol) indicated at the B3LYP/aug-cc-pVTZ level. Shown in ***bold italic*** are the relative energies for the top two structures at PBE0/aug-cc-pVTZ level. The B atom is in gray, and O is in black.

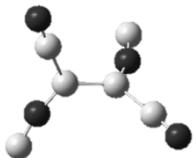




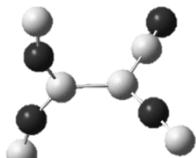
$C_{2v}^1 A_1$
 $+38 \text{ cm}^{-1}$
63.09 kcal/mol



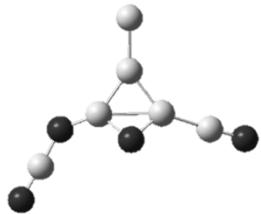
$C_1^1 A$
 $+49 \text{ cm}^{-1}$
67.54 kcal/mol



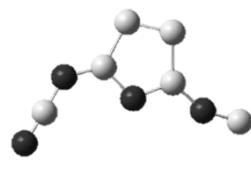
$C_2^1 A$
 $+26 \text{ cm}^{-1}$
72.80 kcal/mol



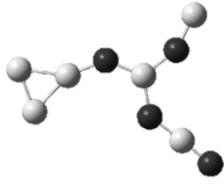
$C_1^1 A$
 $+22 \text{ cm}^{-1}$
88.01 kcal/mol



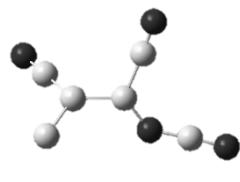
$C_1^1 A$
 $+43 \text{ cm}^{-1}$
92.43 kcal/mol



$C_1^1 A$
 $+48 \text{ cm}^{-1}$
93.68 kcal/mol

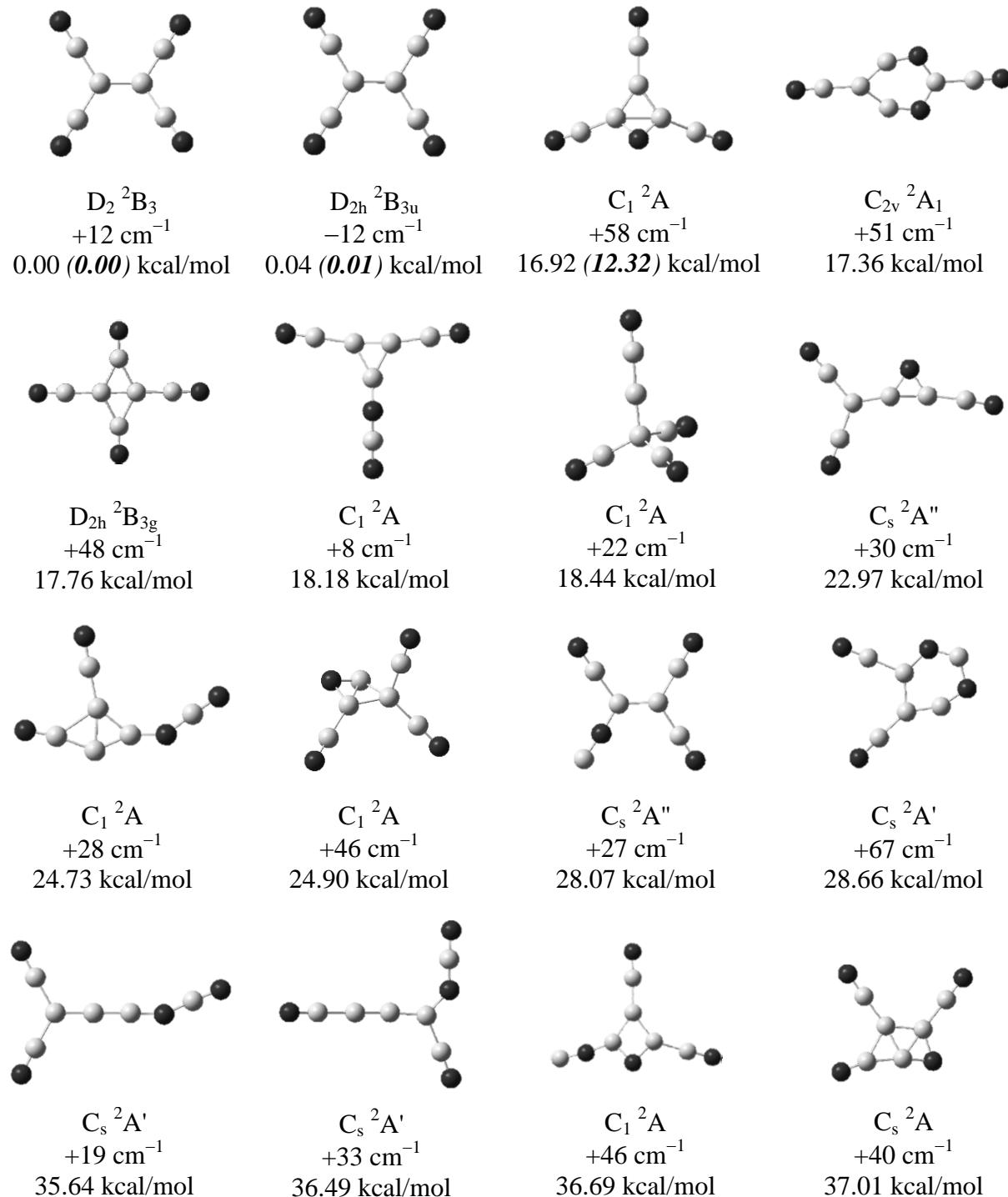


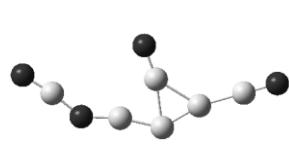
$C_s^1 A'$
 $+25 \text{ cm}^{-1}$
95.55 kcal/mol



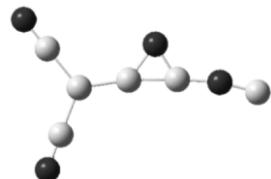
$C_1^1 A$
 $+39 \text{ cm}^{-1}$
95.86 kcal/mol

Figure S2. Representative isomeric structures of B_6O_4^- with their relative energies (in kcal/mol) indicated at the B3LYP/aug-cc-pVTZ level. Shown in ***bold italic*** are the relative energies for the top three structures at PBE0/aug-cc-pVTZ level. The B atom is in gray, and O is in black.

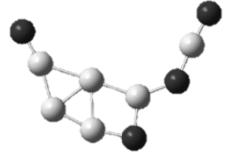




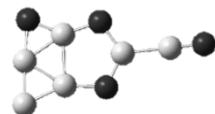
C_s $^2A'$
 $+31\text{ cm}^{-1}$
41.53 kcal/mol



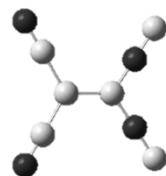
C_s $^2A''$
 $+37\text{ cm}^{-1}$
44.81 kcal/mol



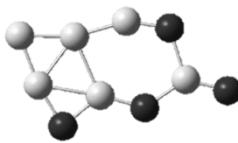
C_s $^2A'$
 $+67\text{ cm}^{-1}$
45.66 kcal/mol



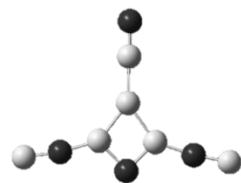
C_s $^2A'$
 $+80\text{ cm}^{-1}$
45.83 kcal/mol



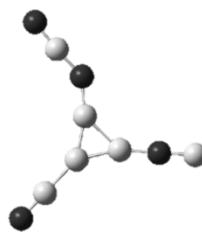
C_{2v} 2B_1
 $+29\text{ cm}^{-1}$
47.42 kcal/mol



C_1 2A
 $+74\text{ cm}^{-1}$
53.43 kcal/mol

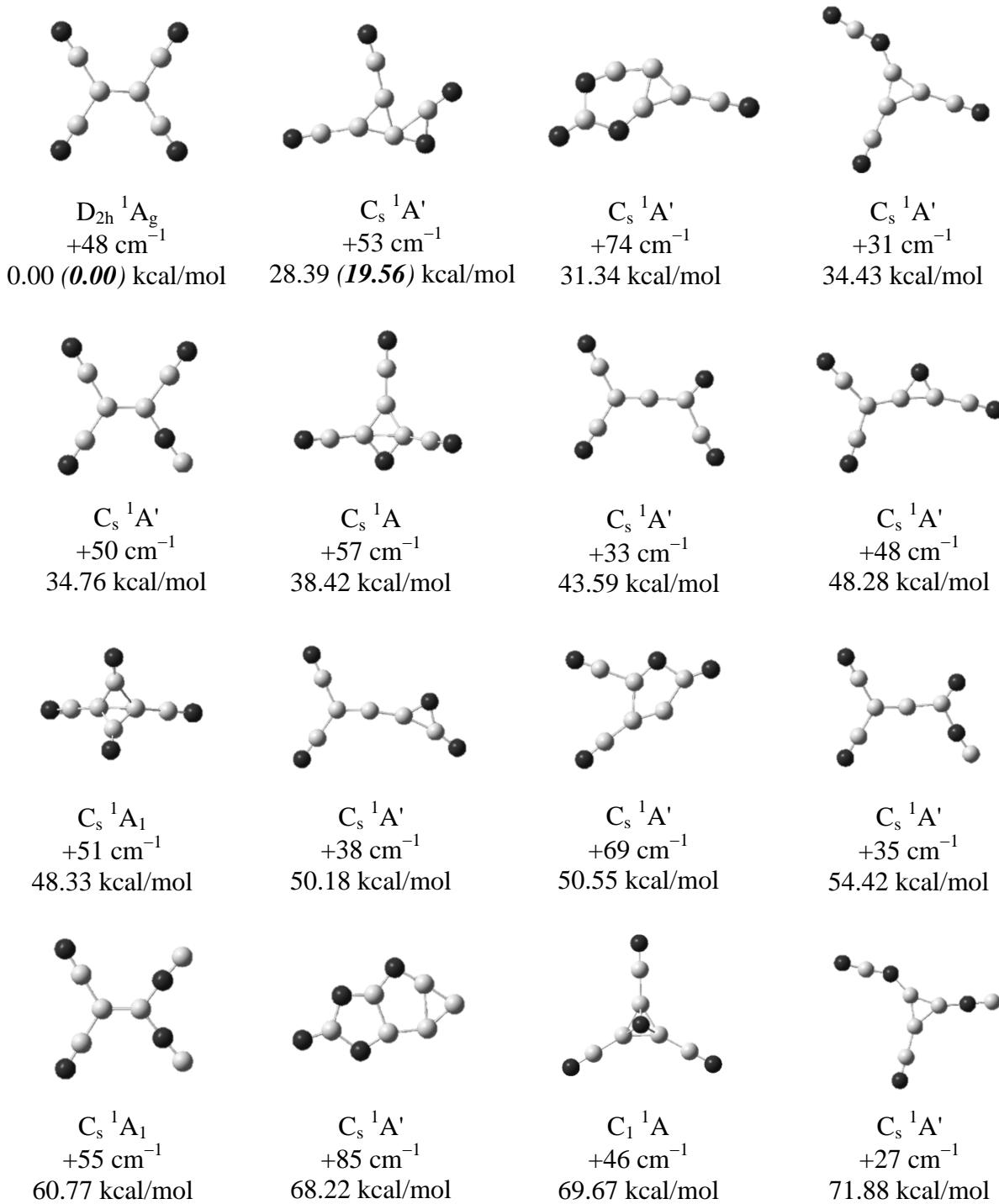


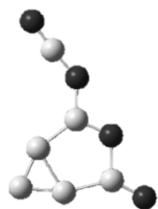
C_{2v} 2B_1
 $+36\text{ cm}^{-1}$
55.56 kcal/mol



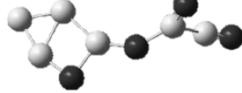
C_s $^2A'$
 $+11\text{ cm}^{-1}$
55.58 kcal/mol

Figure S3. Representative isomeric structures of $\text{B}_6\text{O}_4^{2-}$ with their relative energies (in kcal/mol) indicated at the B3LYP/aug-cc-pVTZ level. Shown in ***bold italic*** are the relative energies for the top two structures at PBE0/aug-cc-pVTZ level. The B atom is in gray, and O is in black.

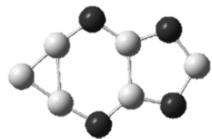




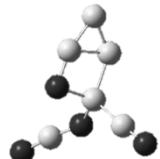
$C_s\ ^1A'$
 $+44\ cm^{-1}$
73.97 kcal/mol



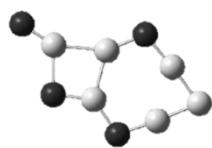
$C_1\ ^1A$
 $+20\ cm^{-1}$
84.16 kcal/mol



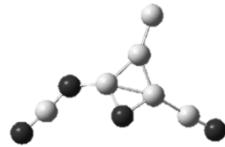
$C_{2v}\ ^1A_1$
 $+125\ cm^{-1}$
84.67 kcal/mol



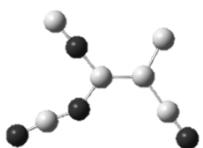
$C_s\ ^1A$
 $+27\ cm^{-1}$
92.16 kcal/mol



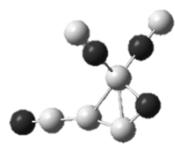
$C_s\ ^1A'$
 $+87\ cm^{-1}$
93.69 kcal/mol



$C_1\ ^1A$
 $+36\ cm^{-1}$
101.26 kcal/mol



$C_s\ ^1A'$
 $+37\ cm^{-1}$
103.85 kcal/mol



$C_1\ ^1A'$
 $+46\ cm^{-1}$
104.81 kcal/mol

Figure S4. Selected canonical molecular orbitals (CMOs) of (a) C_{2v} B_6O_4 (**1**, ${}^1\text{A}_1$) and (b) D_{2h} B_6O_4^- (**2**, ${}^2\text{B}_{3u}$). “SOMO” stands for the singly occupied molecular orbital.

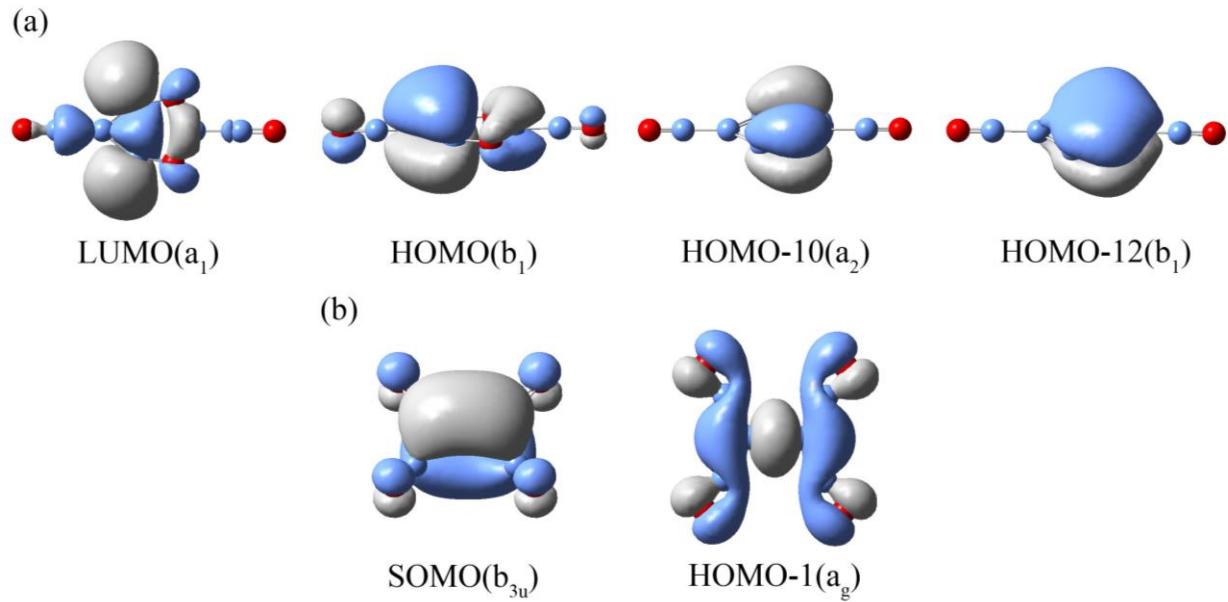


Figure S5. The Wiberg bond indices of C_{2v} B_6O_4 (**1**, 1A_1)

