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

SUPPLEMENTARY INFORMATION

Structures and Chemical Bonding of Boron-Based $B_{12}O$ and $B_{11}Au$ Clusters. A Counterexample in Boronyl Chemistry

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Table S1. Cartesian coordinates for the global-minimum (GM) structures of $B_{12}O$ (**1**, C_1, ^1A) and $B_{11}Au$ (**5**, C_s, $^1A'$) clusters at the B3LYP/B/O/6-311+G(d)/Au/Stuttgart_rsc_1997_ecp+2f1g level.

Table S2. Calculated nucleus-independent chemical shifts (NICSs) of $B_{12}O$ (**1**), $B_{11}Au$ (**5**), and B_{12} clusters, as well as those of benzene molecule, at the B3LYP/6-311+G(d) (with the Stuttgart_rsc_1997_ecp+2f1g basis set for Au) level.

Figure S1. Alternative optimized low-lying structures of $B_{12}O$ cluster. Relative energies are shown in kcal mol^{-1} at the B3LYP/6-311+G(d) level (without parenthesis). Also shown are energetics data for top 5 lowest-energy isomers at the PBE0/6-311+G(d) level (in parentheses), at the B3LYP/cc-pvtz and B3LYP/aug-cc-pvtz levels (in curly brackets), and at the single-point CCSD(T)/cc-pvtz//B3LYP/cc-pvtz level (in square brackets). All energies at the density-functional theory (DFT) levels have been corrected for zero-point energies (ZPEs).

Figure S2. Alternative optimized low-lying structures of $B_{12}O^-$ cluster. Relative energies are shown in kcal mol^{-1} at the B3LYP/6-311+G(d) level (without parenthesis). Also shown are energetics data for top 5 lowest-energy isomers at the PBE0/6-311+G(d) level (in parentheses), at the B3LYP/cc-pvtz and B3LYP/aug-cc-pvtz levels (in curly brackets), and at the single-point CCSD(T)/cc-pvtz//B3LYP/cc-pvtz level (in square brackets). All energies at the DFT levels have been corrected for ZPEs.

Figure S3. Alternative optimized low-lying structures of $B_{11}Au$ cluster. Relative energies are shown in kcal mol^{-1} at the B3LYP/B/6-311+G(d)/Au/Stuttgart level (without parentheses). Also shown are energetics data for top 4 lowest-energy isomers at the PBE0/B/6-311+G(d)/Au/Stuttgart level (in parentheses), at the B3LYP/B/cc-pvtz/Au/cc-pvtz-pp and B3LYP/B/aug-cc-pvtz/Au/Stuttgart levels (in curly brackets), and at the single-point CCSD(T)/cc-pvtz//B3LYP/cc-pvtz (cc-pvtz-pp for Au) level (in square brackets). Here the term "Stuttgart" stands for Stuttgart_rsc_1997_ecp+2f1g. All energies at the DFT levels have been corrected for ZPEs.

Figure S4. Alternative optimized low-lying structures of $B_{11}Au^-$ cluster. Relative energies are shown in kcal mol^{-1} at the B3LYP/B/6-311+G(d)/Au/Stuttgart level (without parentheses). Also shown are energetics data for top 4 lowest-energy isomers at the PBE0/B/6-311+G(d)/Au/Stuttgart level (in parentheses), at the B3LYP/B/cc-pvtz/Au/cc-pvtz-pp and B3LYP/B/aug-cc-pvtz/Au/Stuttgart levels (in curly brackets), and at the single-point CCSD(T)/cc-pvtz//B3LYP/cc-pvtz (cc-pvtz-pp for Au) level (in square brackets). Here the term "Stuttgart" stands for Stuttgart_rsc_1997_ecp+2f1g. All energies at the DFT levels have been corrected for ZPEs.

Figure S5. A primitive bonding scheme for delocalized σ framework in $B_{11}Au$ (**5**) cluster from the adaptive natural density partitioning (AdNDP) analysis. Occupation numbers (ONs) are shown. In this scheme, the σ framework is islanded as three-center

two-electron (3c-2e) bonds. Its refined version is presented in Figure 8(d), in which the islands are expanded to 4c-2e σ bonds with moderately improved ON values.

Figure S6. Simulated photoelectron spectra of (a) $B_{12}O^-$ (**3**) and (b) $B_{11}Au^-$ (**7**) clusters at the time-dependent PBE0/6-311+G(d) (Stuttgart_rsc_1997_ecp+2f1g for Au) level, in comparison with that of (c) B_{12}^- cluster. The simulations were done by fitting the calculated vertical detachment energies (VDEs) with unit-area Gaussian functions of 0.04 eV half-width.

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$B_{12}O$ (**1**, C_1, ^1A)

B	-1.29648500	-0.23696500	0.26746900
B	0.28036100	-0.73495400	0.38481100
B	-2.39523100	-1.36974800	-0.18444300
B	0.71715200	-2.23506300	-0.07567600
B	1.85392500	-1.20479700	-0.06917200
B	0.01848700	0.89031300	0.33710000
B	-1.90068800	1.40531500	-0.06321800
B	-0.61076600	2.37606600	-0.10925200
B	-2.82184500	0.11409700	-0.14768400
B	1.78334400	0.90291800	-0.01293000
B	-0.86819500	-1.95177000	-0.03735500
B	0.91923700	2.21410600	-0.08003400
O	2.70044100	-0.10594900	-0.13100900

$B_{11}Au$ (**5**, C_s, $^1A'$)

B	1.31560600	-0.44088600	0.00000000
B	3.95134700	-1.29708500	0.00000000
B	4.74996500	0.03270300	0.00000000
B	4.31438100	1.49250800	0.00000000
B	3.15399200	2.51663900	0.00000000
B	1.65514900	2.91933200	0.00000000
B	0.30479400	2.21027300	0.00000000
B	1.60693900	1.19931200	0.00000000

B	3.01417100	0.15840200	0.00000000
B	0.00000000	0.62816800	0.00000000
B	2.42916000	-1.50673400	0.00000000
Au	-1.67693100	-0.50079900	0.00000000

Table S2. Calculated nucleus-independent chemical shifts (NICSs) of $B_{12}O$ (**1**), $B_{11}Au$ (**5**), and B_{12} clusters, as well as those of benzene molecule, at the B3LYP/6-311+G(d) (with the Stuttgart_rsc_1997_ecp+2f1g basis set for Au) level.

Species	NICS (ppm)	$NICS_{zz}$ (ppm)
$B_{12}O$ (**1**)[a]	−10.09	−29.10
$B_{11}Au$ (**5**)[b]	−18.80	−50.46
B_{12}[c]	−12.77	−43.19
C_6H_6[d]	−10.14	−28.99

[a] Calculated at 1 Å above the center of inner B_3 triangular ring.

[b] Calculated at 1 Å above the center of 11 boron atoms.

[c] Calculated at 1 Å above the center of inner B_3 triangular ring.

[d] Calculated at 1 Å above the ring center.

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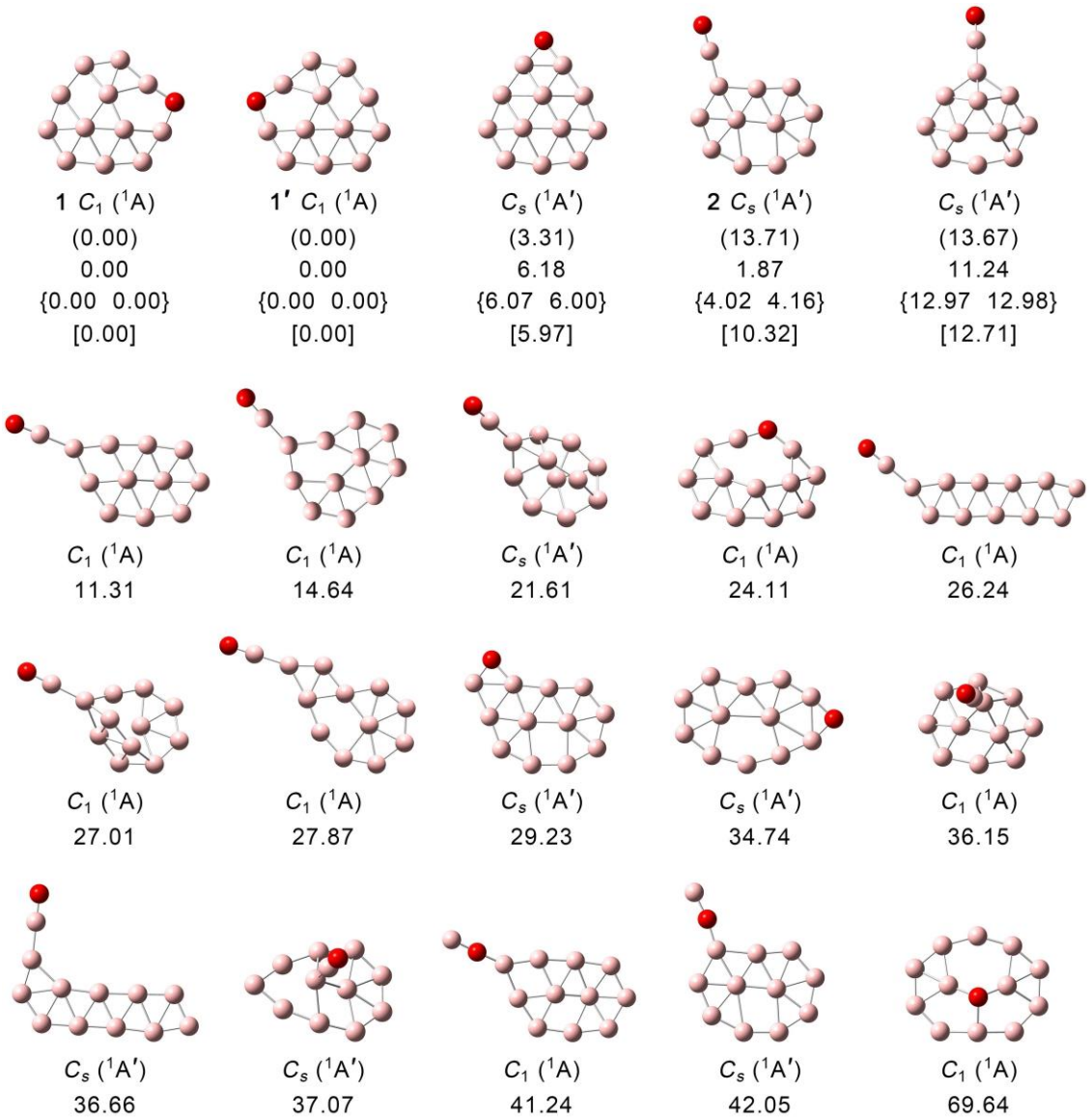
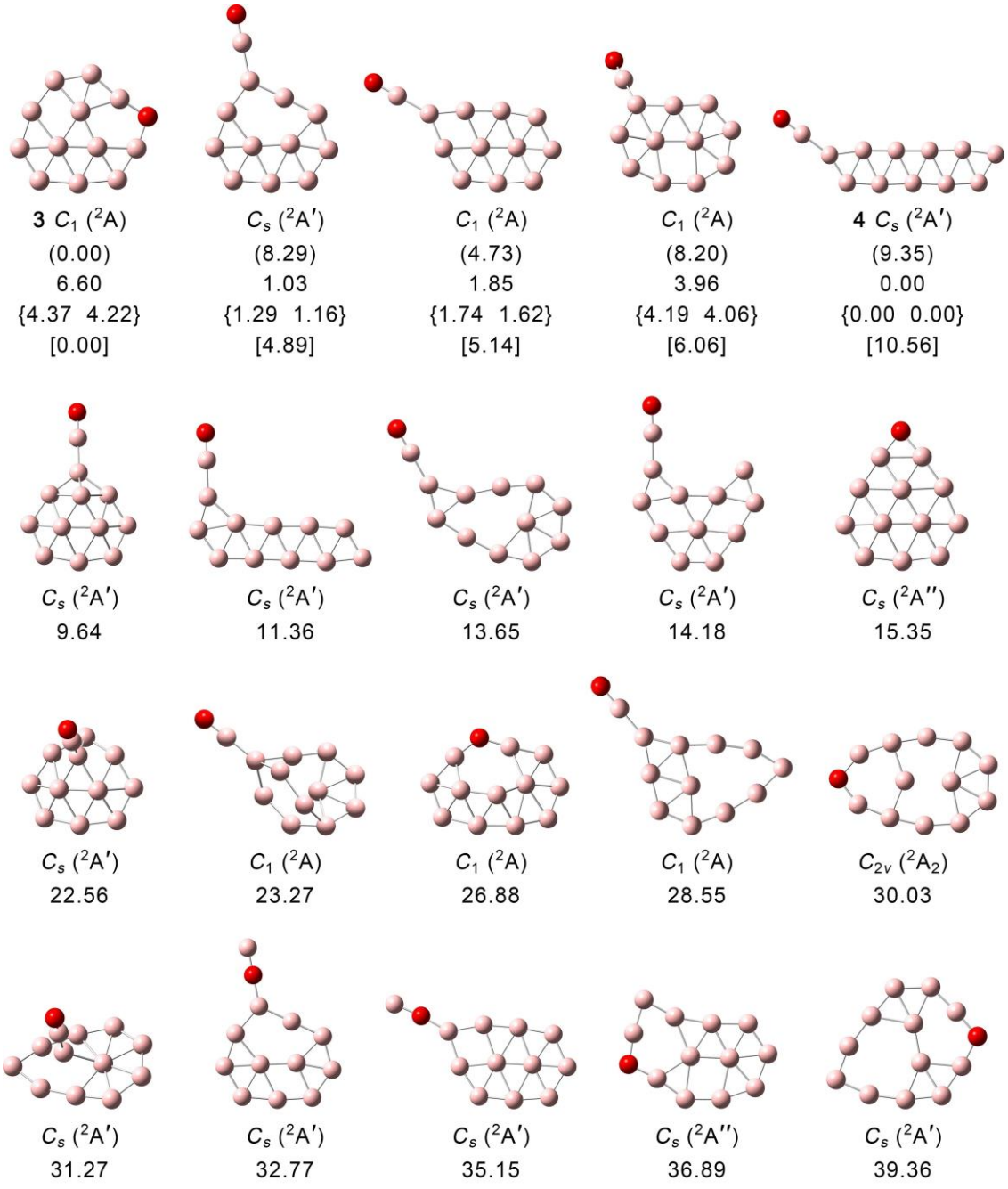


Figure S2. Alternative optimized low-lying structures of $B_{12}O^-$ cluster. Relative energies are shown in kcal mol^{-1} at the B3LYP/6-311+G(d) level (without parenthesis). Also shown are energetics data for top 5 lowest-energy isomers at the PBE0/6-311+G(d) level (in parentheses), at the B3LYP/cc-pvtz and B3LYP/aug-cc-pvtz levels (in curly brackets), and at the single-point CCSD(T)/cc-pvtz//B3LYP/cc-pvtz level (in square brackets). All energies at the DFT levels have been corrected for ZPEs.



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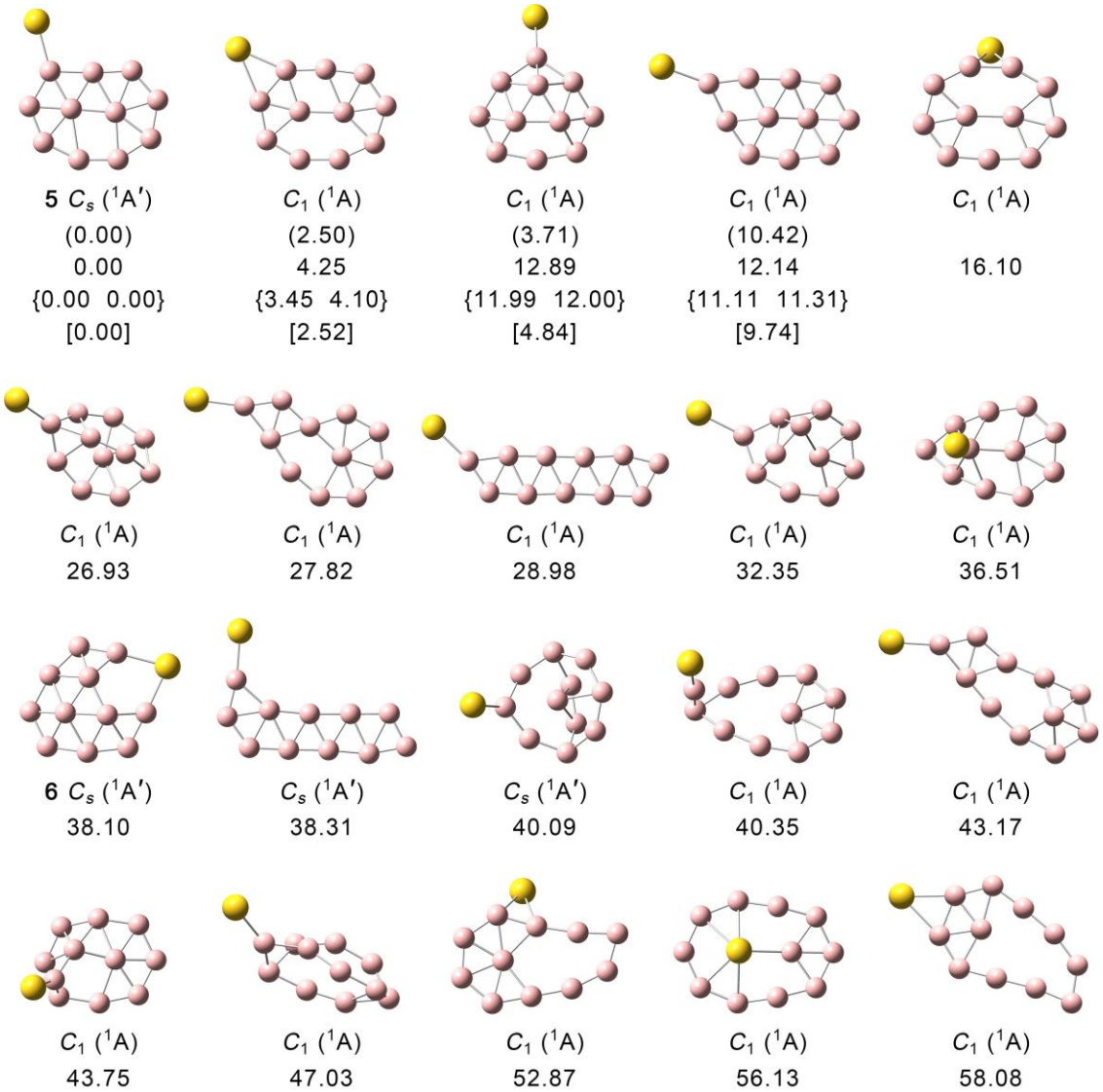

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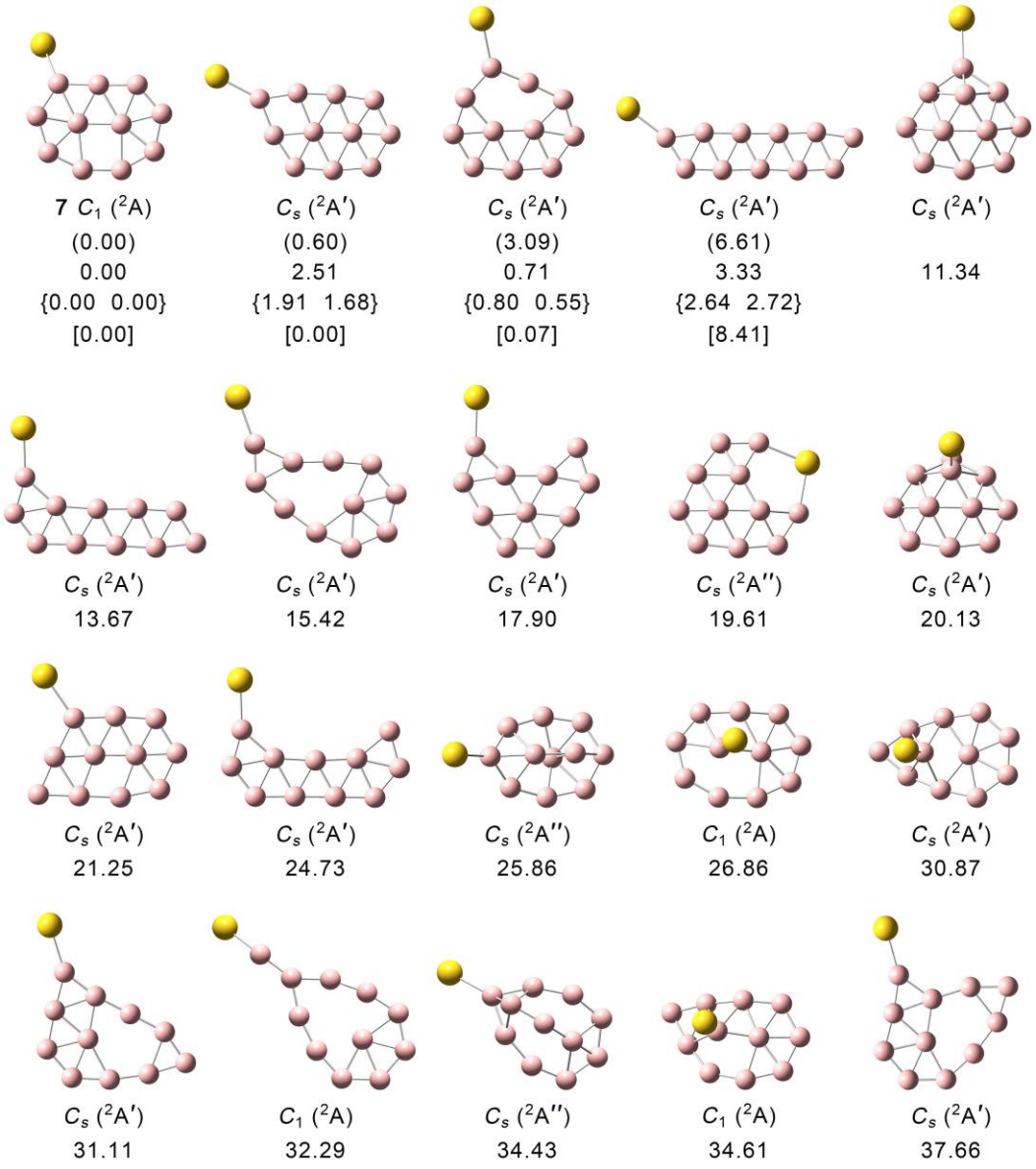

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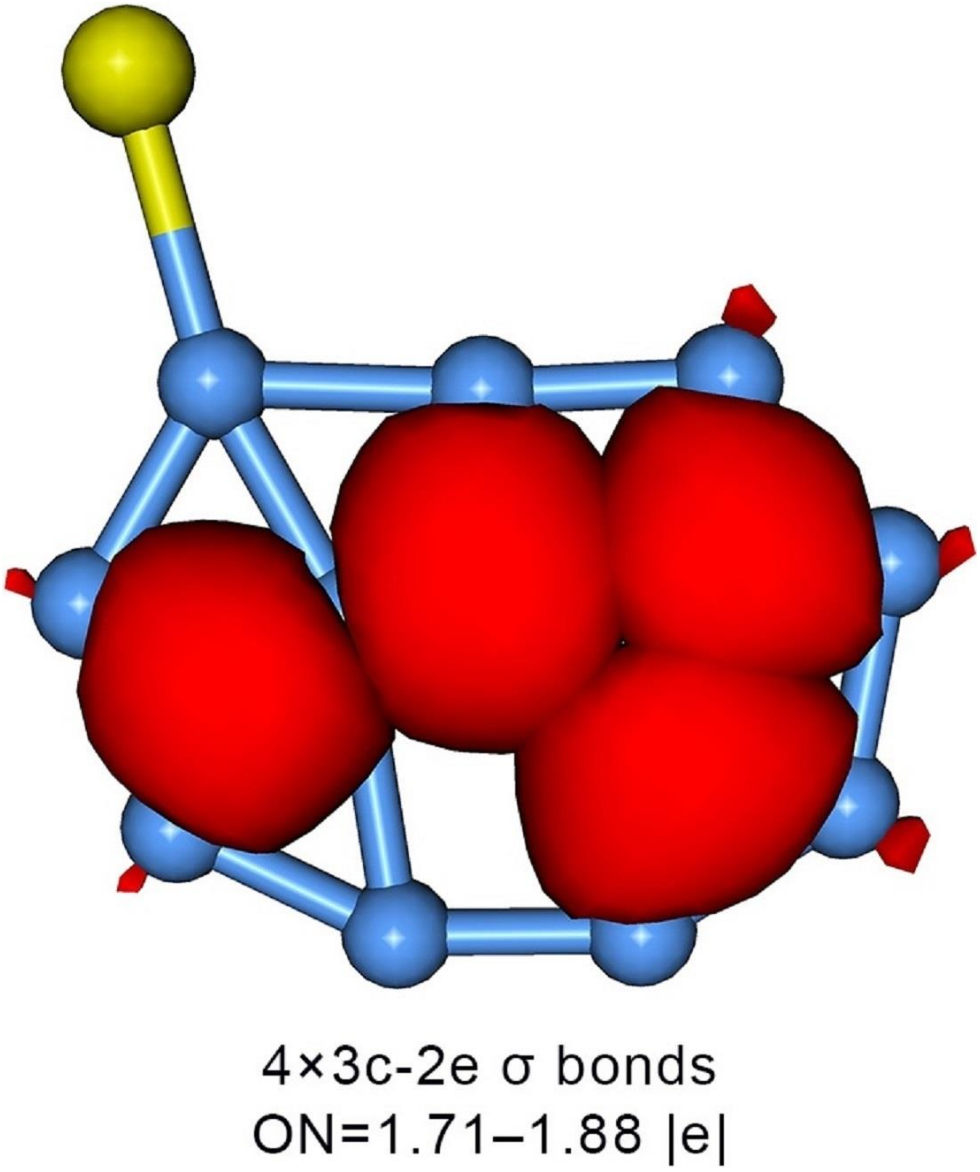

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