Chem150L: Final

March 7, 2020

Electronic Structure of a New Carborane Radical

a) Perform an initial geometry optimization of $meta$-$C_2B_{10}H_{11}$ using def2-SV(P) basis sets and TPSS/RI. (8)

   Performed geometry optimization and verified.

b) Confirm that the converged structure is a minimum by analytical second derivative calculations. What point group symmetry, if any, does the radical have? (4)
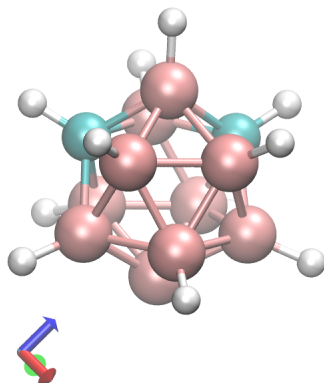
   C_s point group symmetry.

Figure 1: Geometry optimized $meta$-$C_2B_{10}H_{11}$ with RI-TPSS/def2-SV(P) basis sets.

c) Refine the structure by re-optimizing it using def2-TZVP basis sets and the TPSSh. Use the refined methodology for the following property calculations. (4)

   Performed geometry optimization and verified.

d) Investigate the bonding in the cluster core by visually inspecting the orbitals and their energies. Identify and plot the low-lying totally symmetric delocalized valence orbital expected from the Wade rules. Can the electronic structure of the radical be described by localized two-electron two-center bonds? (4)
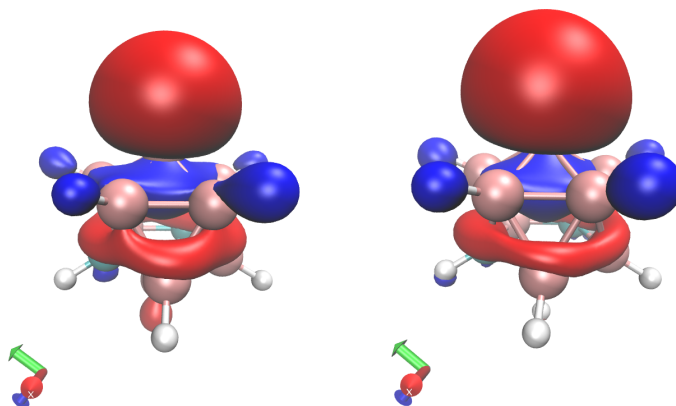
Figure 2: Molecular orbitals of the HOMO (left) and LUMO (right) for $meta$-$C_2B_{10}H_{11}$. HOMO energy is -5.18 eV and LUMO energy is -2.36 eV.

e) Perform a population analysis of the spin density and plot it in 3 dimensions. Do your results support the hypothesis of a boron-centered, localized radical? (4)
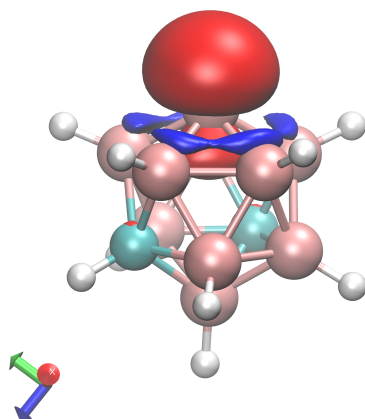

Figure 3: Spin density of the $meta$-$C_2B_{10}H_{11}$.

Population analysis of the spin density on the boron without the terminal hydrogen is given in Table 1. Yes, the population analysis and the spin density plot support the hypothesis of a boron-centered, localized radical.

Table 1: Population analysis of the spin-unrestricted calculation for the spin density $(D^\alpha - D^\beta)$ for the boron with the terminal hydrogen in $meta$-$C_2B_{10}H_{11}$.

Atom	Total	n(s)	n(p)	n(d)
B	0.834	-0.022	0.846	0.011

f) Investigate the redox chemistry of the radical by computing the first vertical ionization potential and electron affinity (using self-consistent energy calculations for the cation and the anion). (4)

Table 2: Ionization potential and electron affinity reported in eV.

Molecule	Ionization Potential	Electron Affinity
$meta$-$C_2B_{10}H_{11}$	7.744	0.495

g) Simulate and plot the low-energy UV spectrum by computing the first 10 dipole-allowed excitations and broadening the obtained oscillator strengths with Gaussians using 0.16 eV linewidth. Hint: Specifying the data group `$spectrum nm` in the control file will result in a separate file spectrum containing the excitation energies and oscillator strengths. Assign the lowest-energy band in the spectrum based on the dominant occupied-unoccupied orbital pairs involved in the underlying transition. (8)
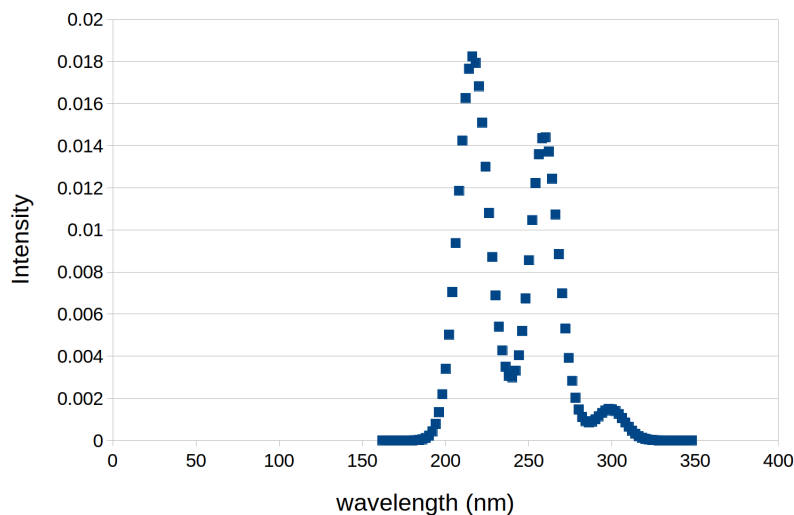

Figure 4: UV spectrum of the $meta$-$C_2B_{10}H_{11}$ of the first 10 dipole-allowed excitations and broadening the obtained oscillator strengths.