Universität Bielefeld

Pyramidality of the Boron Atom in 3-Methyl-1-boraadamantane

UNEX Project

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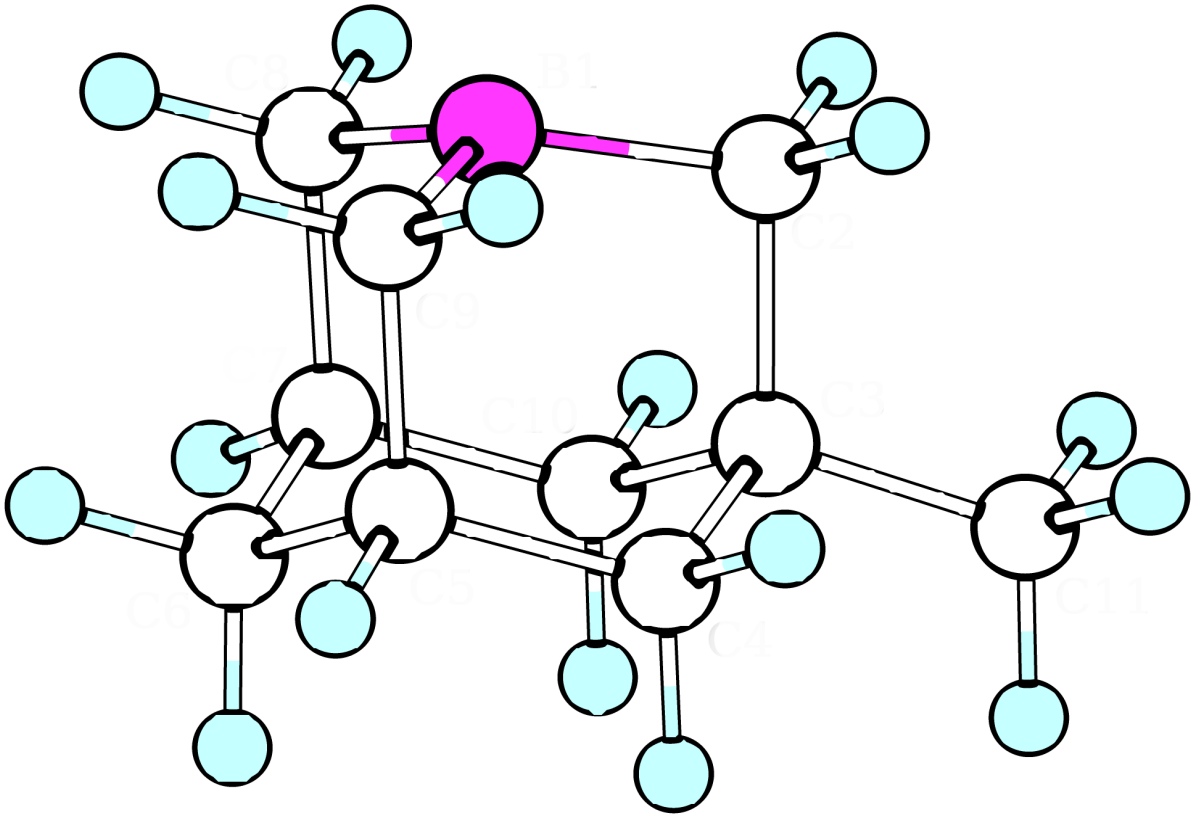
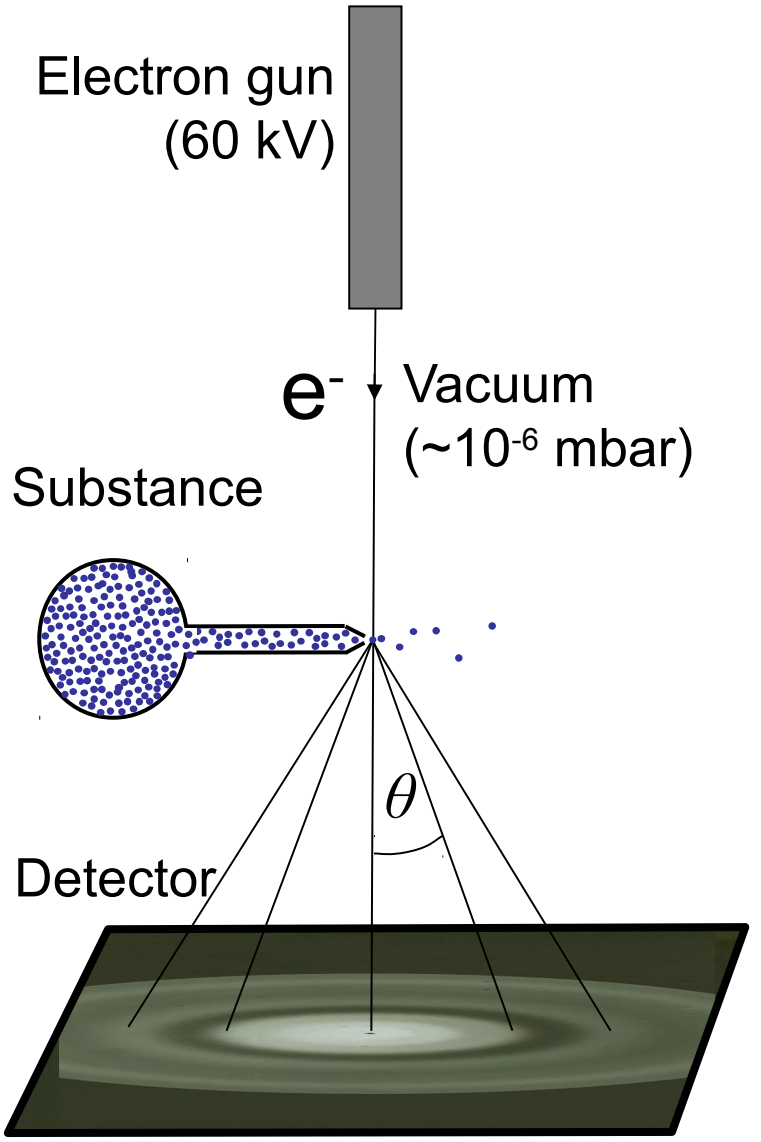
Our main goals

1. Structure of the molecules in gas phase.
2. Testing of a new method for structure refinements in GED.



GED Experiment in Bielefeld



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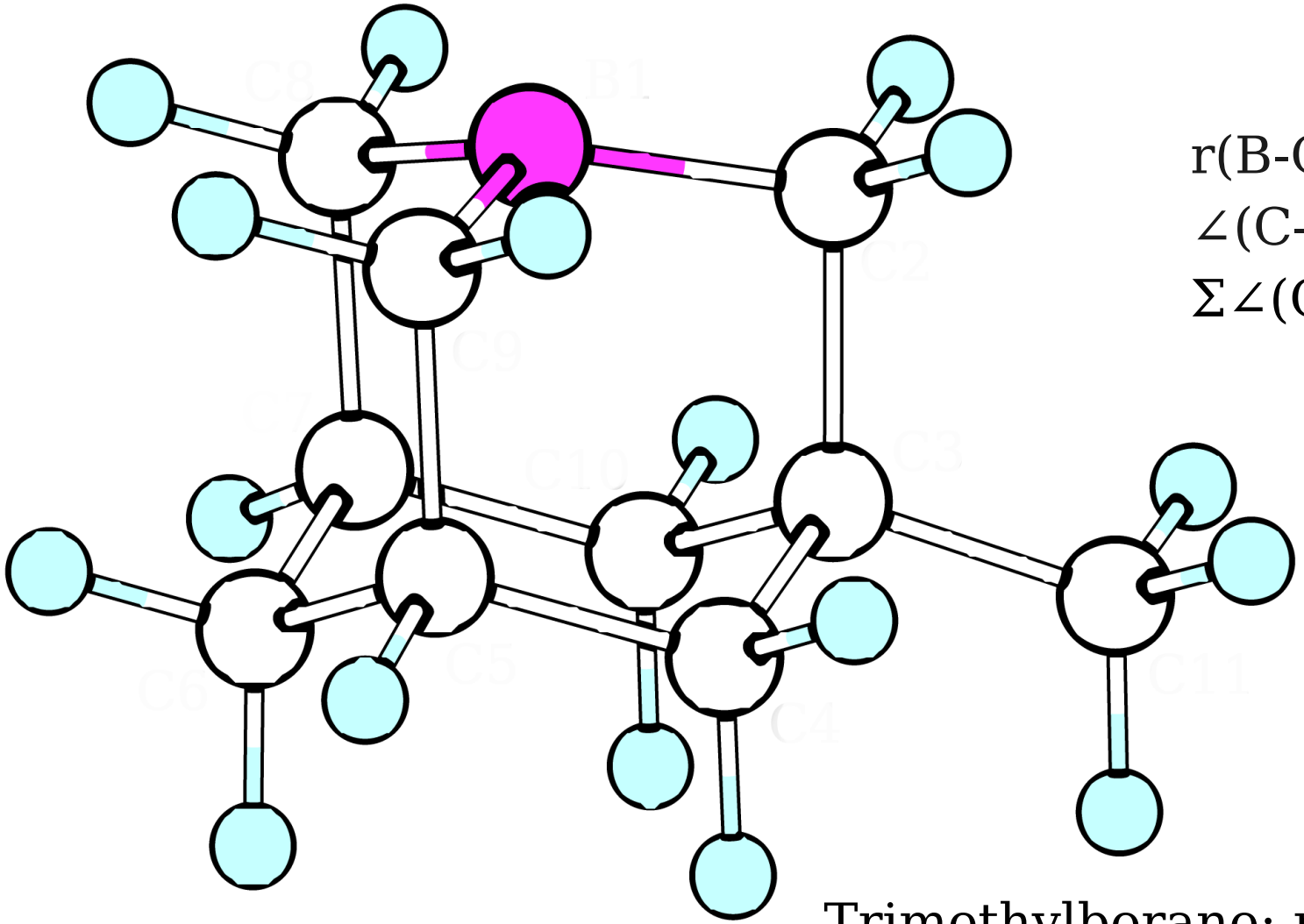
3-Methyl-1-boraadamantane: Experimental Equilibrium Structure



$r(B\text{-}C)_{av}$ = 1.556(5)Å

$\angle(C\text{-}B\text{-}C)_{av}$ = 116.5(2)°

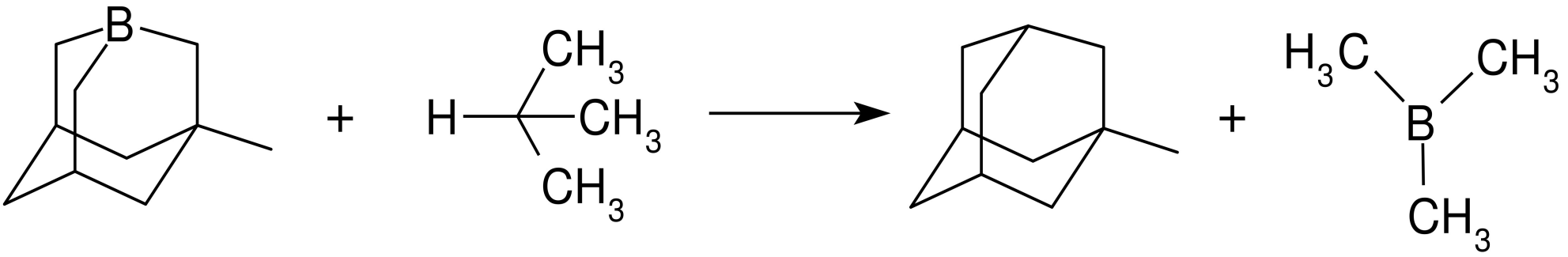
$\Sigma\angle(C\text{-}B\text{-}C)$ = 349.4(4)°

Trimethylborane: $r_g(B\text{-}C)$ = 1.578(3) Å

Trivinylborane: $r_a(B\text{-}C)$ = 1.558(3) Å

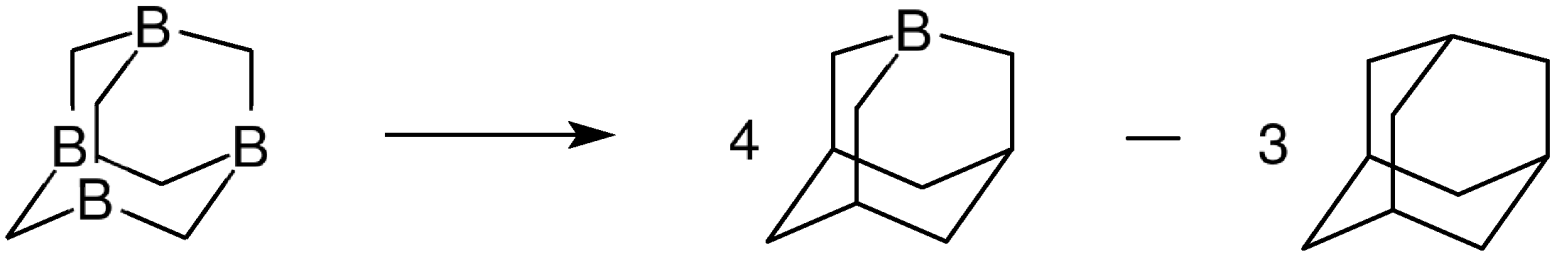
Adamantane: $\angle(C\text{-}C_{tert}\text{-}C)$ = 109.8(5)°

Strain energy: Isodesmic reactions



$\Delta H°_{r,298}$ (G4) = -14.1 kcal/mol

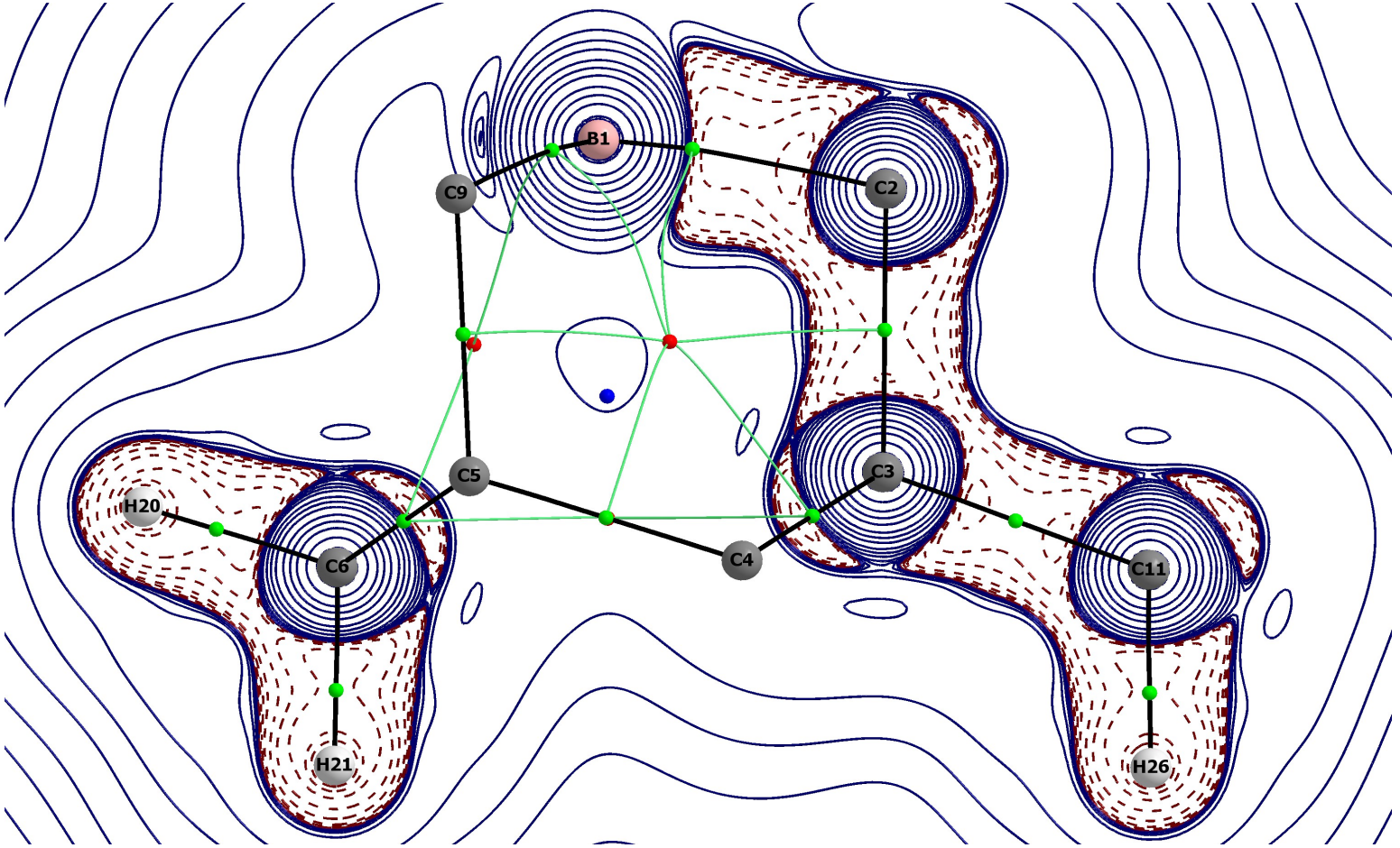
However,



$\Delta H°_{r,298}$ = 34.6 kcal/mol *

*Wang, Y.; Wu, J. I.-C.; Li, Q.; Schleyer, P. von R. *Organic Letters* 2010, **12**, 1320–1323.

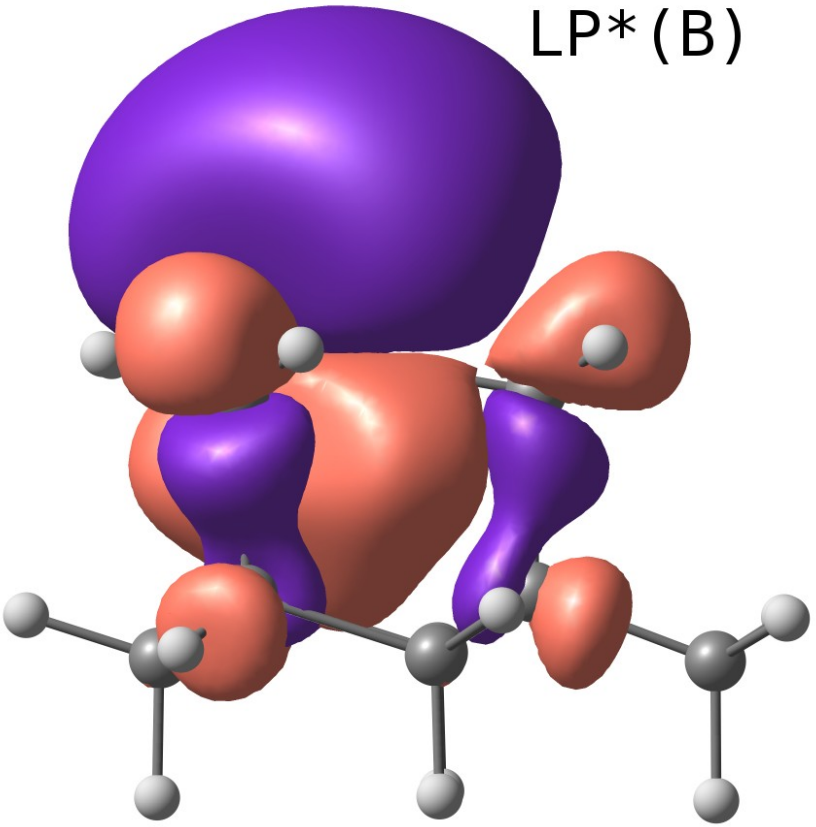
AIM Analysis

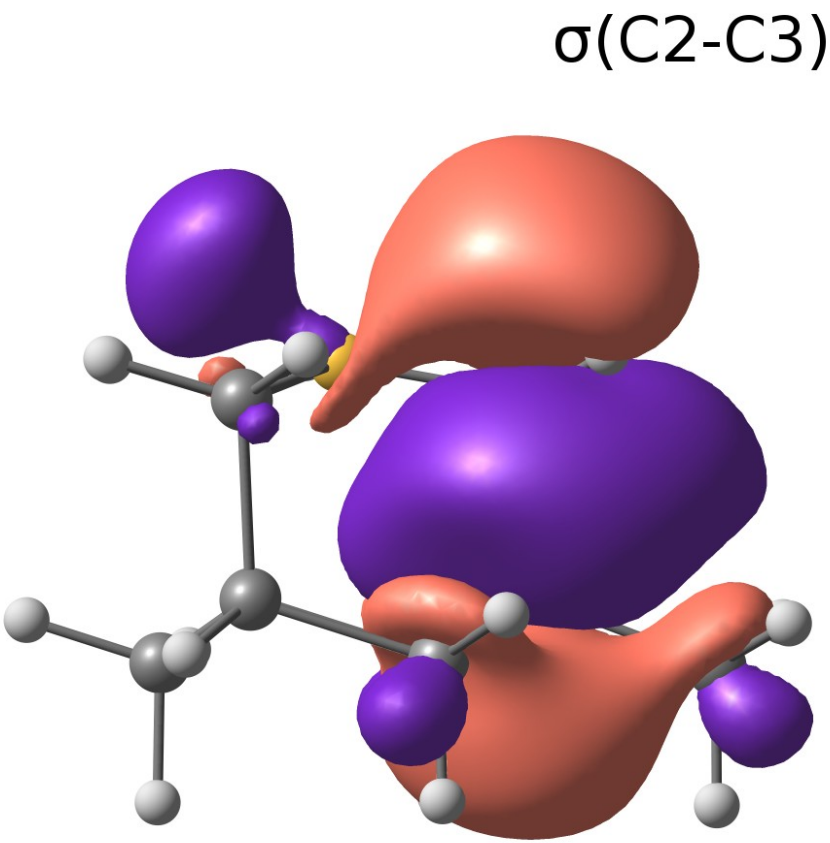


$\angle(\text{C-B-C})_{av}$ = 119.0 (AIM) vs. 116.5(2) (GED)

B-C bond ellipticity: 0.26

NBO Analysis

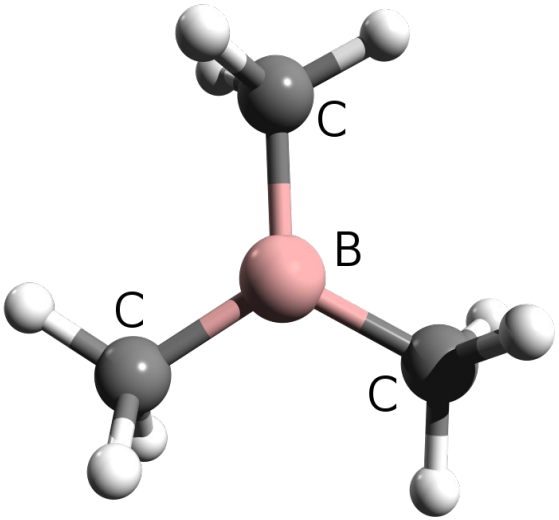


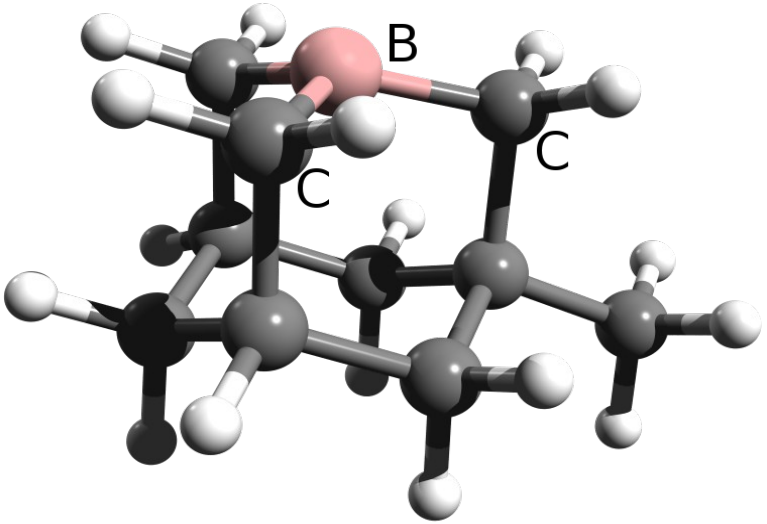


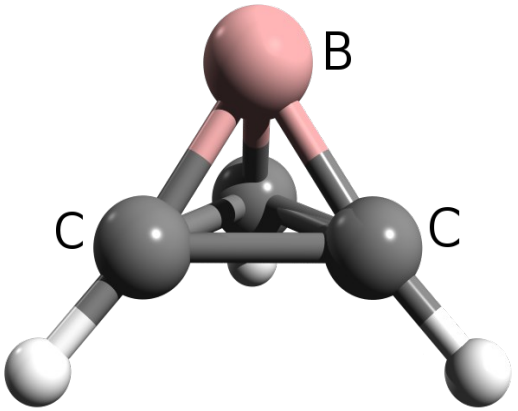
E_2 = 15.4 kcal/mol

∠ Lp*/σ(B-C) = 88.2°, i.e. even less then 90.0!
= 101.1° (HF/3-21G*) Wagner, et all., JACS, 2003

Comparison with BMe_3 and BC_3H_3







∠(C-B-C):

120.0	116.5(2)	65.2

σ(B-C) electronic configuration:

sp^2(B)-$sp^{1.9}$(C)	sp^2(B)-$sp^{2.1}$(C)	sp^2(B)-$sp^{2.3}$(C)

Charges,

AIM:

2.12	2.06	1.76

NBO:

0.93	0.94	0.73

Results

1) The boron atom in 3-methyl-1-boraadamantane is not planar,
2) but the molecule is not so strained as expected,
3) due to the bending of the B-C bonds,
4) because of hyperconjugation of $Lp^{*}(B)$ and σ(C-C),
5) which leads to the shortening of the B-C bonds as well.