Universität Bielefeld

Correlation of Experiment and Theory in Structural Chemistry: the Case of 3-Methyl-1-boraadamantane

UNEX Project

Yury V. Vishnevskiy

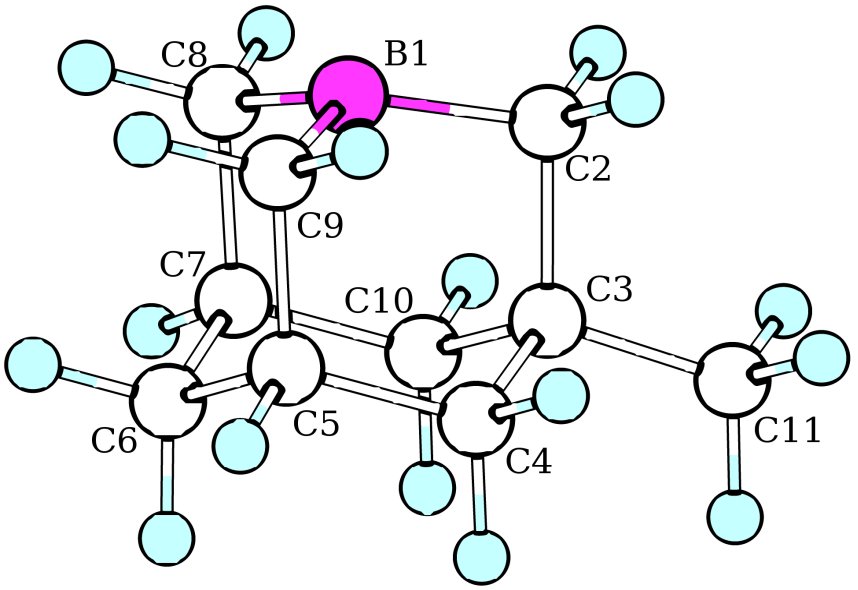
Bielefeld, June 6th 2011

Universität Bielefeld

3-Methyl-1-boraadamantane

Problems:

1. “Pyramidality” of the boron atom.
2. There is neither XRD structure nor hope to have it.
3. Difficult object for GED.



Our main objectives:

1. Development of a new method for structure refinement.
2. Experimental molecular structure in the gas phase.
3. Theoretical investigation of the molecule.

ORGANIC LETTERS

2009
Vol. 11, No. 13
2872−2875

Design of Bicyclic and Cage Boron Compounds Based on Allylboration of Acetylenes with Allyldichloroboranes

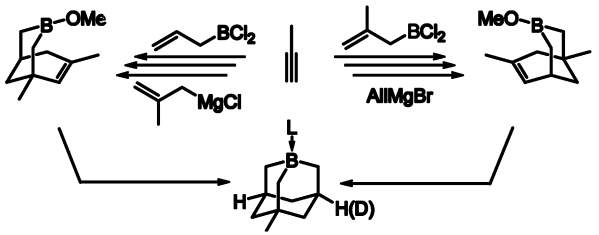
Sergey Yu. Erdyakov,[†] Anatolii V. Ignatenko,[†] Tamara V. Potapova,[†] Konstantin A. Lyssenko,[‡] Mikhail E. Gurskii,[†] and Yuri N. Bubnov*[,†,‡]

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia 119991, and A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia 119991

bor@ioc.ac.ru; bubnov@ineos.ac.ru

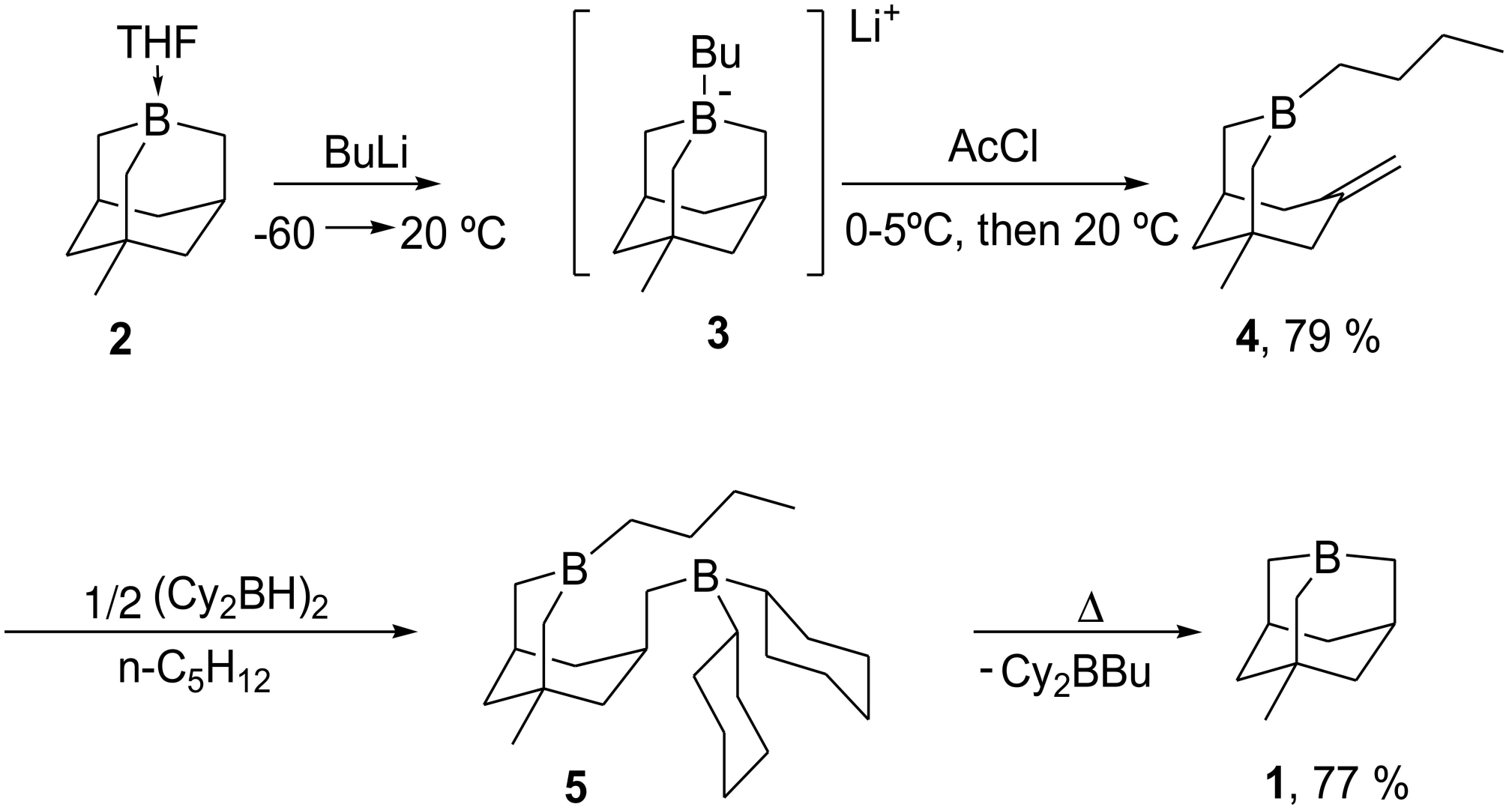
Received April 12, 2009

ABSTRACT



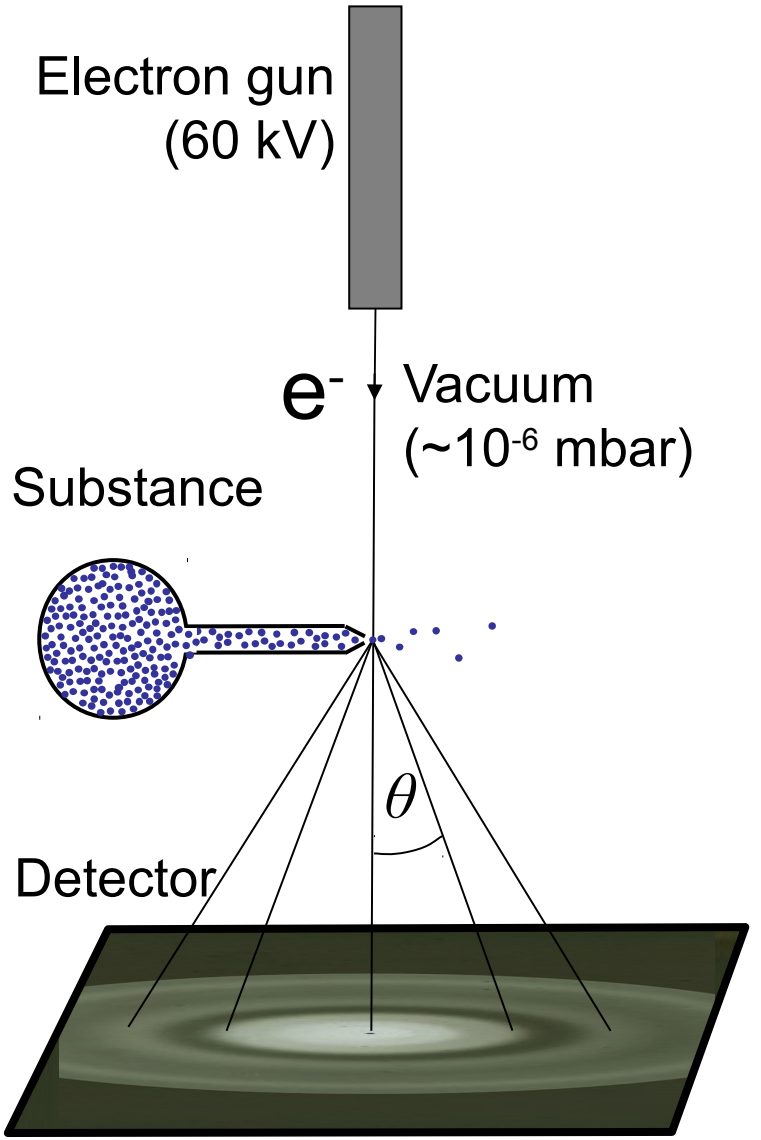
Allylboration of acetylenes with allyldichloroboranes has been proposed as a first step of allylboron−acetylene condensation and a way to design condensation products from stage to stage. The chemistry has been applied to the synthesis of isomeric 3-borabicyclo[3.3.1]non-6-enes transformed into 3-methyl-1-boraadamantane and [5-D]-3-methyl-1-boraadamantane derivatives.

Synthesis, part 2

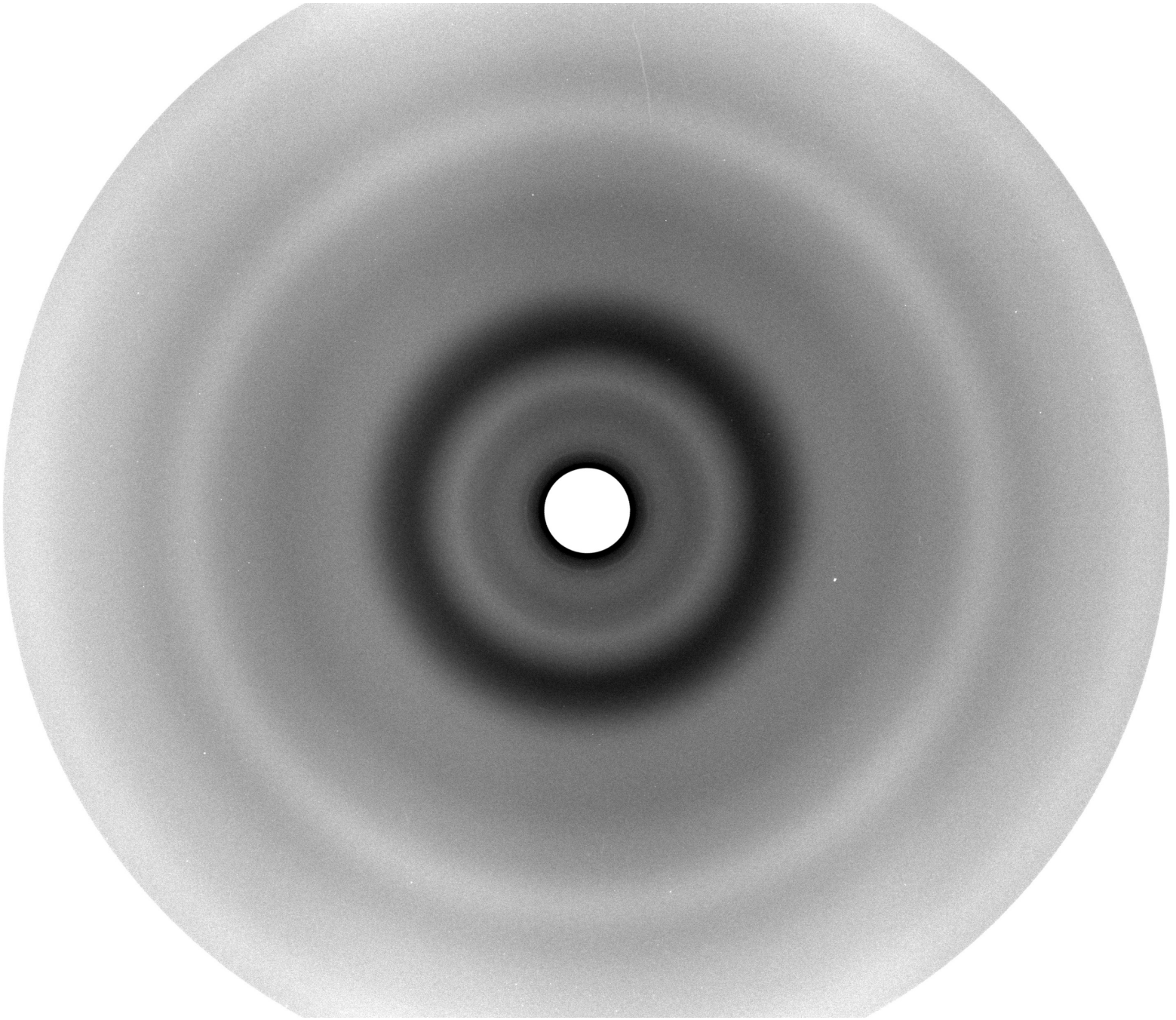


Cy = cyclohexyl

GED Experiment



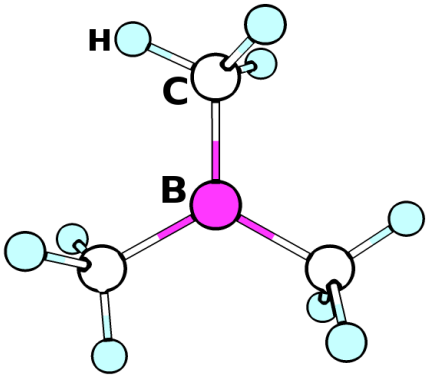
An example of diffraction pattern

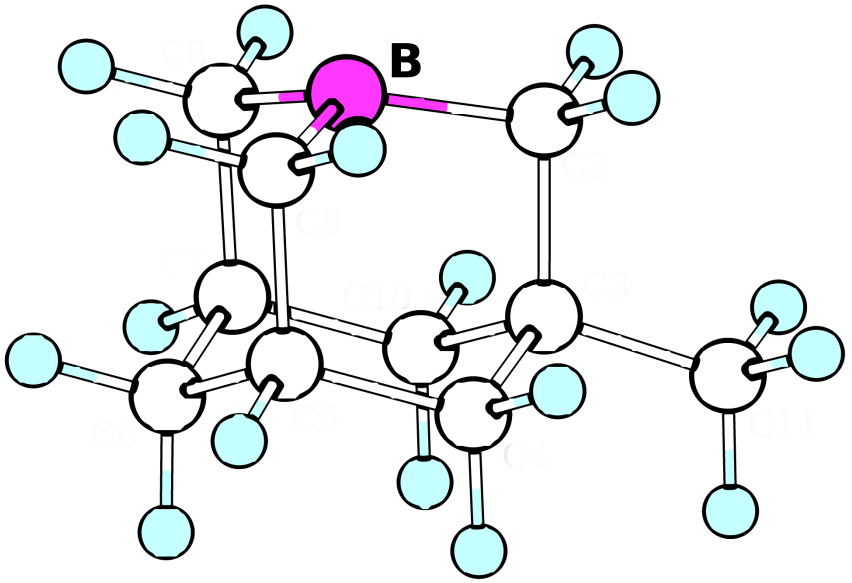


Experimental structure: “pyramidality” of the boron atom

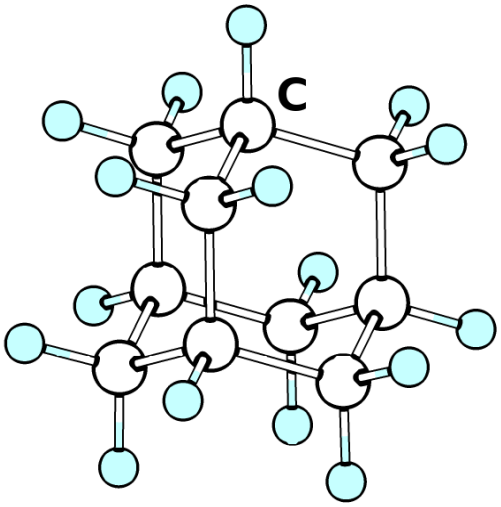
3-Methyl-1-boraadamantane

Trimethylborane





Adamantane



∠(C-X-C), degrees

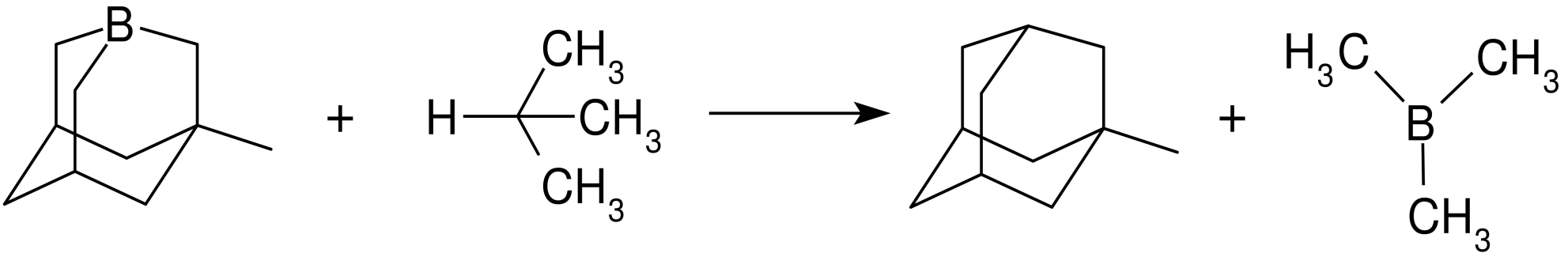
120.0 > 116.5(2) > 109.8(5)

Σ∠(C-X-C), degrees

360.0 > 349.4(4) > 329.4(10)

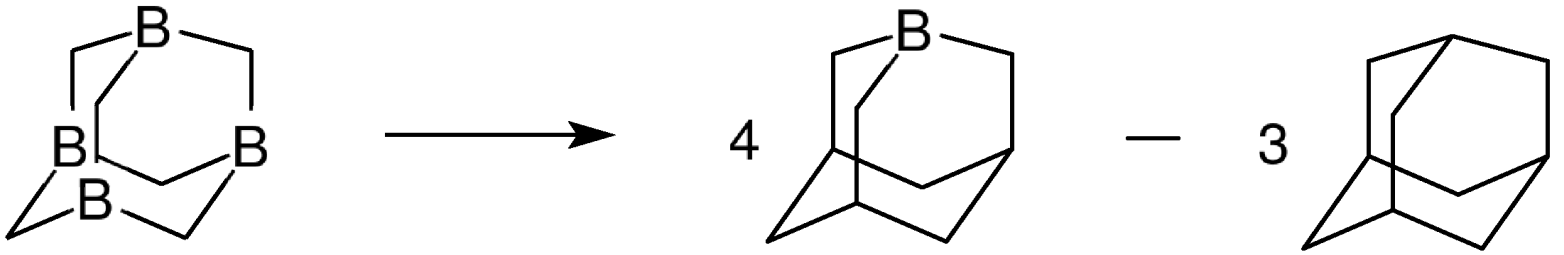
I. Hargittai, K. Hedberg, *J. Chem. Soc., Chem. Commun.* (1971) 1499.

Strain energy: Isodesmic reactions



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

However,



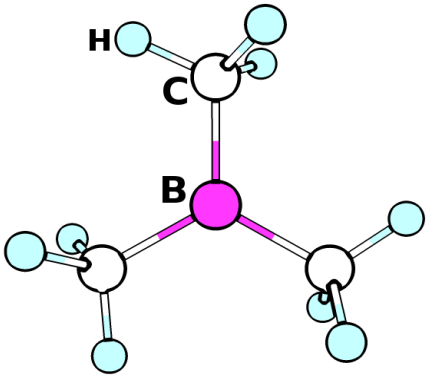
$\Delta H°_{r,298}$ (B3LYP/6-311+G**) = 34.6 kcal/mol

$\Delta H°_{r,298}$ (G4) = 35.9 kcal/mol

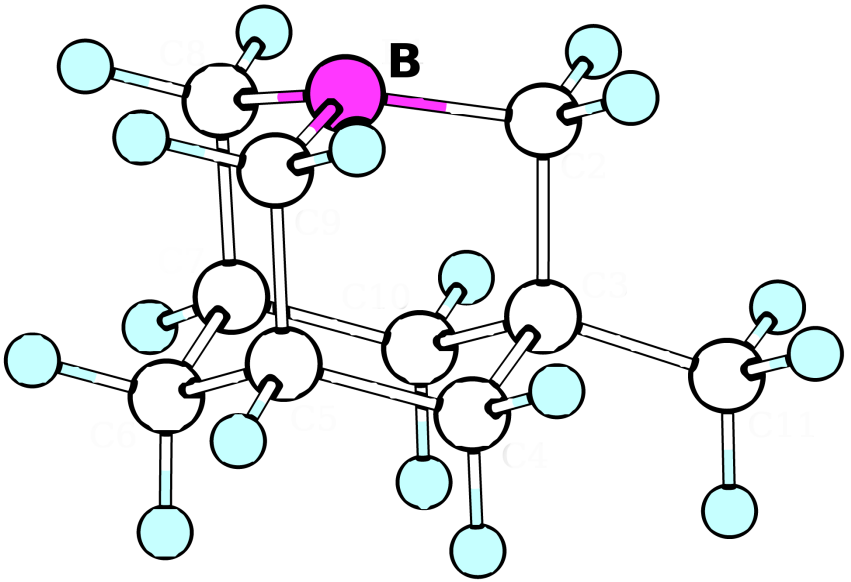
Y. Wang, J. I.-C. Wu, Q. Li, P. von R. Schleyer, *Organic Letters* (2010) **12**, 1320.

Experimental structure: B-C bonds

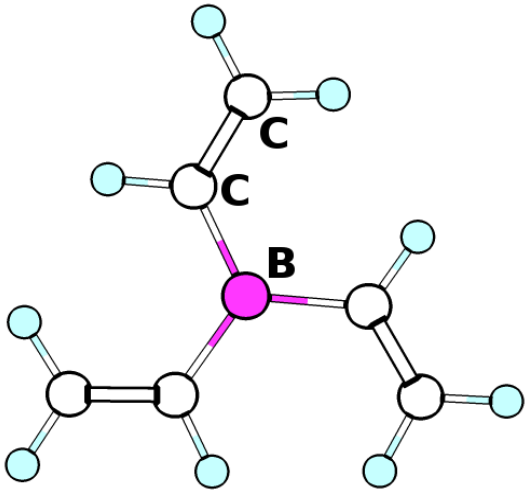
Trimethylborane



3-Methyl-1-boraadamantane



Trivinylborane



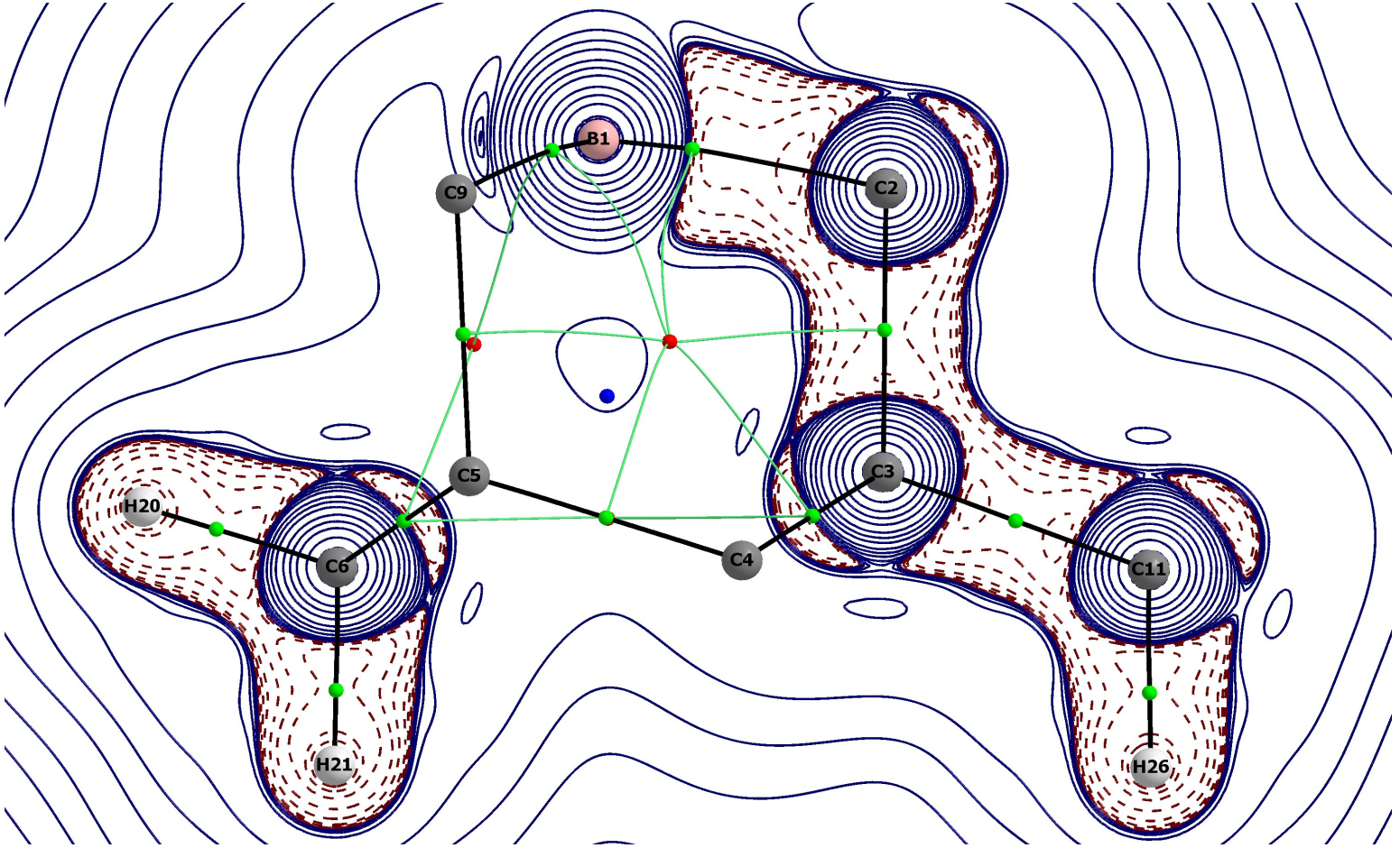
r_g(B-C), Å:

1.578(3) > 1.565(5) > 1.560(3)

L. S. Bartell and B. L. Carroll, *J. Chem. Phys.* (1965) 42, 3076.
A. Foord, B. Beagley, W. Reade and I. A. Steer, *J. Mol. Struct.* (1975) 24, 131.

Analysis of electron density: QTAIM

$\nabla^2\rho$

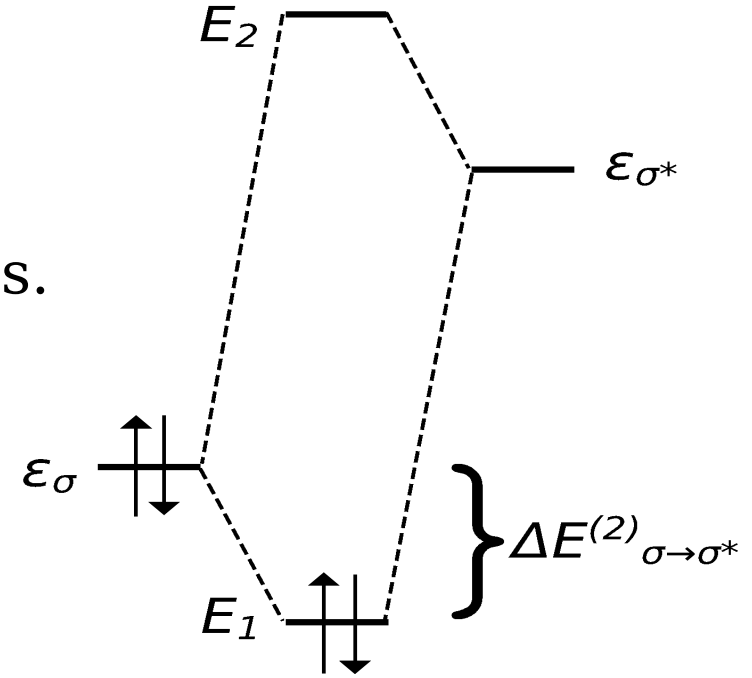


$\angle(\text{C-B-C})_{av}$ = 119.0 (QTAIM) vs. 116.5(2) (GED)

B-C bond ellipticity: 0.26 (C-C in benzene: 0.21; in ethylene: 0.38)

Analysis of orbitals. What is NBO?

- Localized orbitals.
- Perturbation theory energy analysis.
- Directionality and “Bond bending” analysis.
- Natural population analysis.



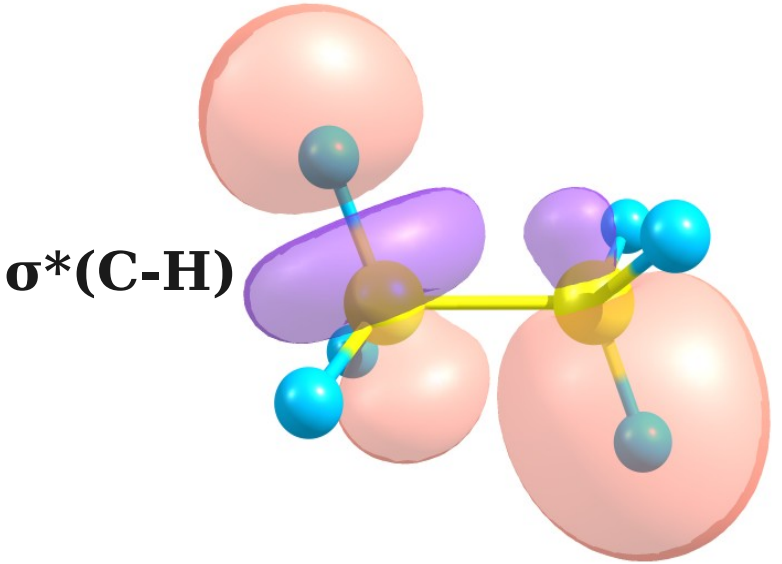
Example:

Nature (2001), v. **411**, p. 565:

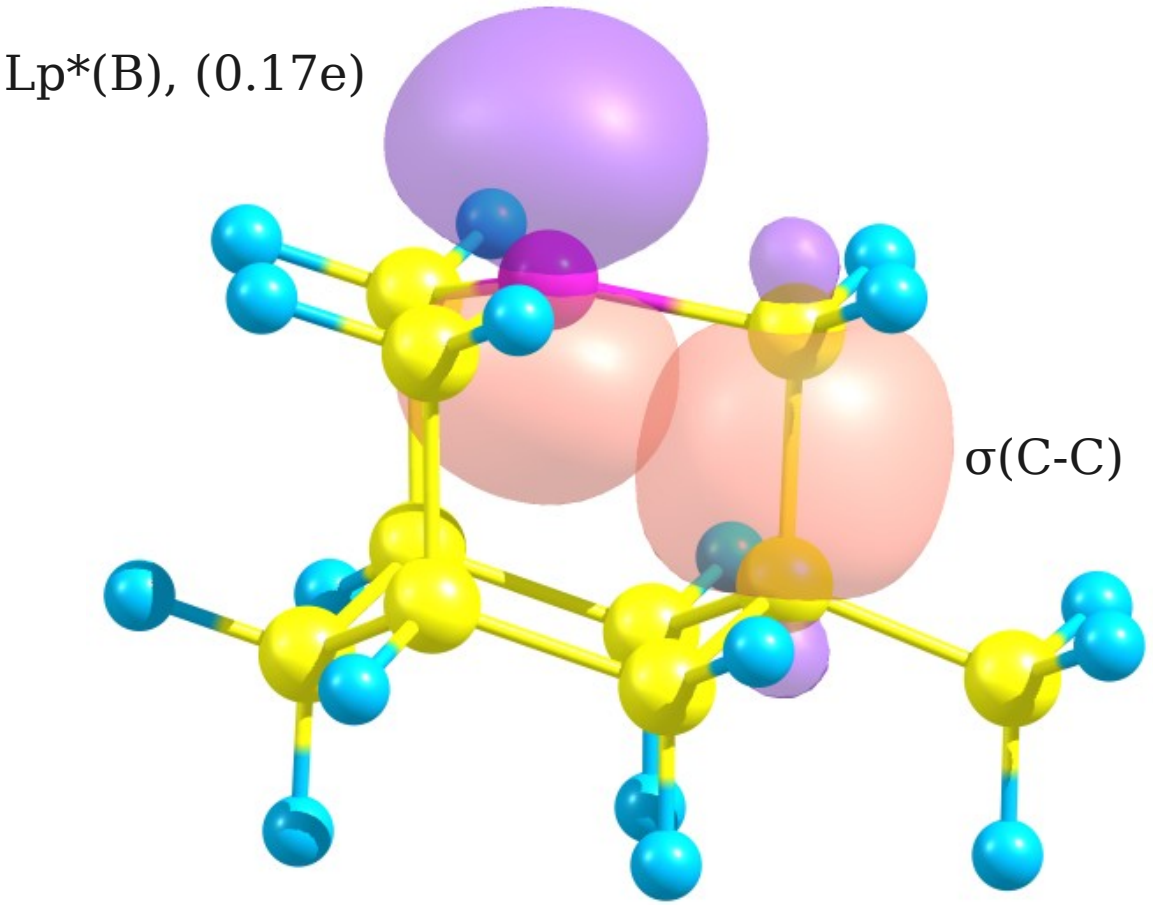
Hyperconjugation not steric repulsion leads to the staggered structure of ethane

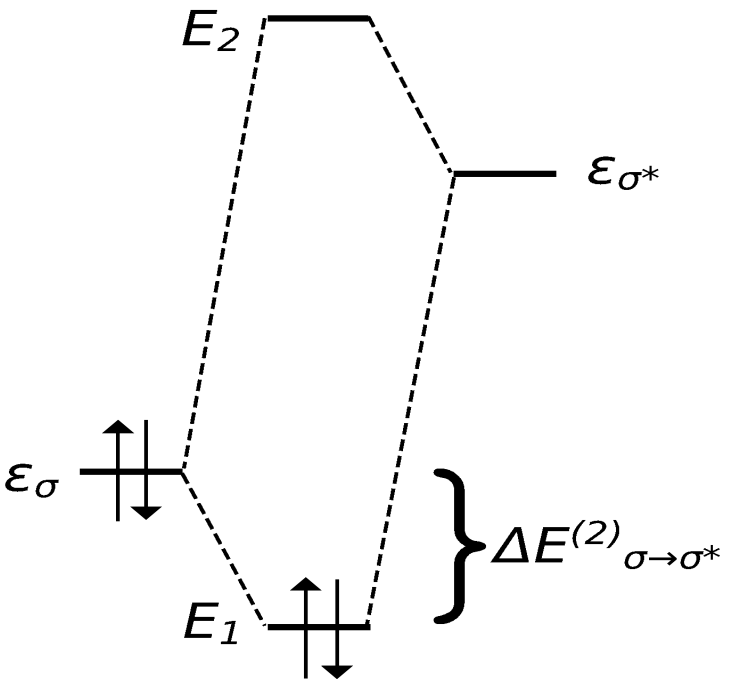
Vojislava Pophristic & Lionel Goodman

Wright and Rieman Chemistry Laboratories, Rutgers University, New Brunswick, New Jersey 08903, USA



Analysis of orbitals: NBO

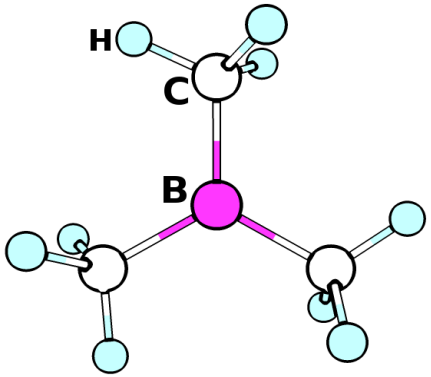


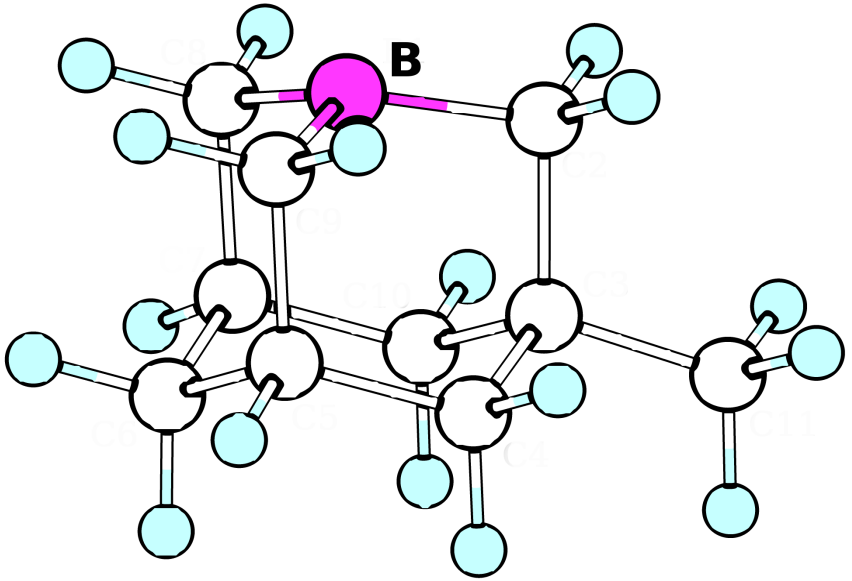


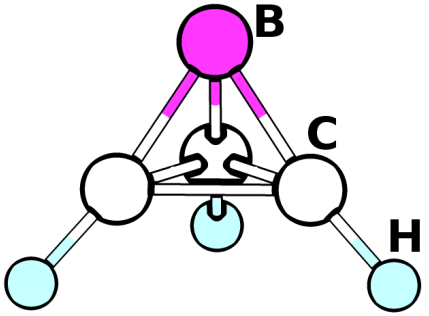
$\Delta E^{(2)}$ = 15.4 kcal/mol

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

B charges,

AIM:

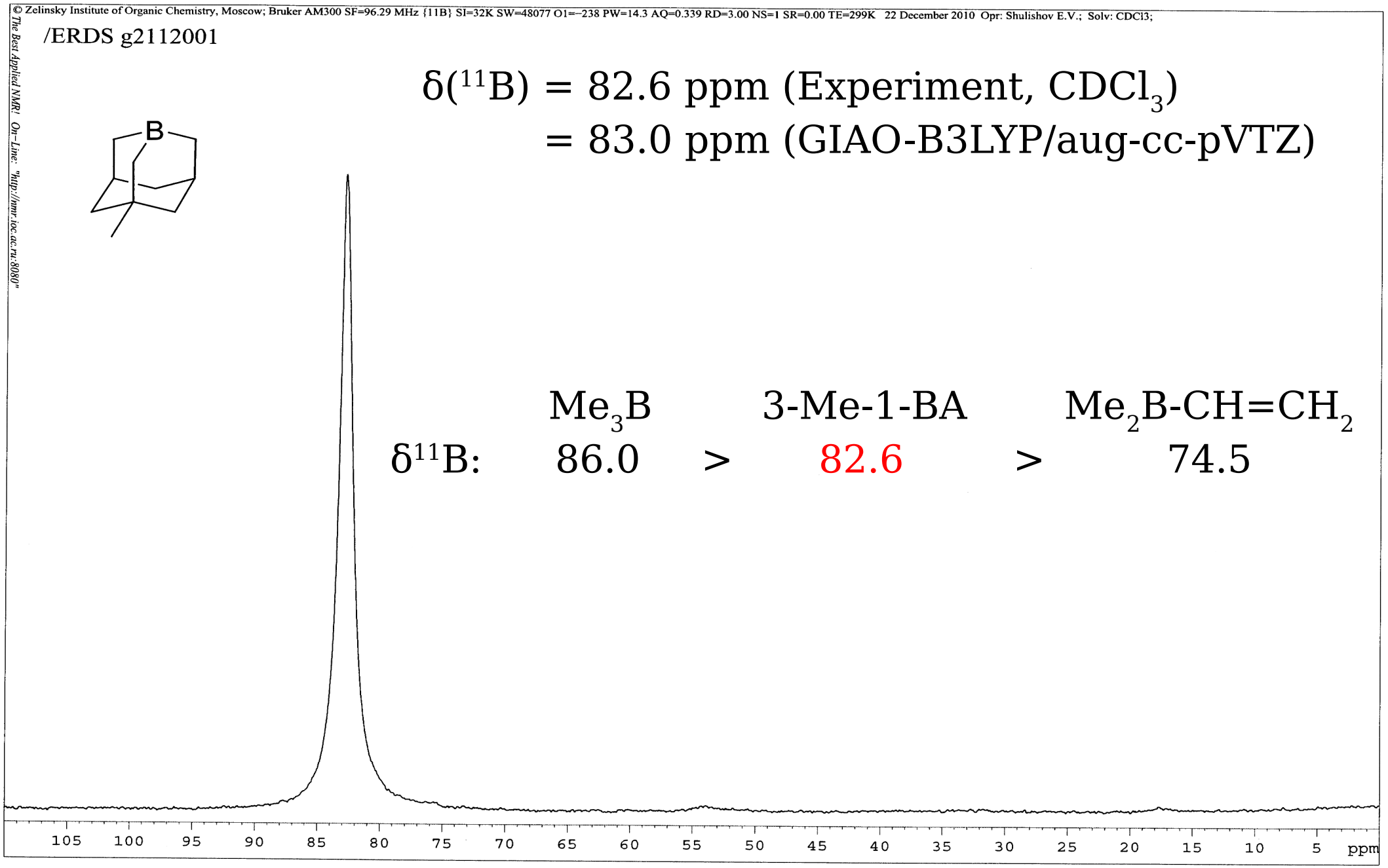
2.12	2.06	1.76

NBO:

0.93	0.94	0.73

Universität Bielefeld

^{11}B NMR



$\delta(^{11}B)$ = 82.6 ppm (Experiment, $CDCl_3$)

= 83.0 ppm (GIAO-B3LYP/aug-cc-pVTZ)

	Me_3B		3-Me-1-BA		Me_2B-CH=CH_2
$\delta^{11}B$:	86.0	>	82.6	>	74.5

B. Wrackmeyer, in Annual Reports on NMR Spectroscopy (G. A. Webb ed.), Academic Press, Vol. 20, 1988, pp. 61 – 203.

Outline