Universität Bielefeld

Structural chemistry of 1,5-diazabicyclo[3.1.0]hexane derivatives from a perspective of gas-phase electron diffraction

UNEX Project

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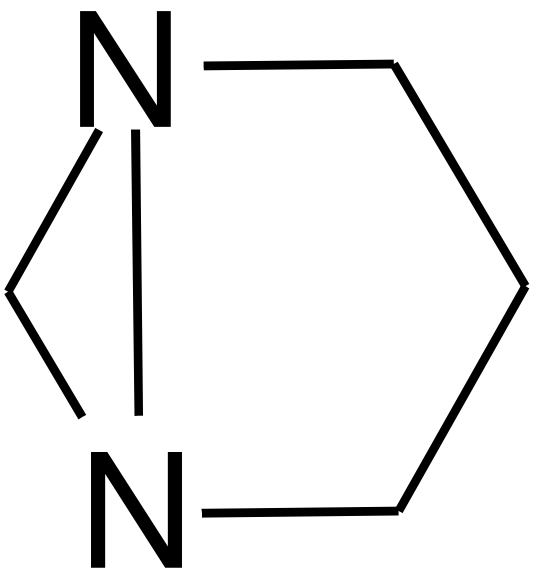
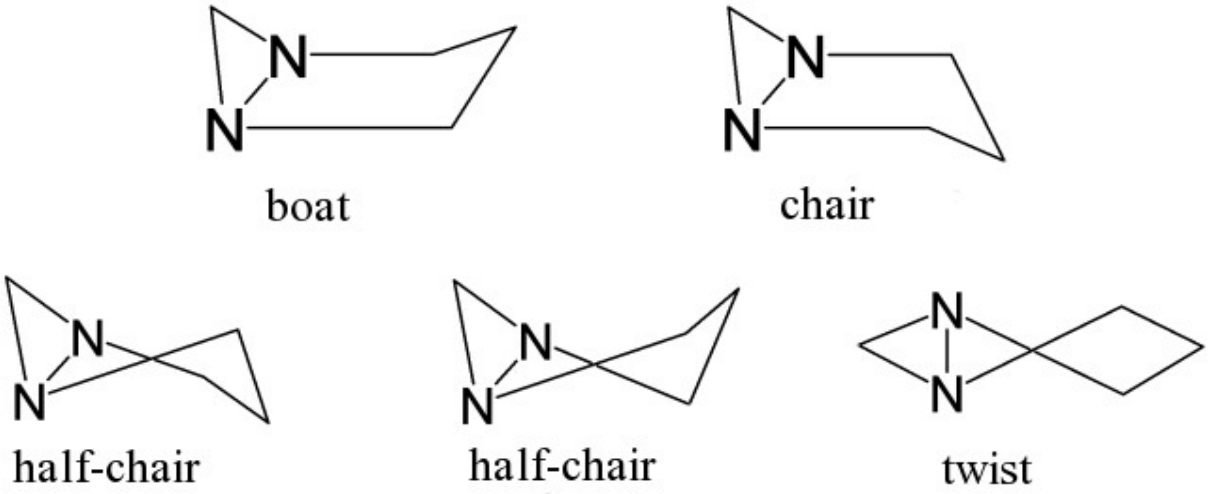
Graz, September 25th 2011

Universität Bielefeld

1,5-diazabicyclo[3.1.0]hexane (DABH)



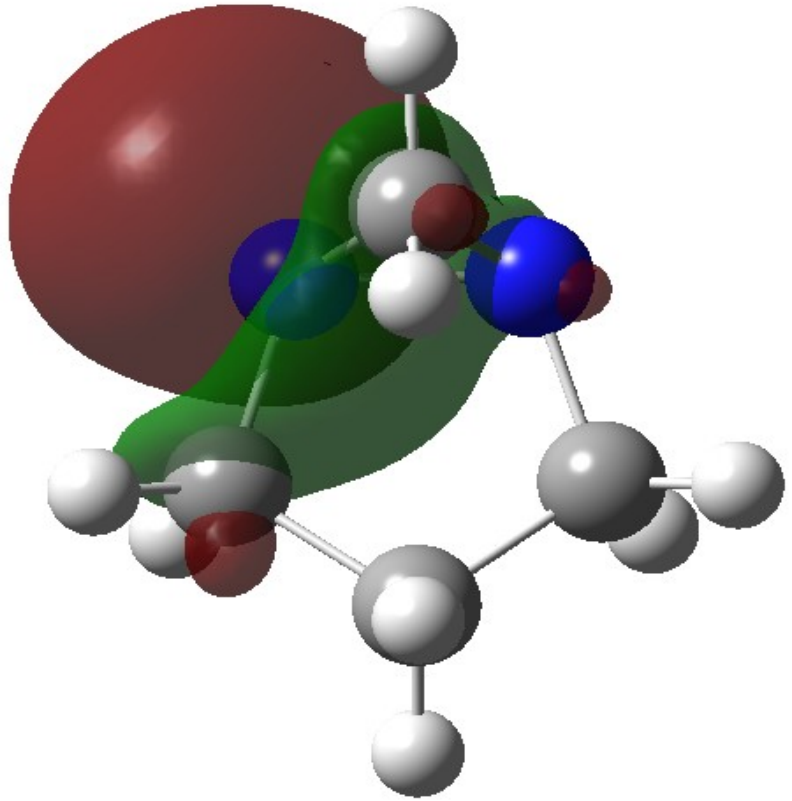
DABH: Conformations

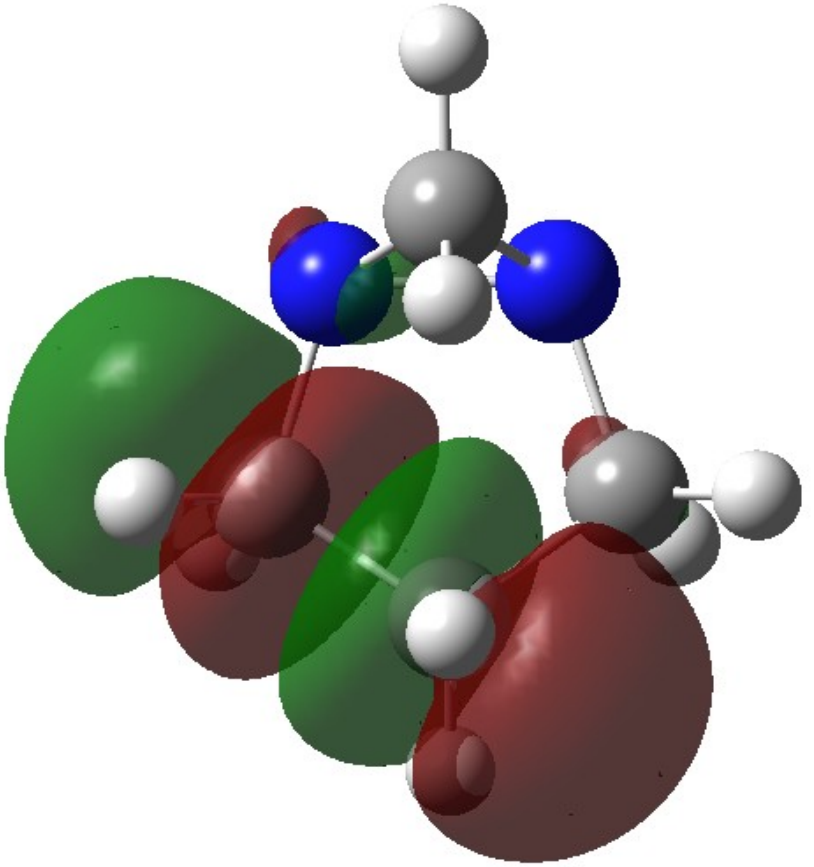


Method	Stable conformation	Reference
^{1}H- and ^{13}C-NMR	boat	[1]
IR	half-chair	[2]
PE, AM1	half-chair	[3]
PE, ^{1}H-NMR	half-chair	[4]
GED	boat	[5]

[1] G. V. Shustov, S. N. Denisenko,I. I. Chervin, N. L. Asfandiarov and R. G. Kostyanovsky, *Tetrahedron*, **41**, N. 23, (1985) 5719-5731.
[2] H.-P. Koopman and P. Rademacher, *Spectrochimica Acta*, **32**A, (1976) 157- 161.
[3] S. N. Denisenko, G. Kaupp, A. J. Bittner and P. Rademacher, *J. Mol. Struct.*, **240**, (1990), 305-312.
[4] P. Rademacher and H. Koopman, *Chem. Ber.*, **108**, (1975), 1557-1569.
[5] Yu. V. Vishnevskiy, N. Vogt, J. Vogt, A. N. Rykov, V. V. Kuznetsov, N. N. Makhova, L. V. Vilkov, *J. Phys. Chem. A*, **112**, (2008) 5243-5250.

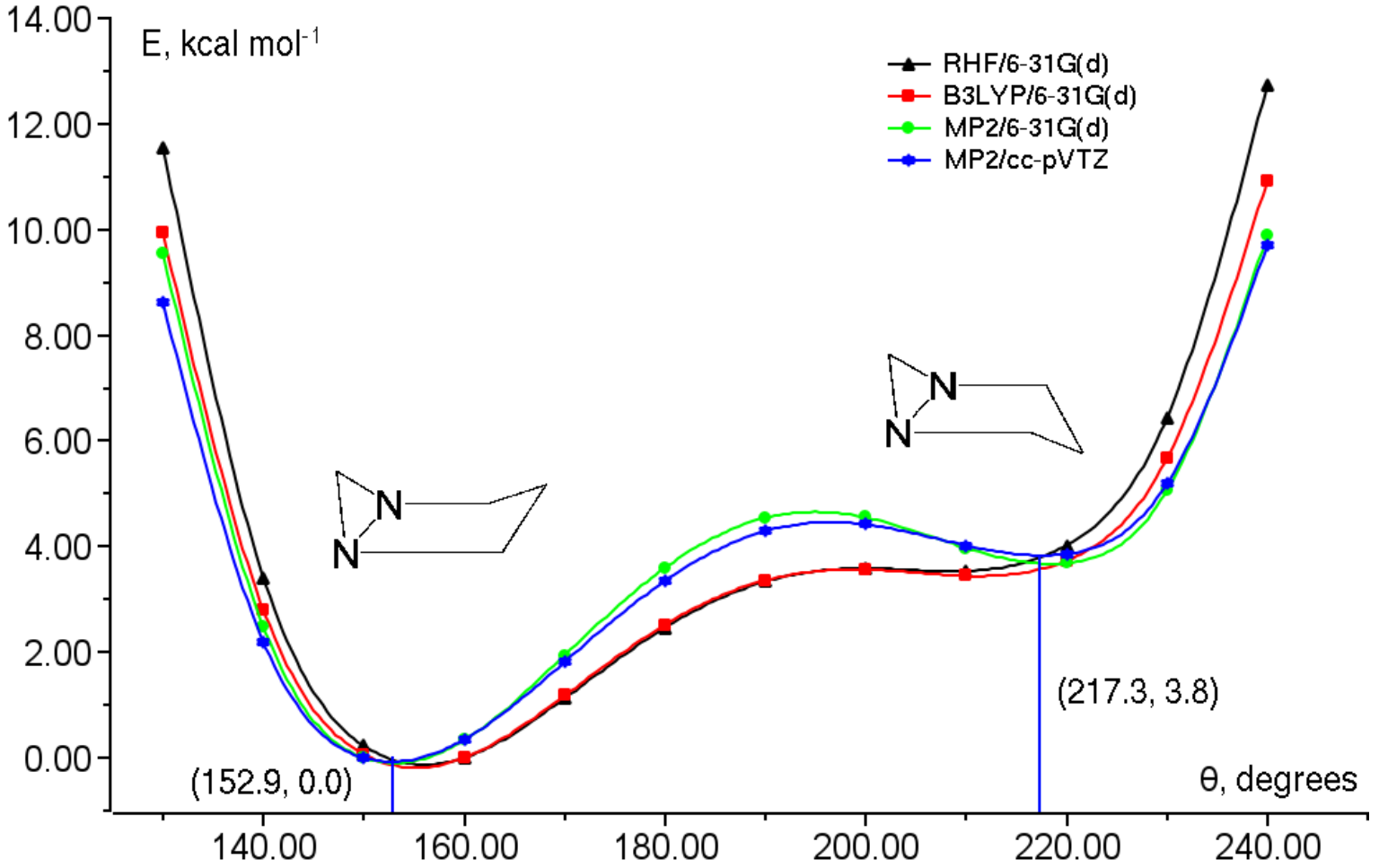
DABH: NBO analysis





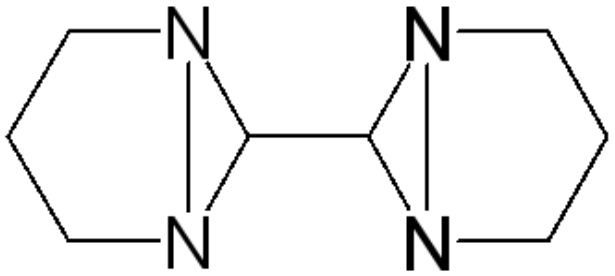
$n(N) \rightarrow \sigma^*(C\text{-}C)$: $E^{(2)} = 4$ kcal/mol

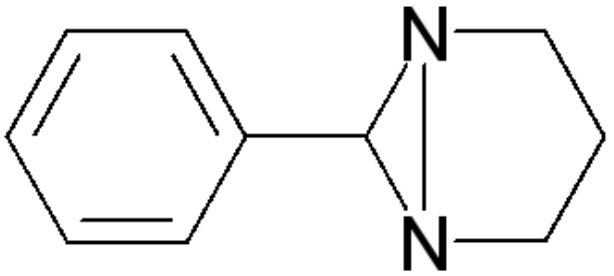
DABH: Potential

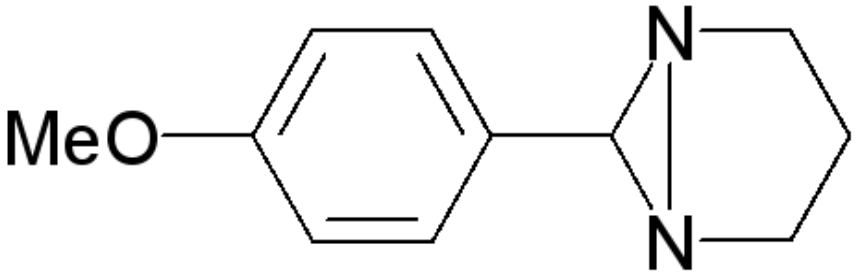


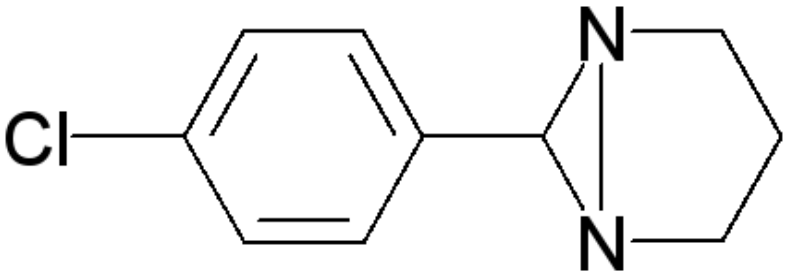
Is there a chair conformer?

DABH: Derivatives



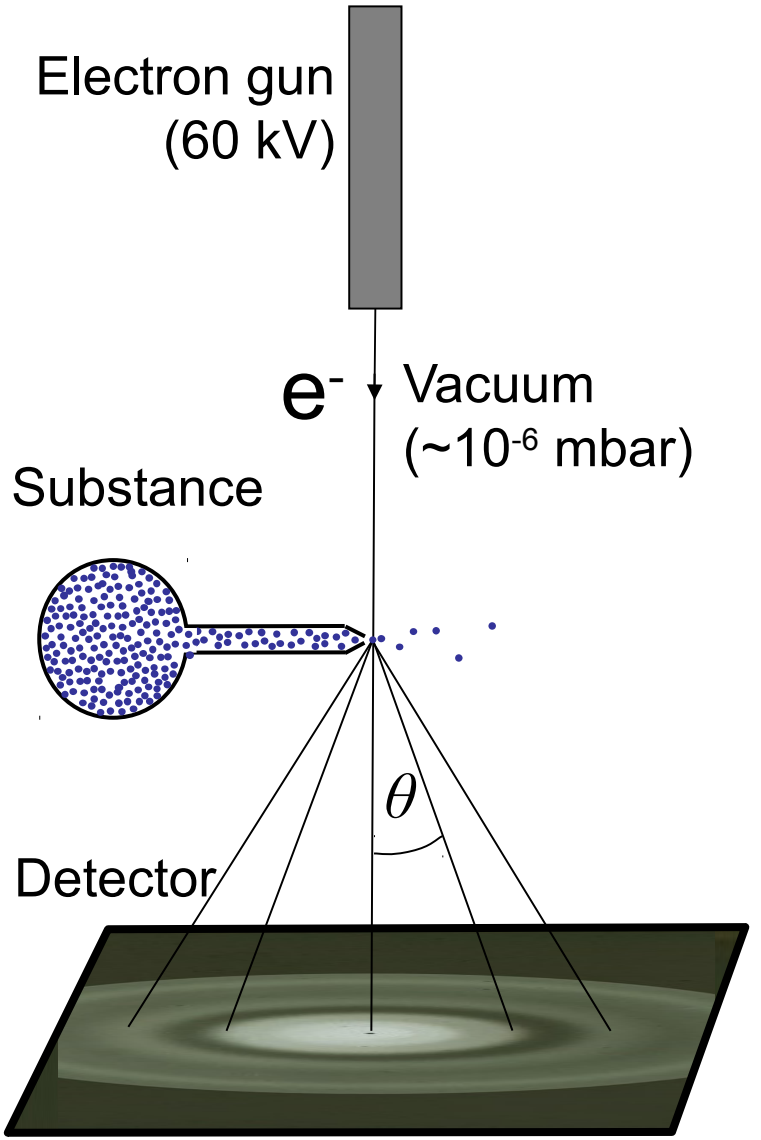




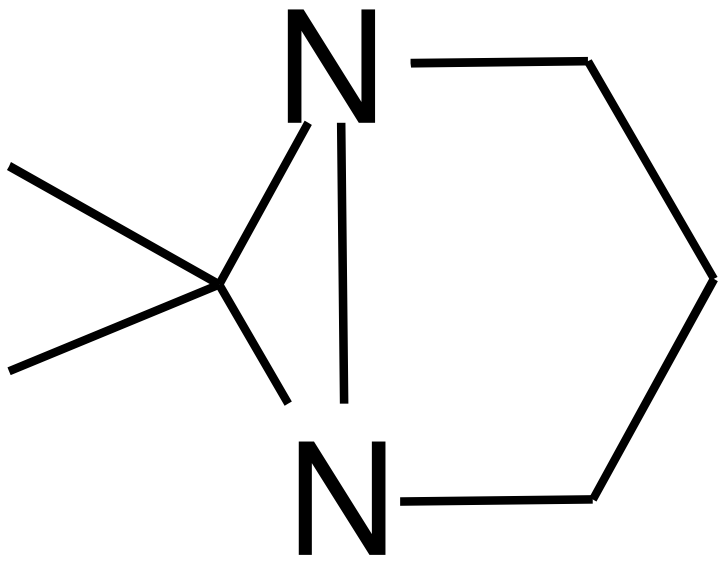


All have *boat* conformation.

GED Experiment



6,6-dimethyl-DABH



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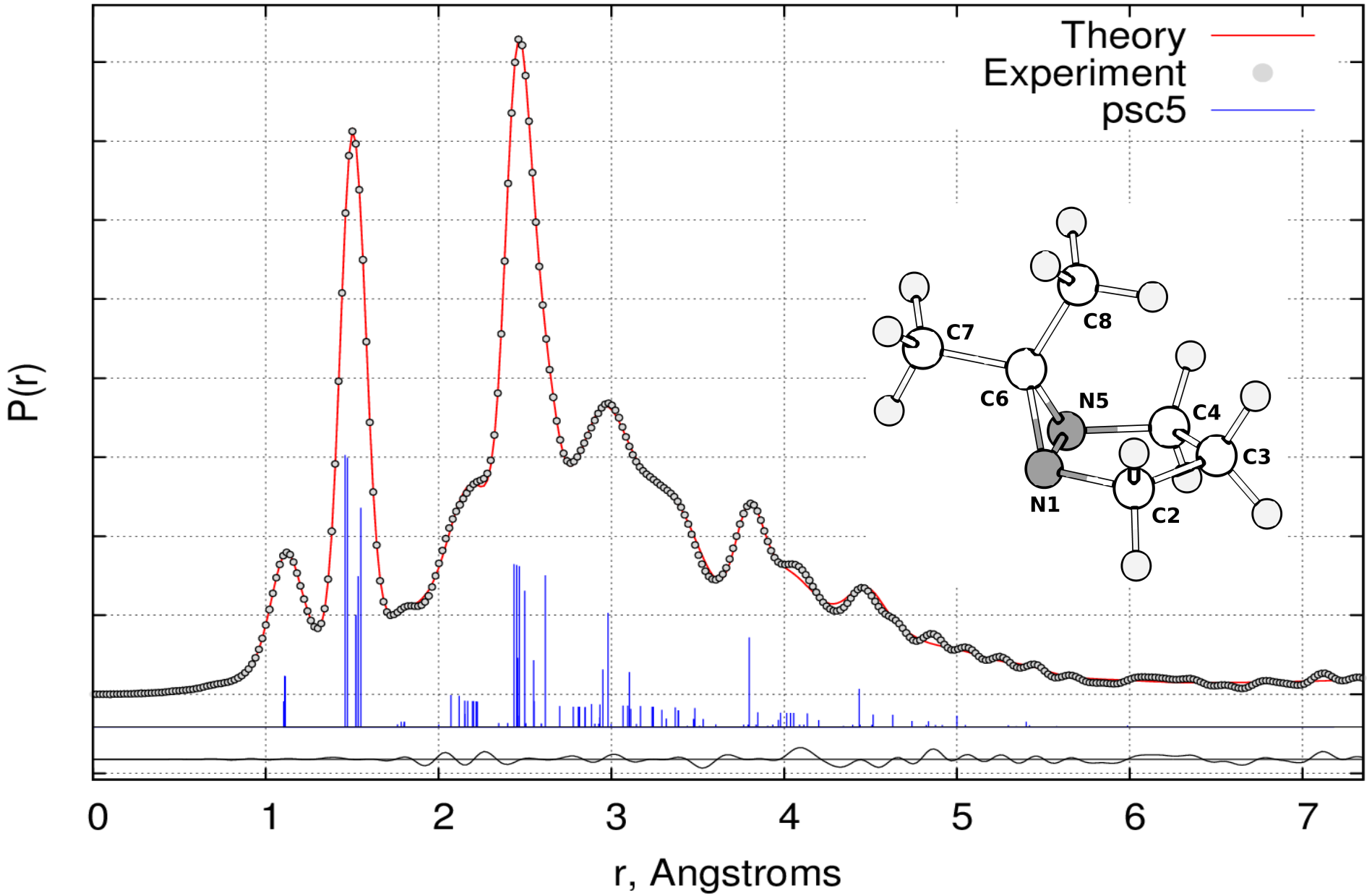
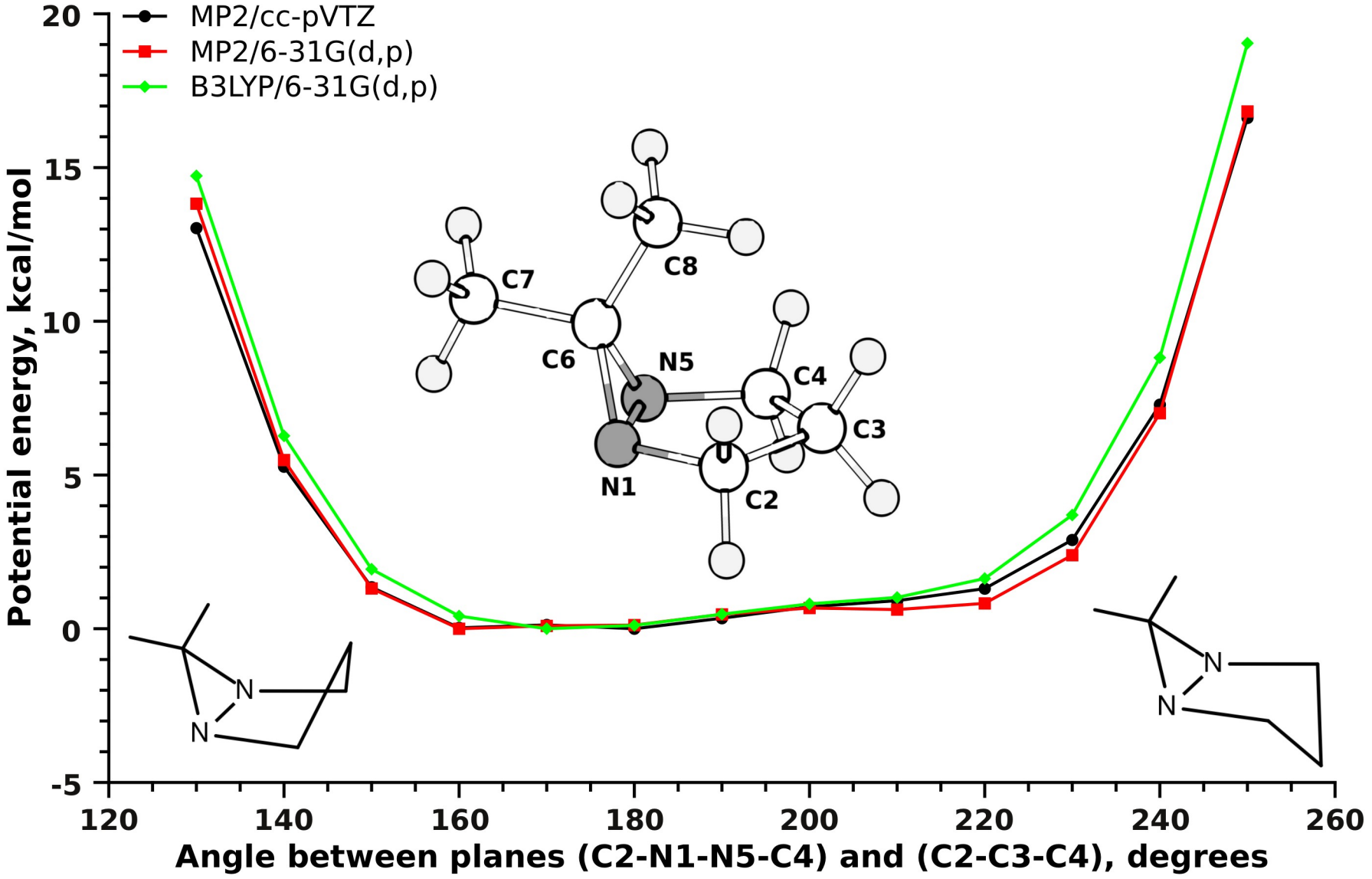
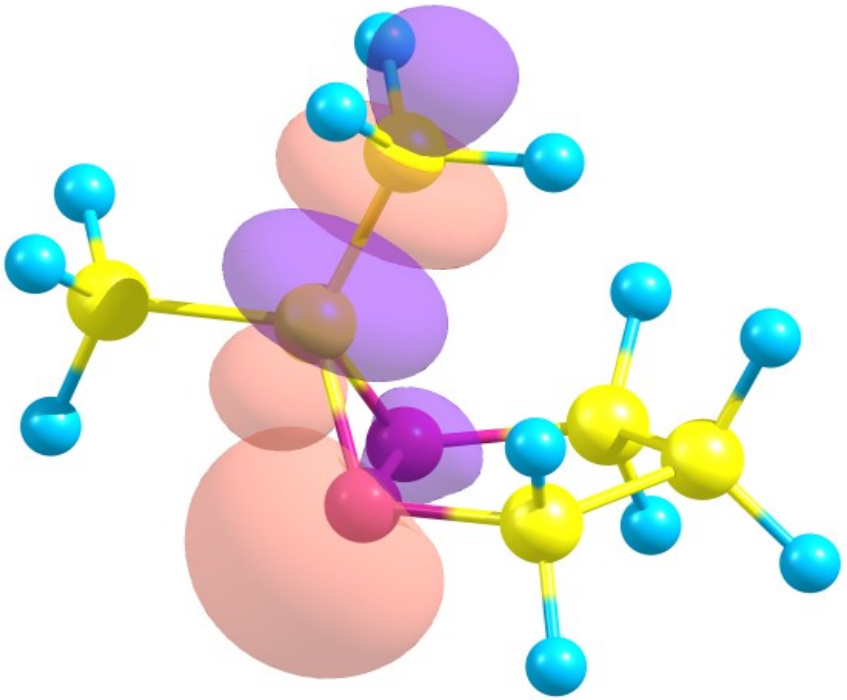
6,6-dimethyl-DABH

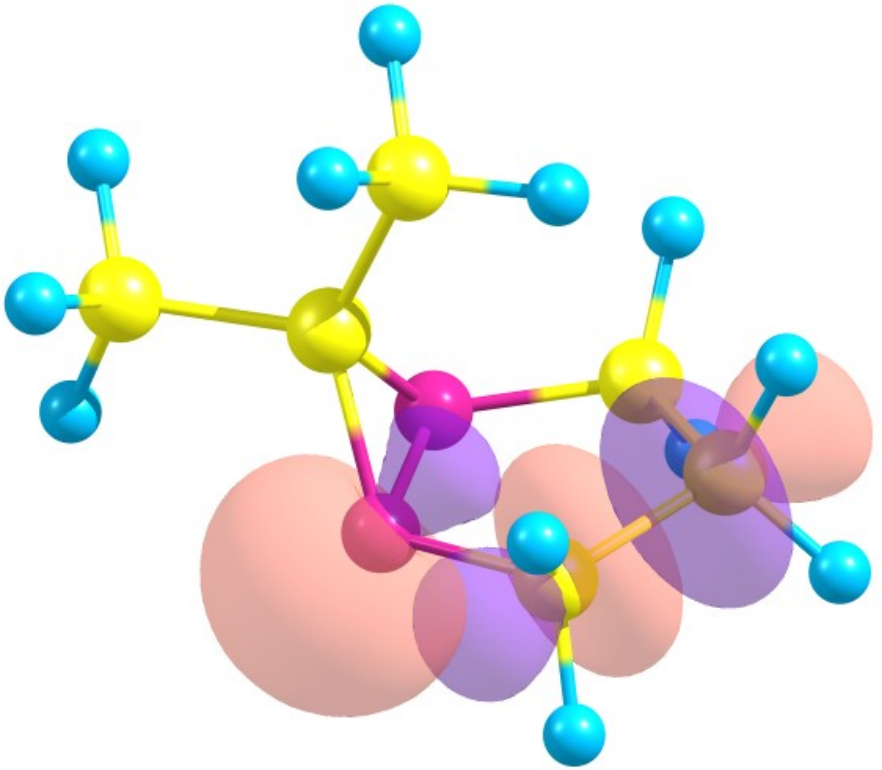


6,6-dimethyl-DABH



6,6-dimethyl-DABH: n(N)→σ*(C-C)





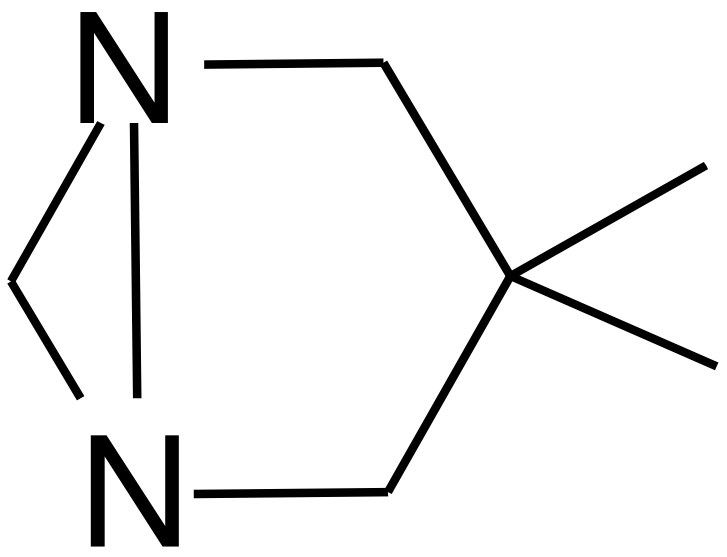
n = 0.035 e

0.022 e

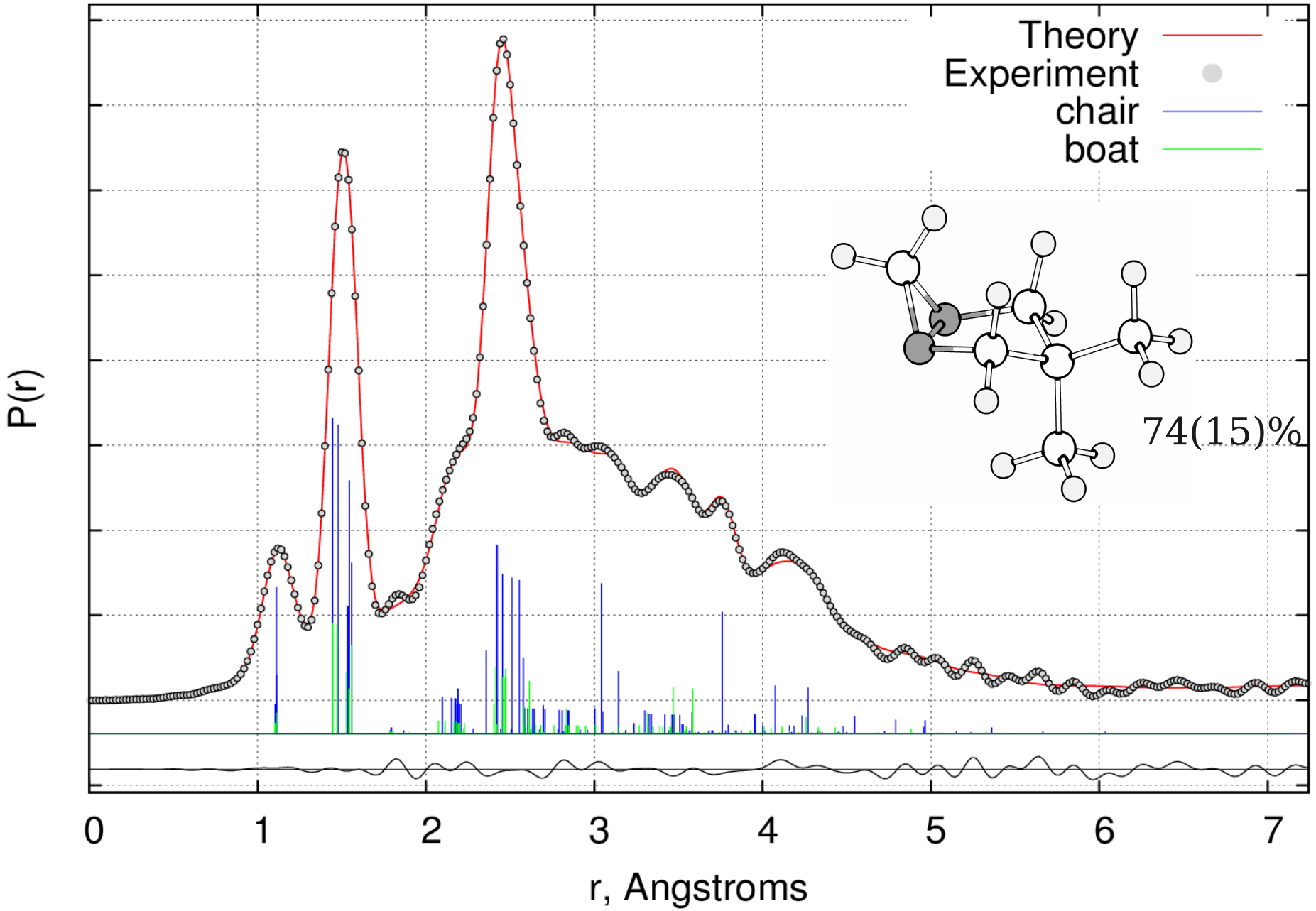
E^2 = 4.6 kcal/mol

3.5 kcal/mol

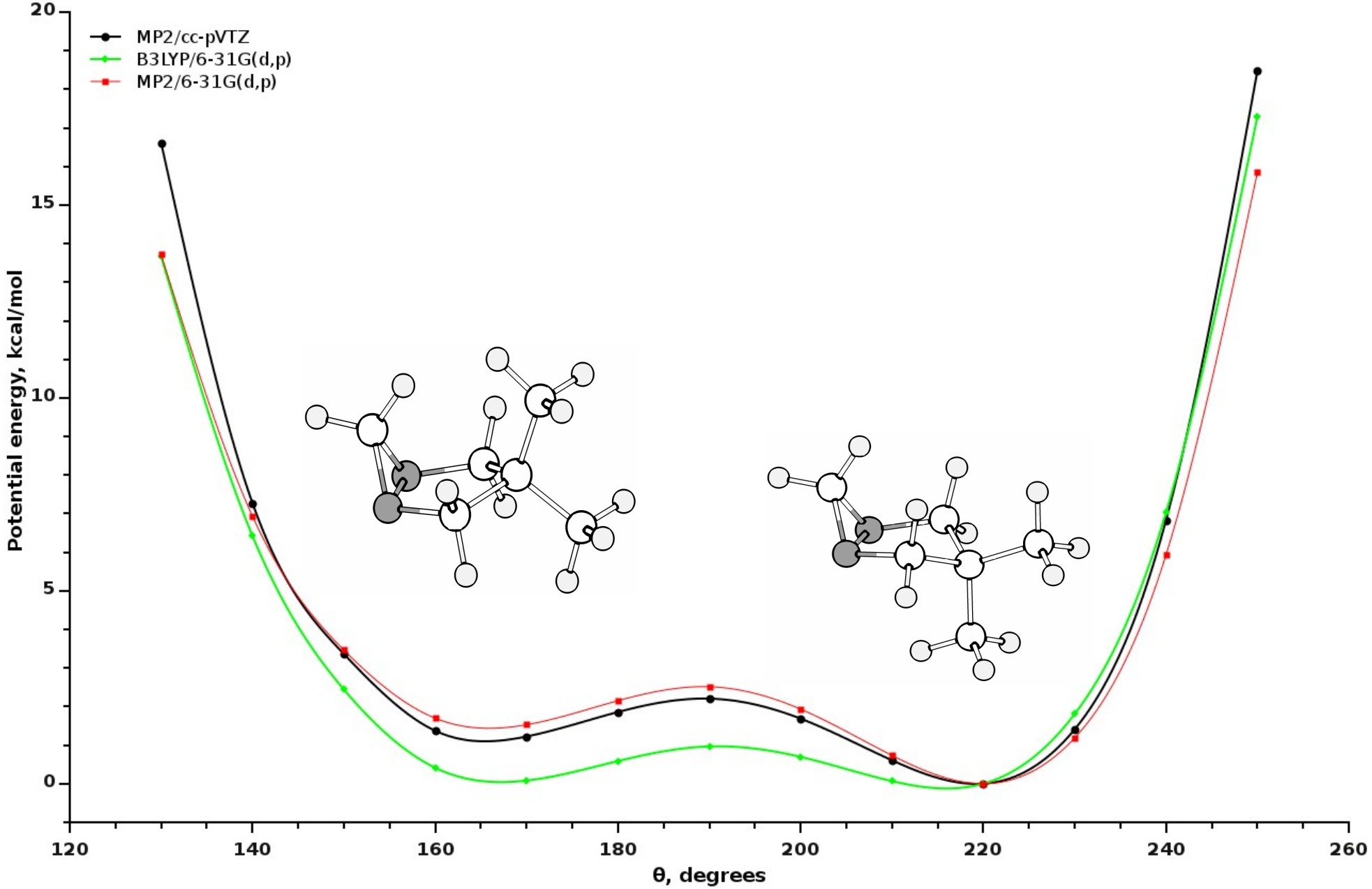
3,3-dimethyl-DABH



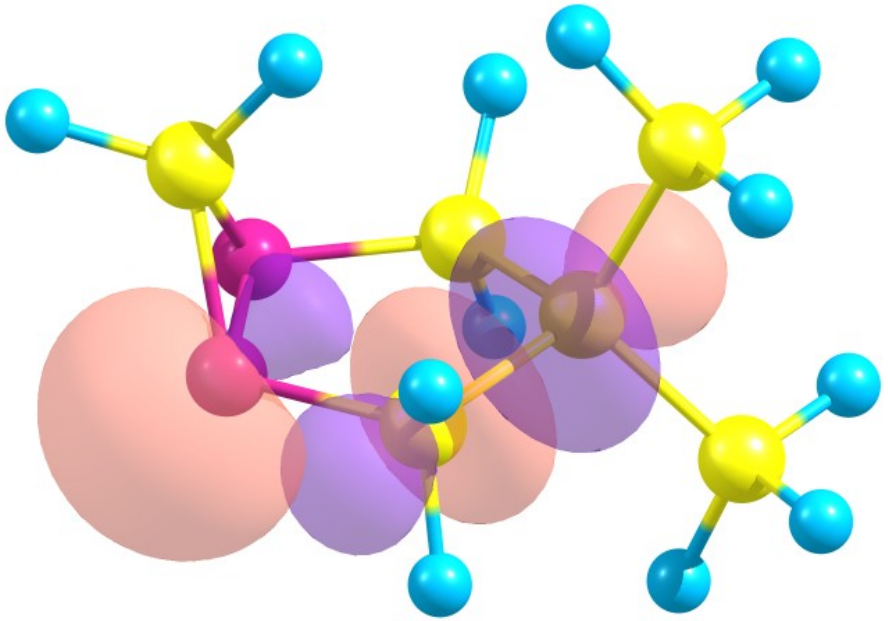
3,3-dimethyl-DABH: GED



3,3-dimethyl-DABH: Potential

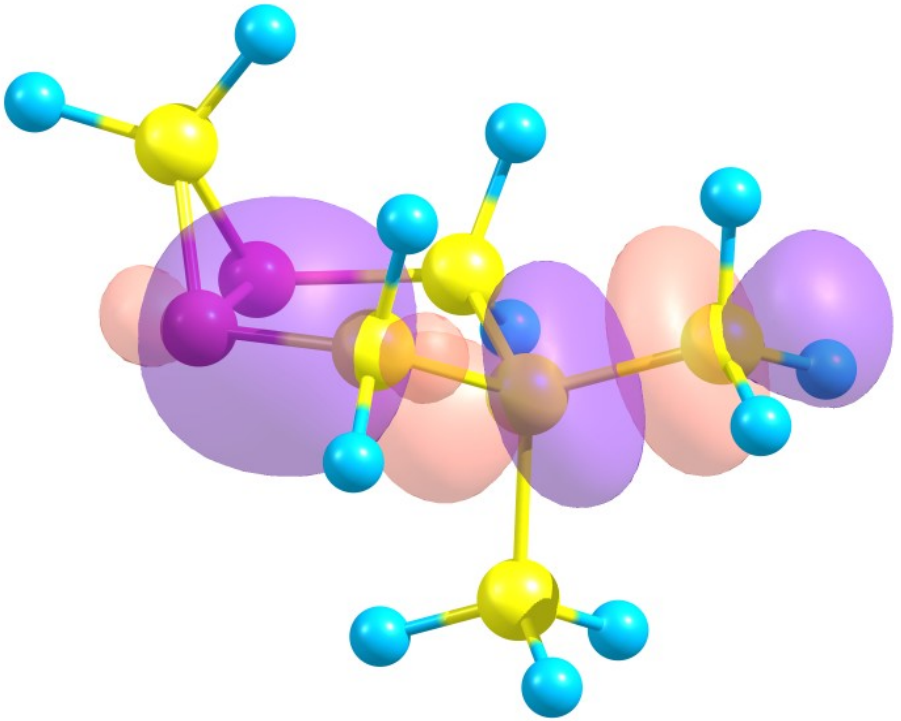


3,3-dimethyl-DABH: NBO



Boat

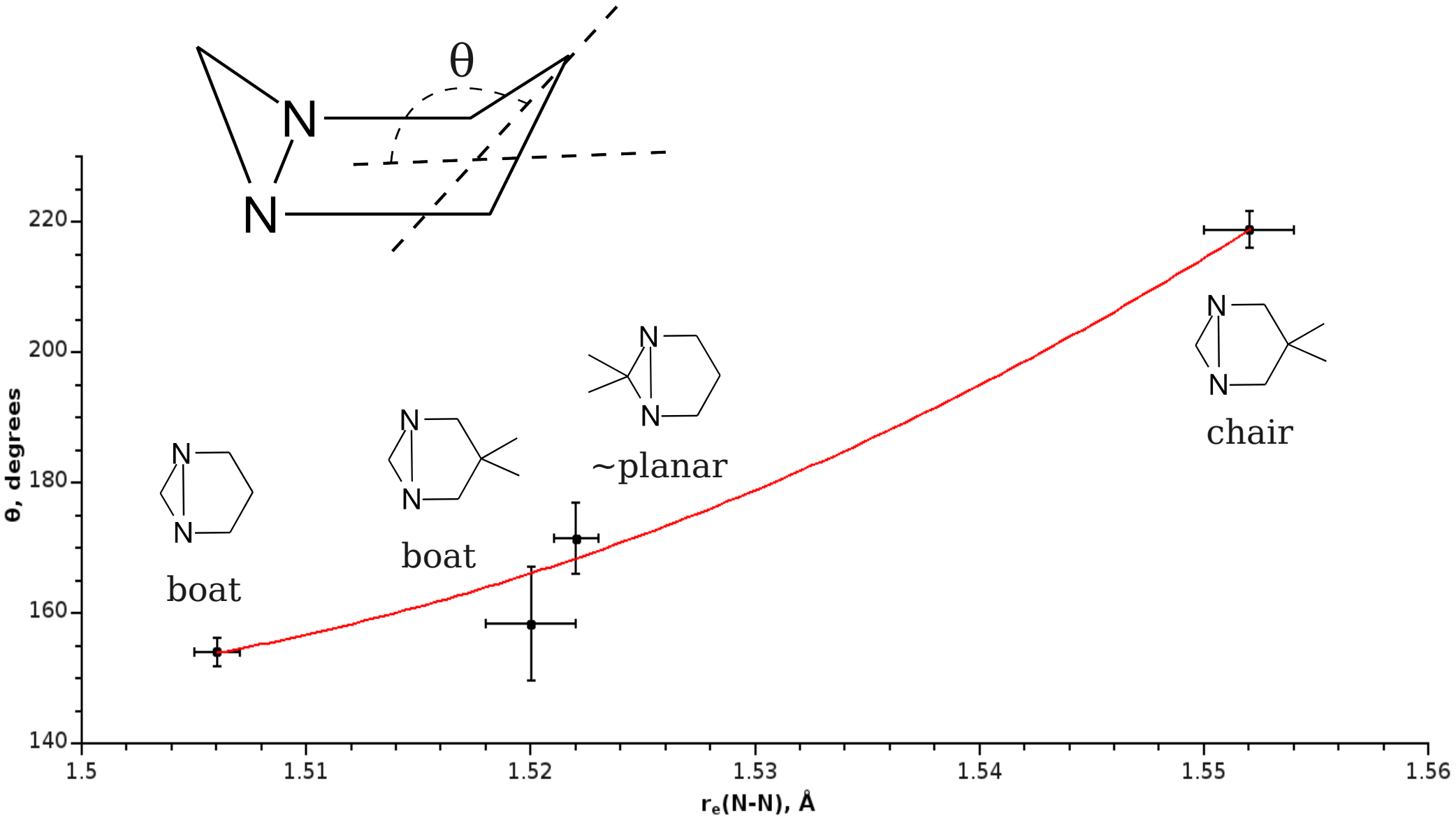
$n(N) \rightarrow \sigma^*(C\text{-}C)$



Chair

$\sigma(N\text{-}C) \rightarrow \sigma^*(C\text{-}C_m)$

Conformation vs. r(N-N)



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Acknowledgments

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The END