Universität Bielefeld

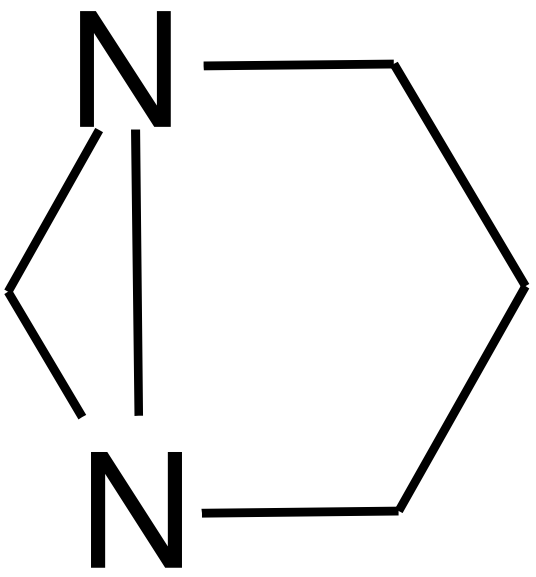
Strukturchemie einiger 1,5-diazabicyclo[3.1.0]hexan Derivate vom Standpunkt der Elektronenbeugung

Yury V. Vishnevskiy

Bielefeld, 29. November 2011

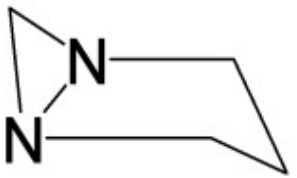
Universität Bielefeld

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

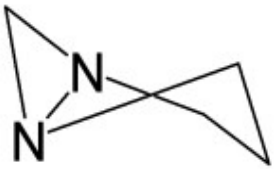


DABH Konformationen

Wanne



Sessel



Halb-Sessel I

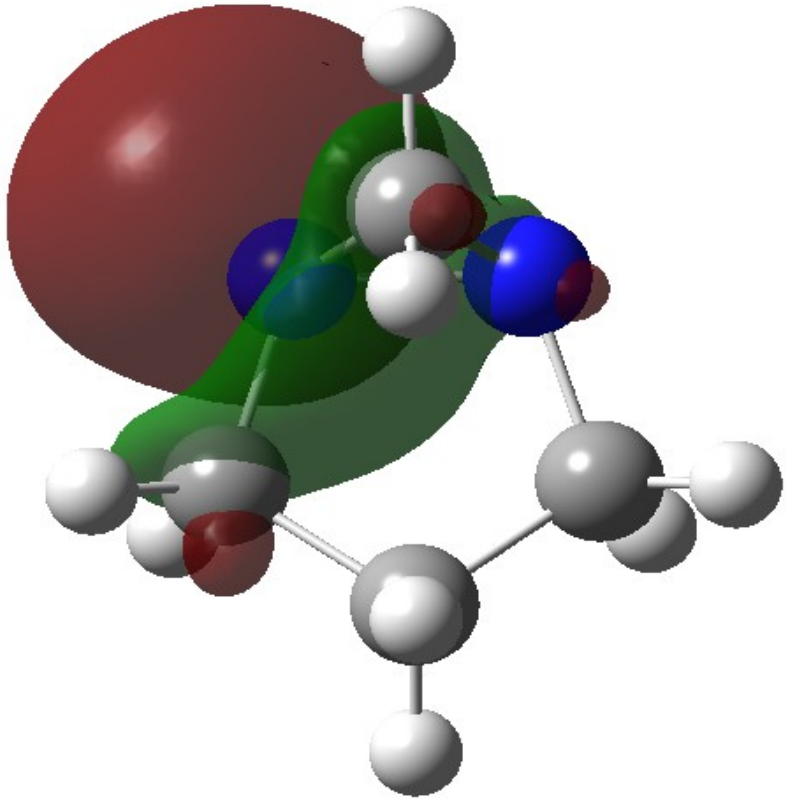
Halb-Sessel II

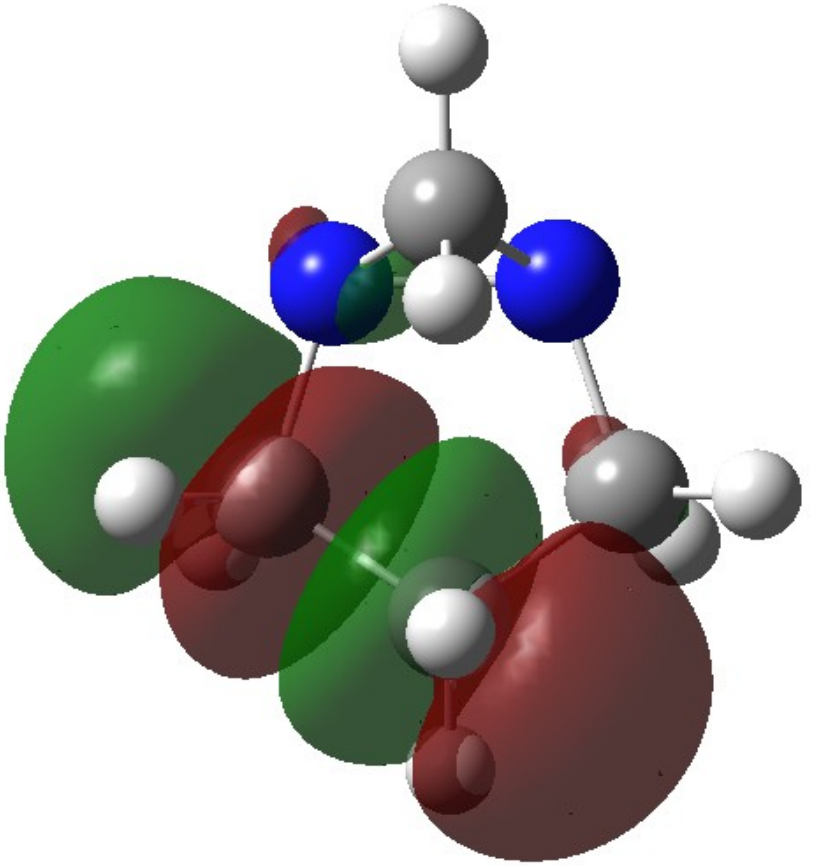
Twist

Methode	**Stabile Konformation**
^{1}H- und ^{13}C-NMR	Wanne
IR	Halb-Sessel
PE, AM1	Halb-Sessel
PE, ^{1}H-NMR	Halb-Sessel
GED	Wanne

[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.

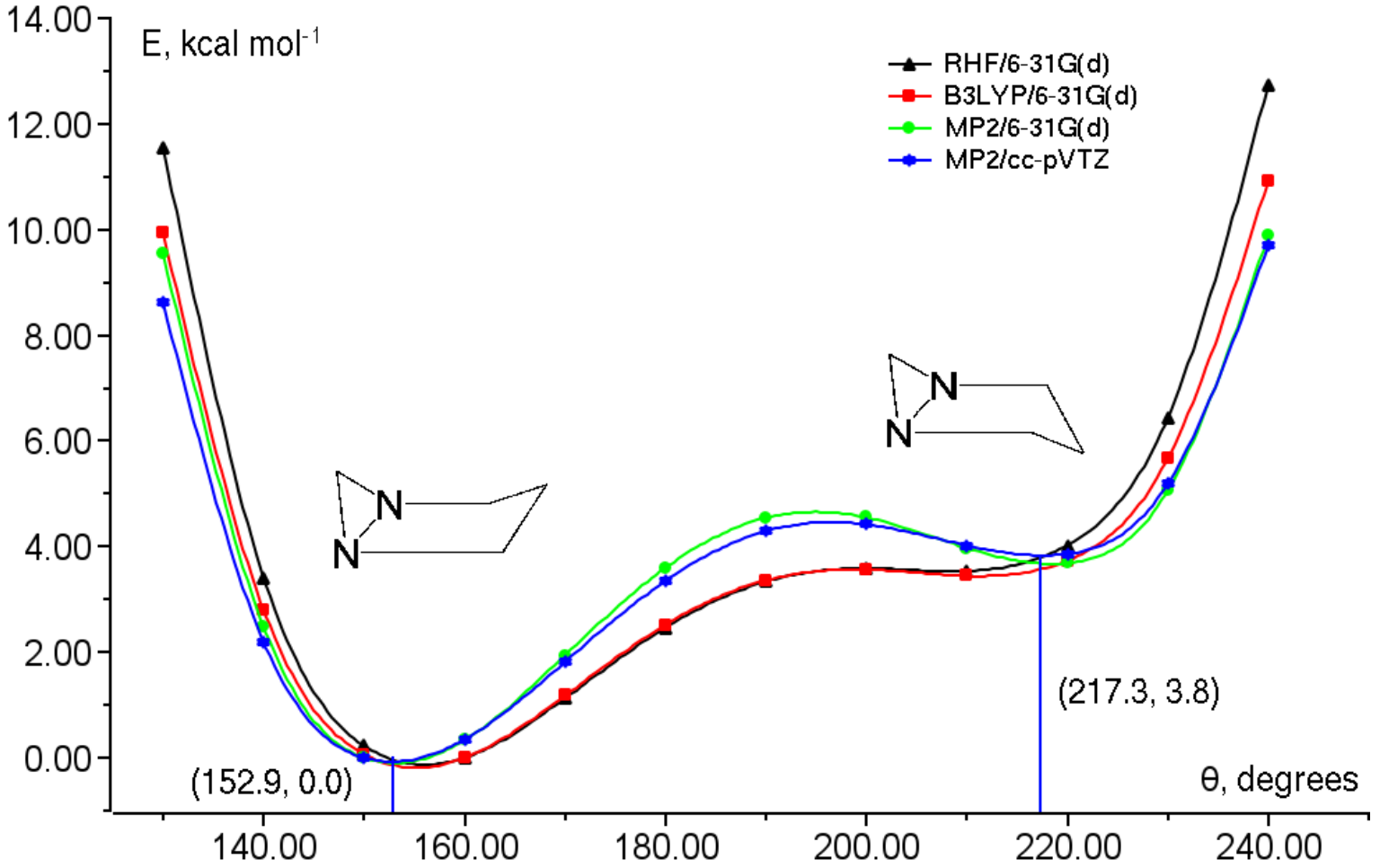
DABH: Wieso Wanne?



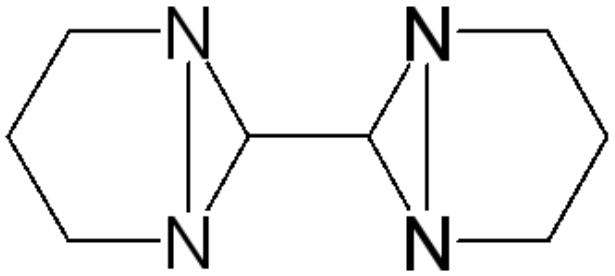


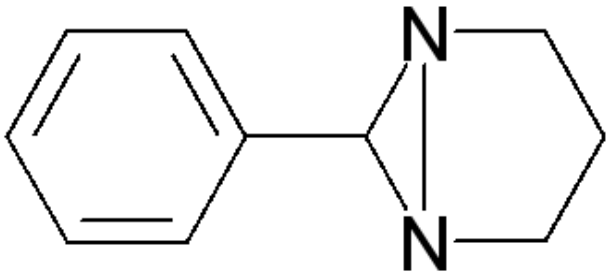
Der anomere Effekt: n(N)→σ*(C-C): $E^{(2)}$ = 4 kcal/mol

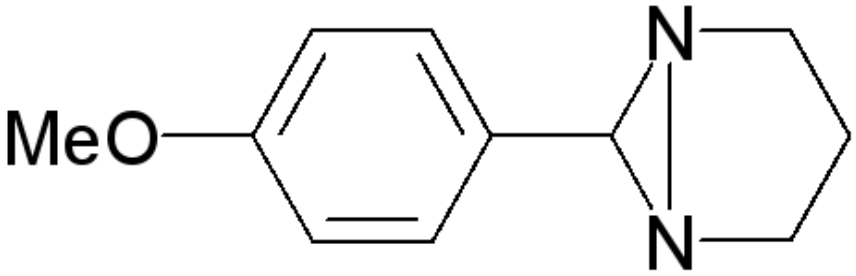
DABH: Gibt es andere Konformationen?

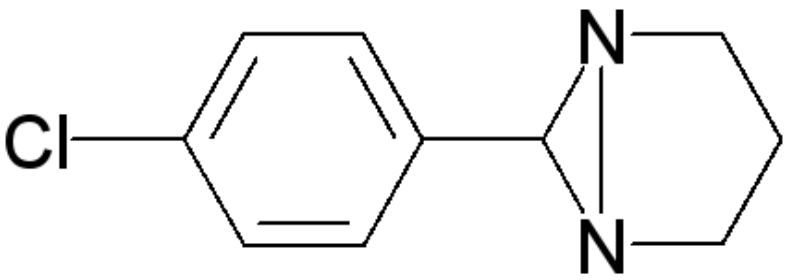


Bekannte Derivate von DABH



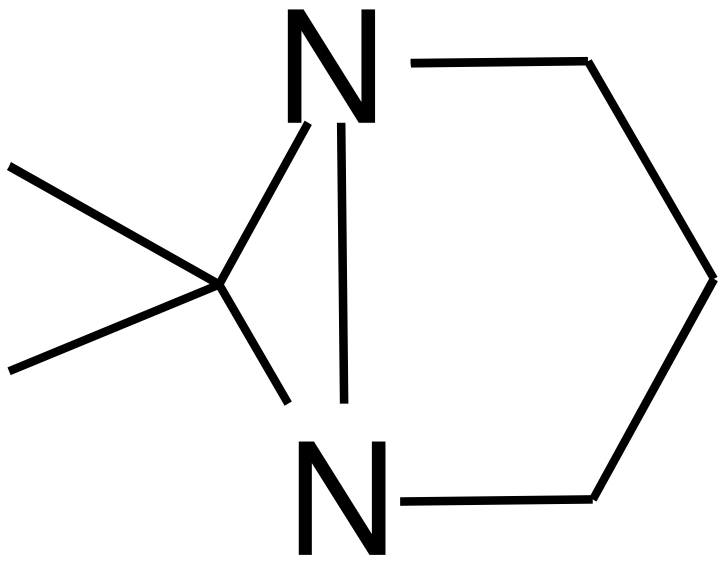






Alle haben Wanne Konformation.

6,6-dimethyl-DABH



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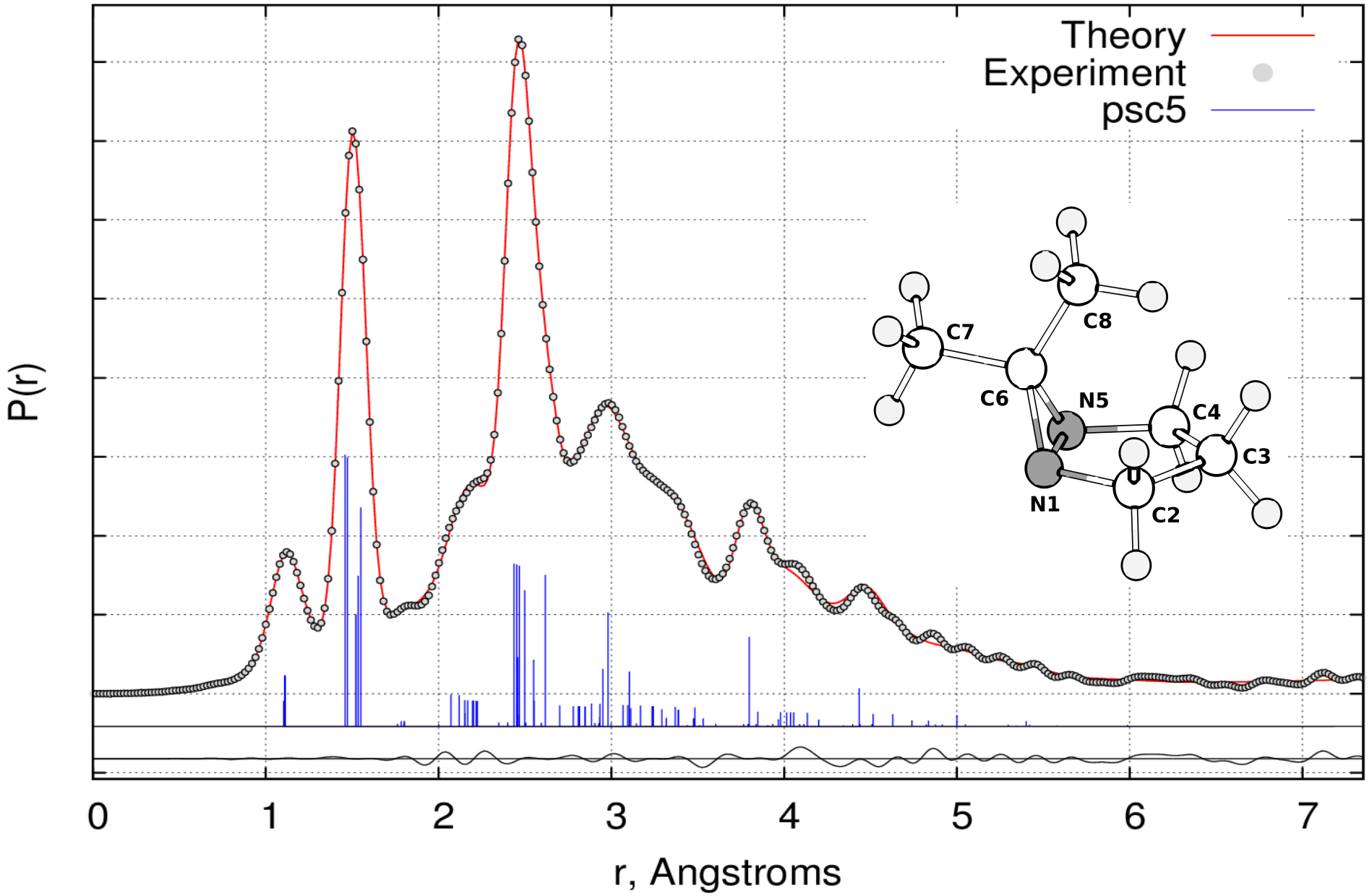
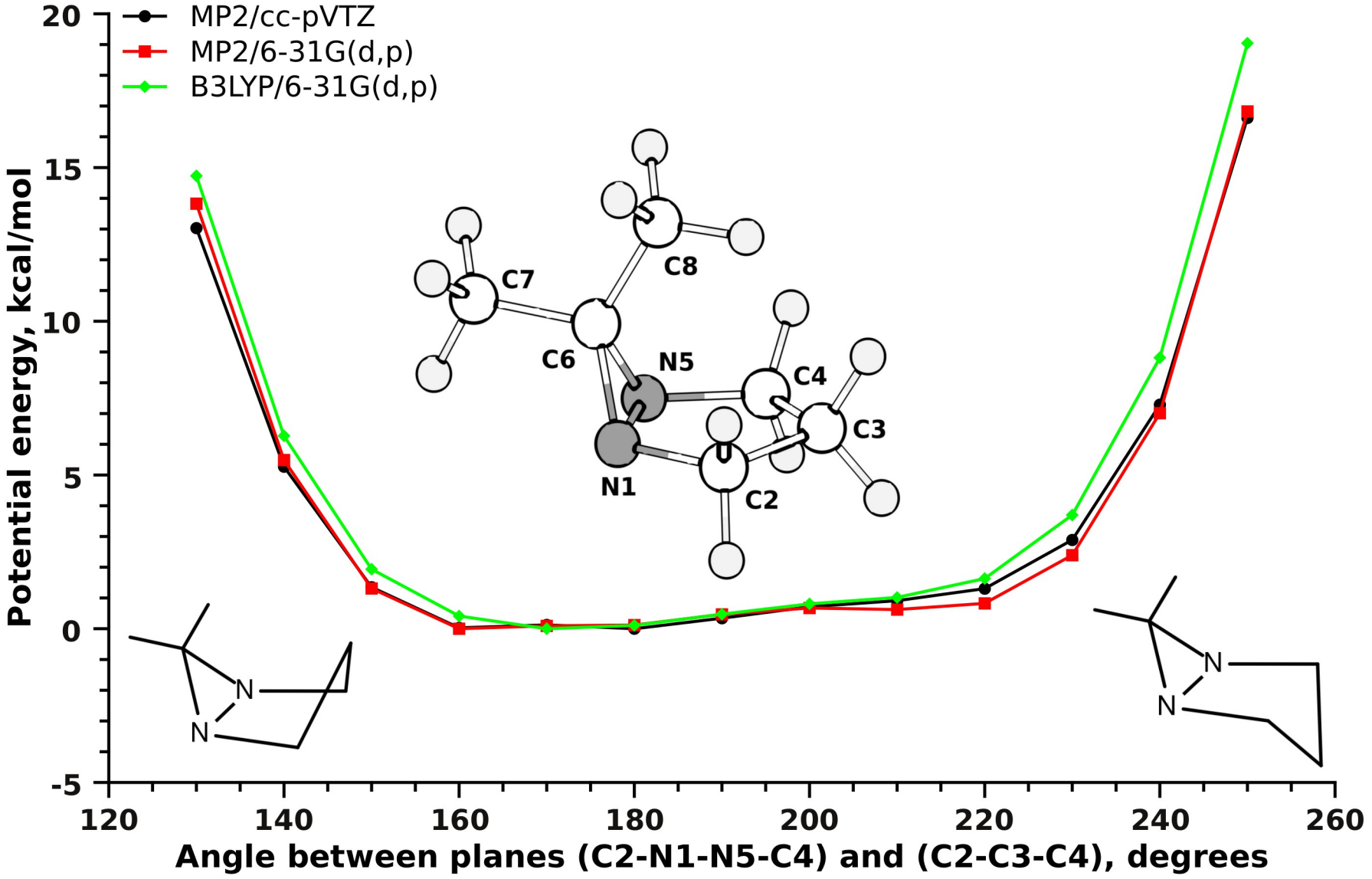
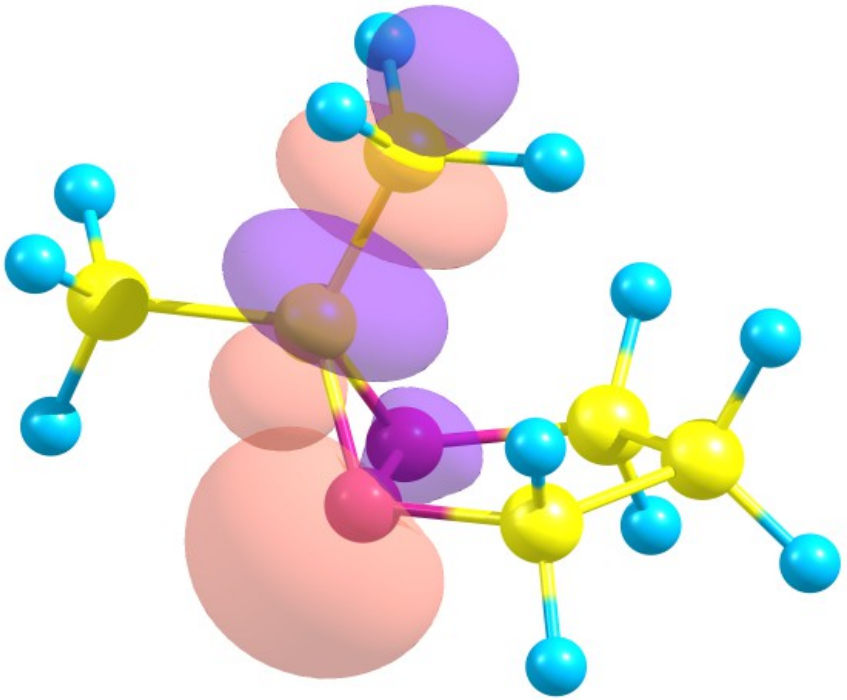
6,6-dimethyl-DABH

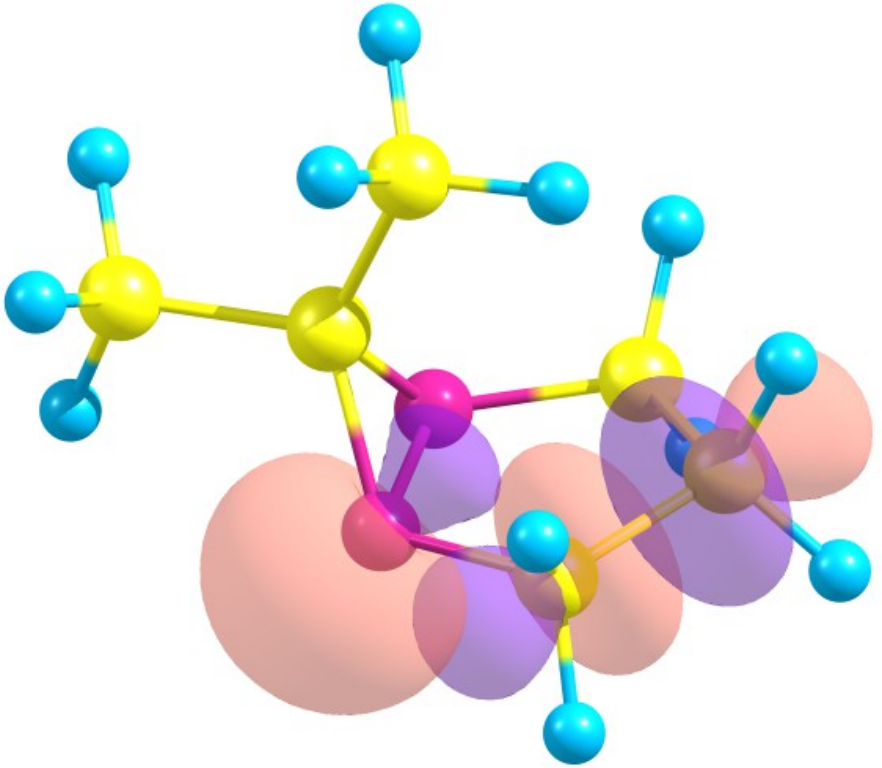


6,6-dimethyl-DABH



6,6-dimethyl-DABH: n(N)→σ*(C-C)





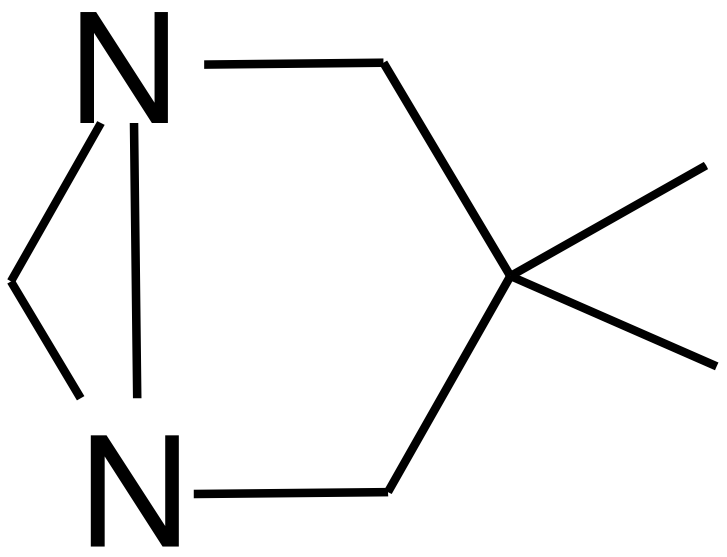
n = 0.035 e

0.022 e

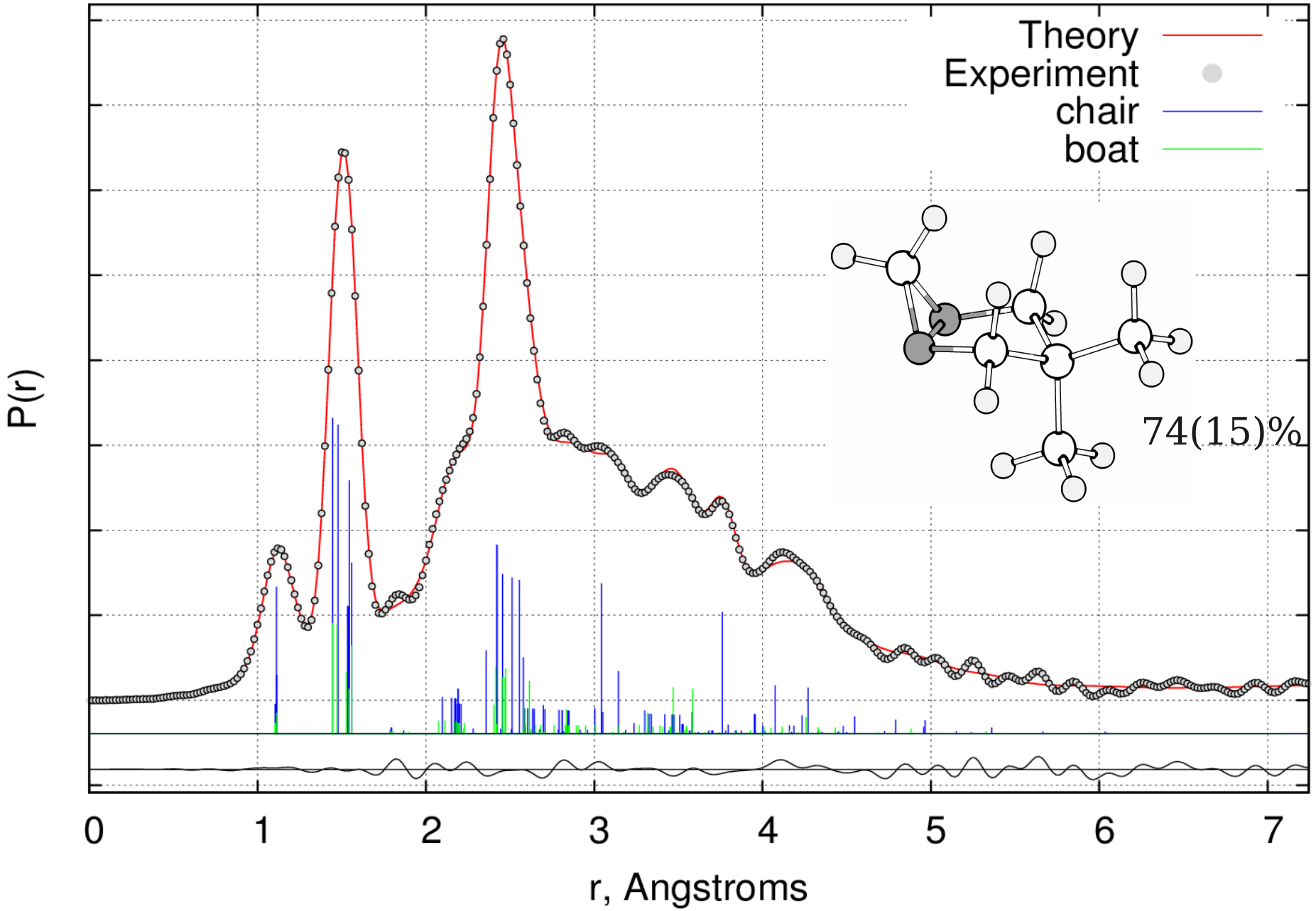
E^2 = 4.6 kcal/mol

3.5 kcal/mol

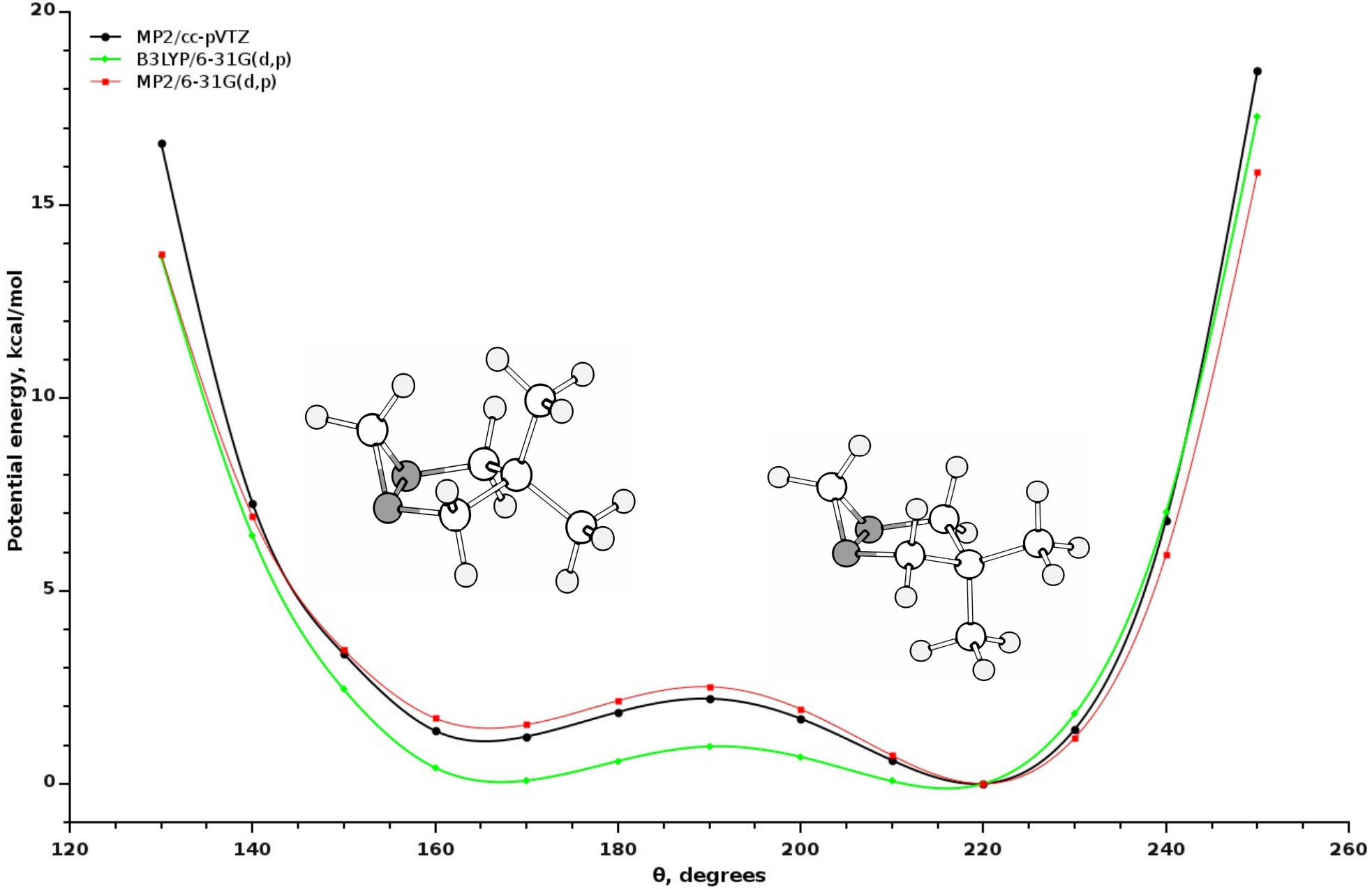
3,3-dimethyl-DABH



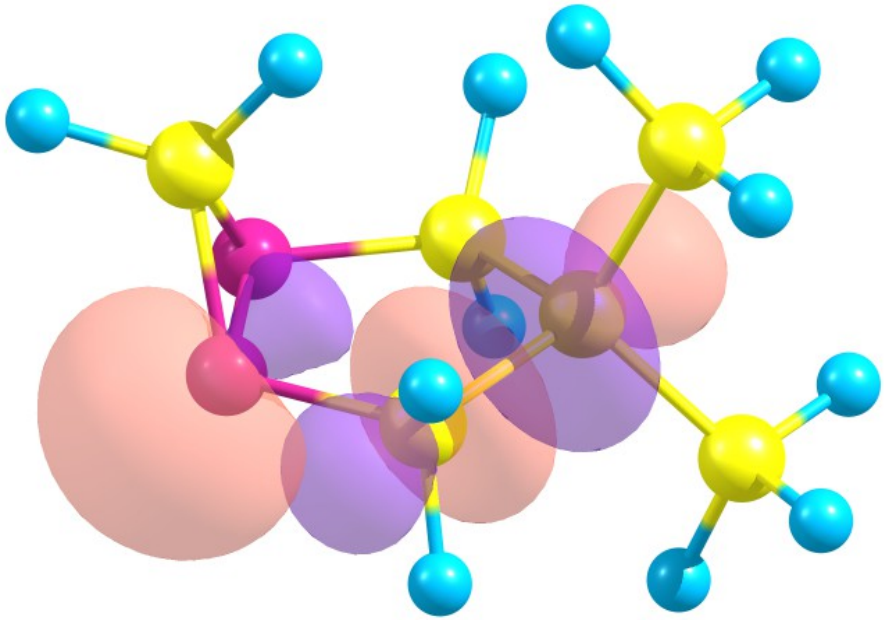
3,3-dimethyl-DABH: GED



3,3-dimethyl-DABH: Potential

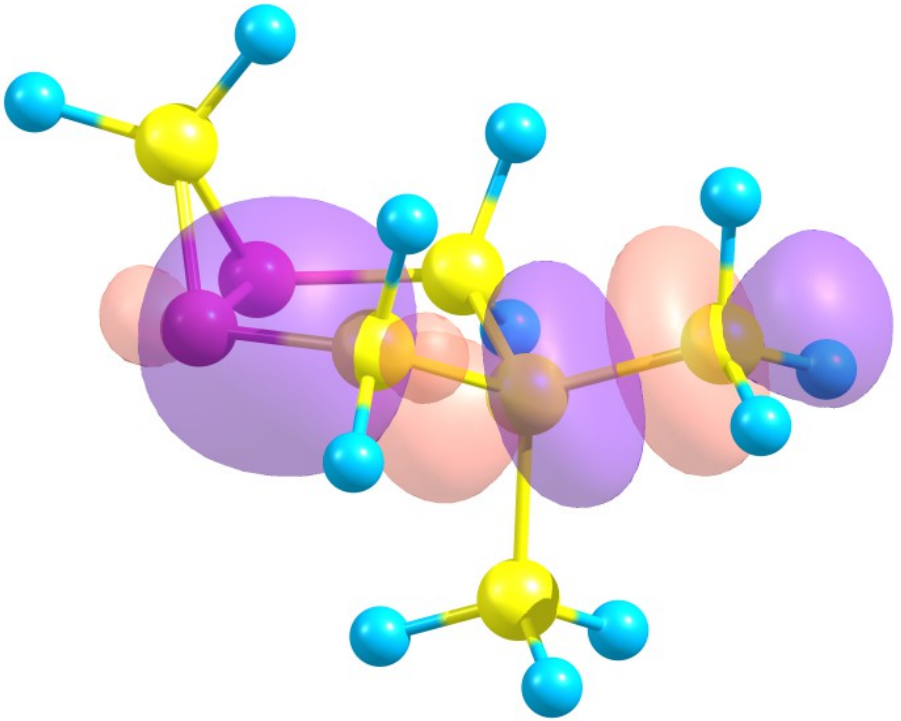


3,3-dimethyl-DABH: NBO



Wanne

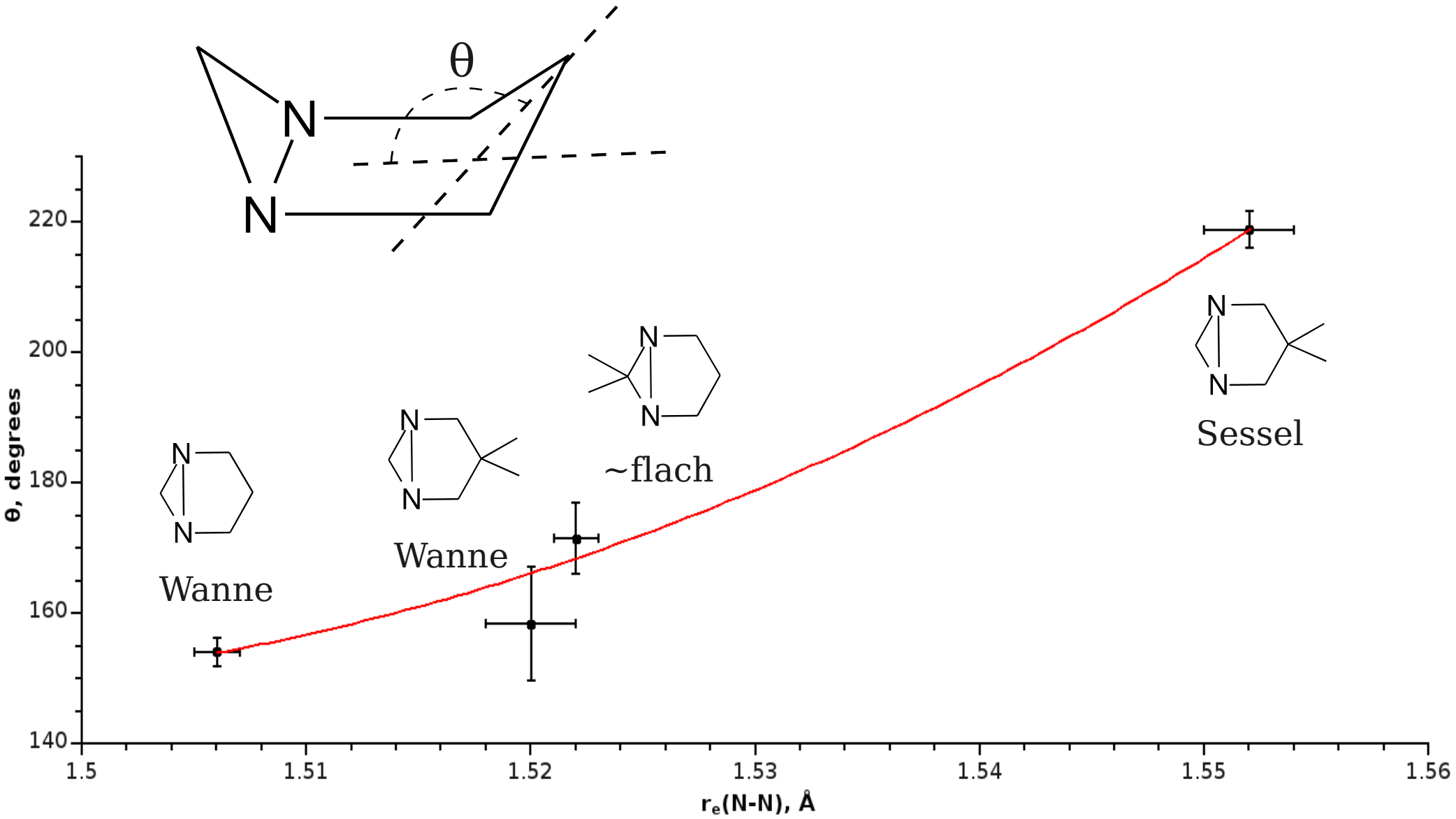
$n(N) \rightarrow \sigma^*(C\text{-}C)$



Sessel

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

Konformation gegen r(N-N)



Danke für die Aufmerksamkeit!