

**BRING
BALANCE
TO THE
FORCE!**

TALK PRESENTED BY
JAN M. SCHÜMANN, MSc.

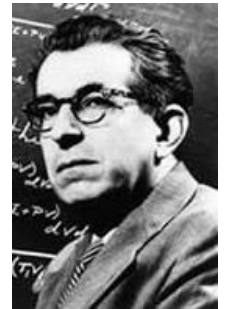
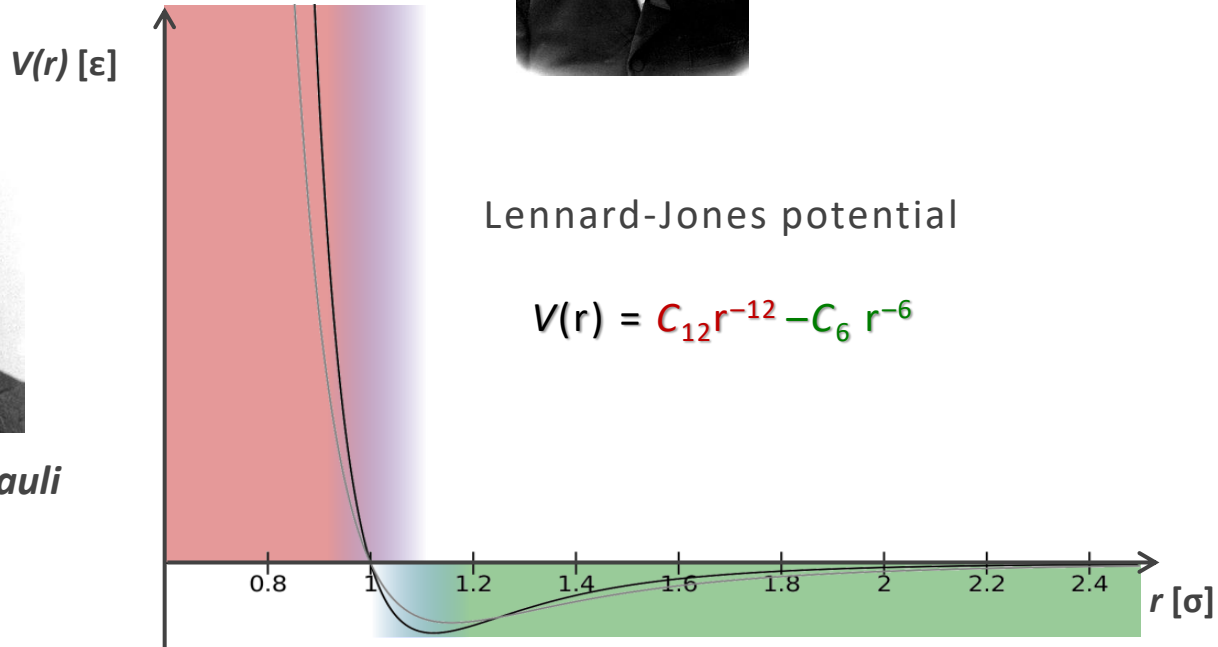
S19TH GROUP SEMINAR
SEPTEMBER 18TH, 2020



J. D. van der Waals



Wolfgang Pauli



Fritz London

Dispersion = attractive part of the vdW-potential

Zur Theorie und Systematik der Molekularkräfte.

Von F. London in Berlin.

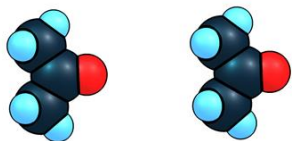
Mit 9 Abbildungen. (Eingegangen am 11. Mai 1930.)



Die Molekularkräfte zerlegen sich in drei wesentlich verschiedene Bestandteile,
...a short-period interaction in the form of a mutual perturbation of the

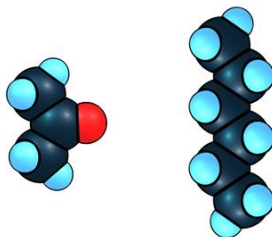
electron movement whose energy contribution is the major attractive
component for simple non-polar or weakly polar molecules.

Keesom Force



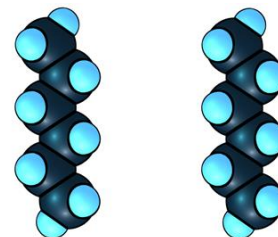
Permanent dipole – Permanent dipole

Debye Force



Permanent dipole – Induced dipole

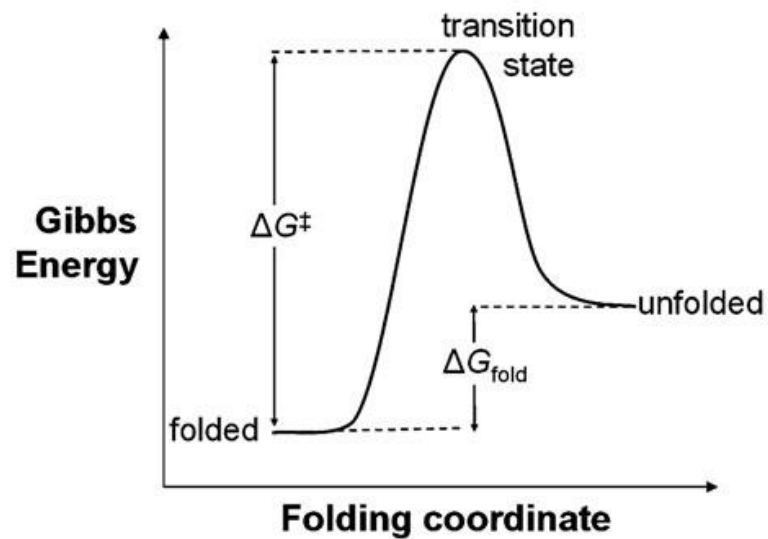
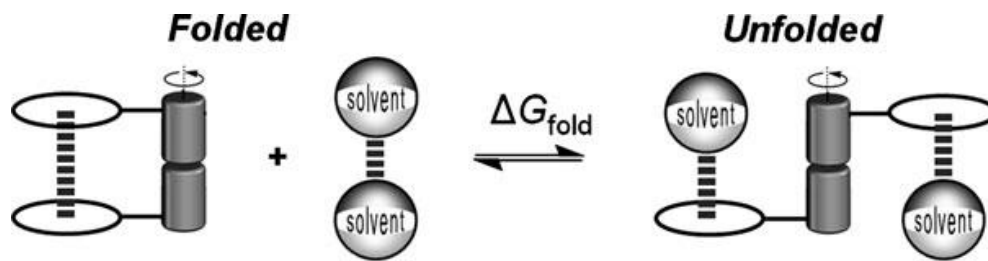
London Dispersion



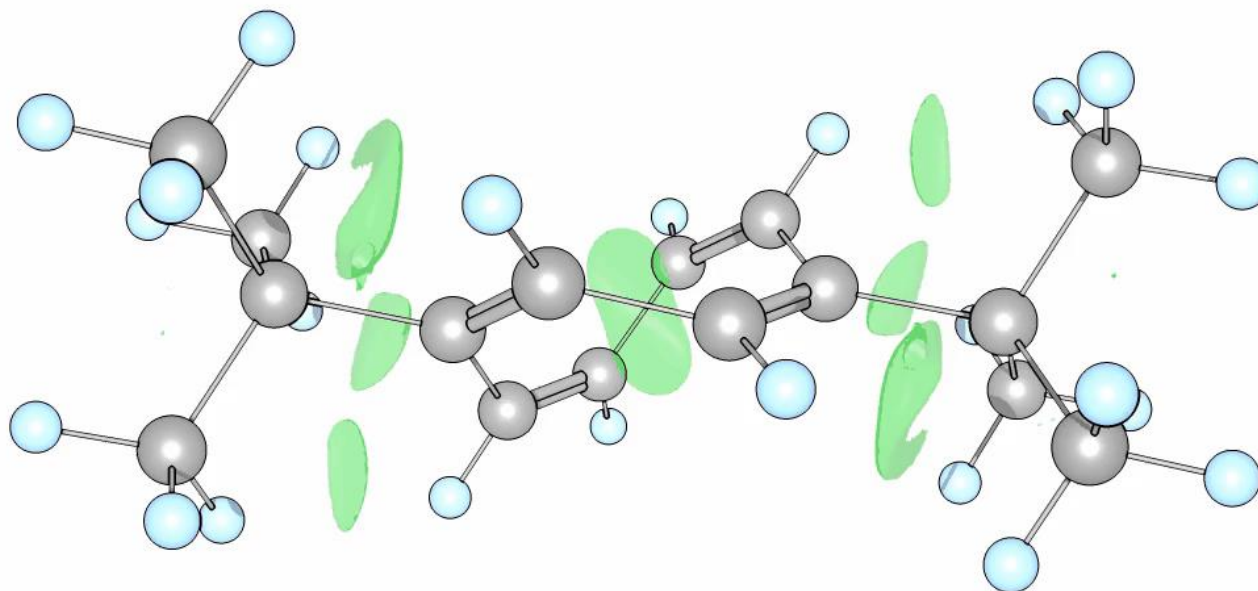
Induced dipole – induced dipole

...this can be estimated with the f -values of the dispersion formula derived
from optical measurements...

...these forces correspond to the attractive part of the van-der-Waals
potential...







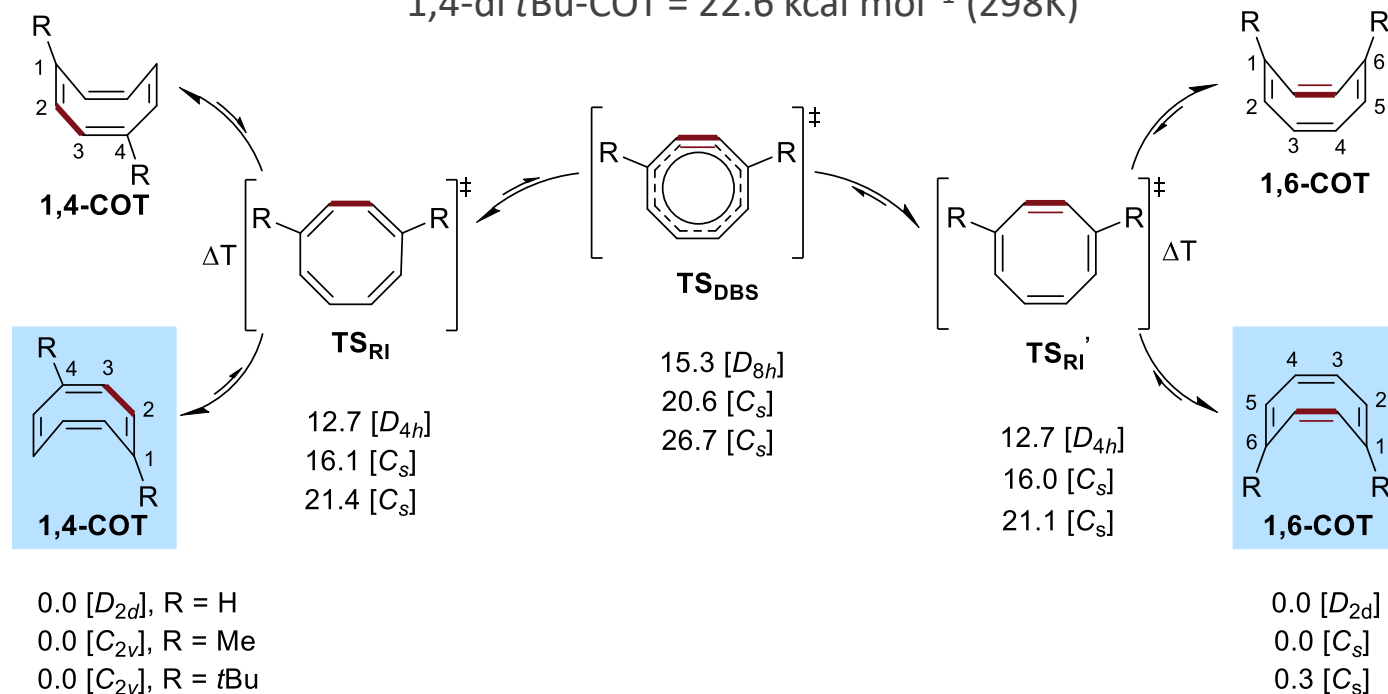


Experimental values $\Delta G^\ddagger$ for DBS

COT = 13.7 kcal mol⁻¹ (268K)

1,4-di Me-COT = 17.3 kcal mol⁻¹ (325K)

1,4-di *t*Bu-COT = 22.6 kcal mol⁻¹ (298K)

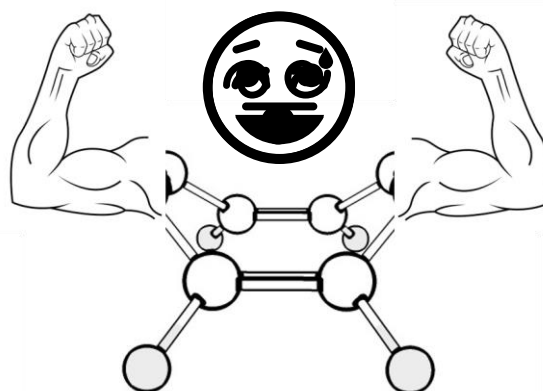


NEVPT2(8,8)/6-311G(d,p)//CASSCF(8,8)/6-31G(d)

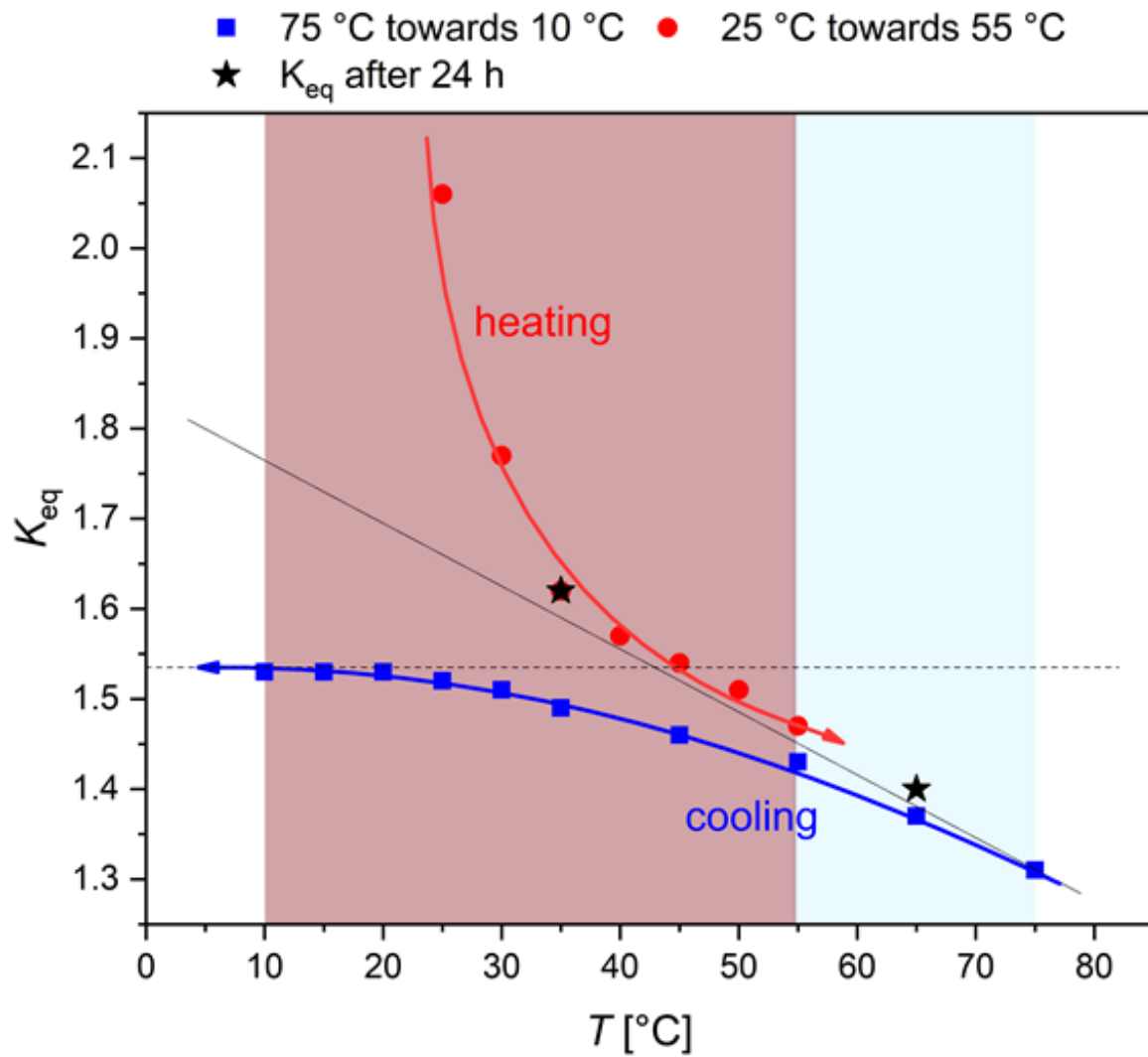
Folding pathway for 1,4 di-substituted cyclooctatetraene. Computed double bond valence shift (DBS) and ring inversion (RI) of cyclooctatetraene enthalpies ($\Delta E + ZPVE$ in kcal mol⁻¹).

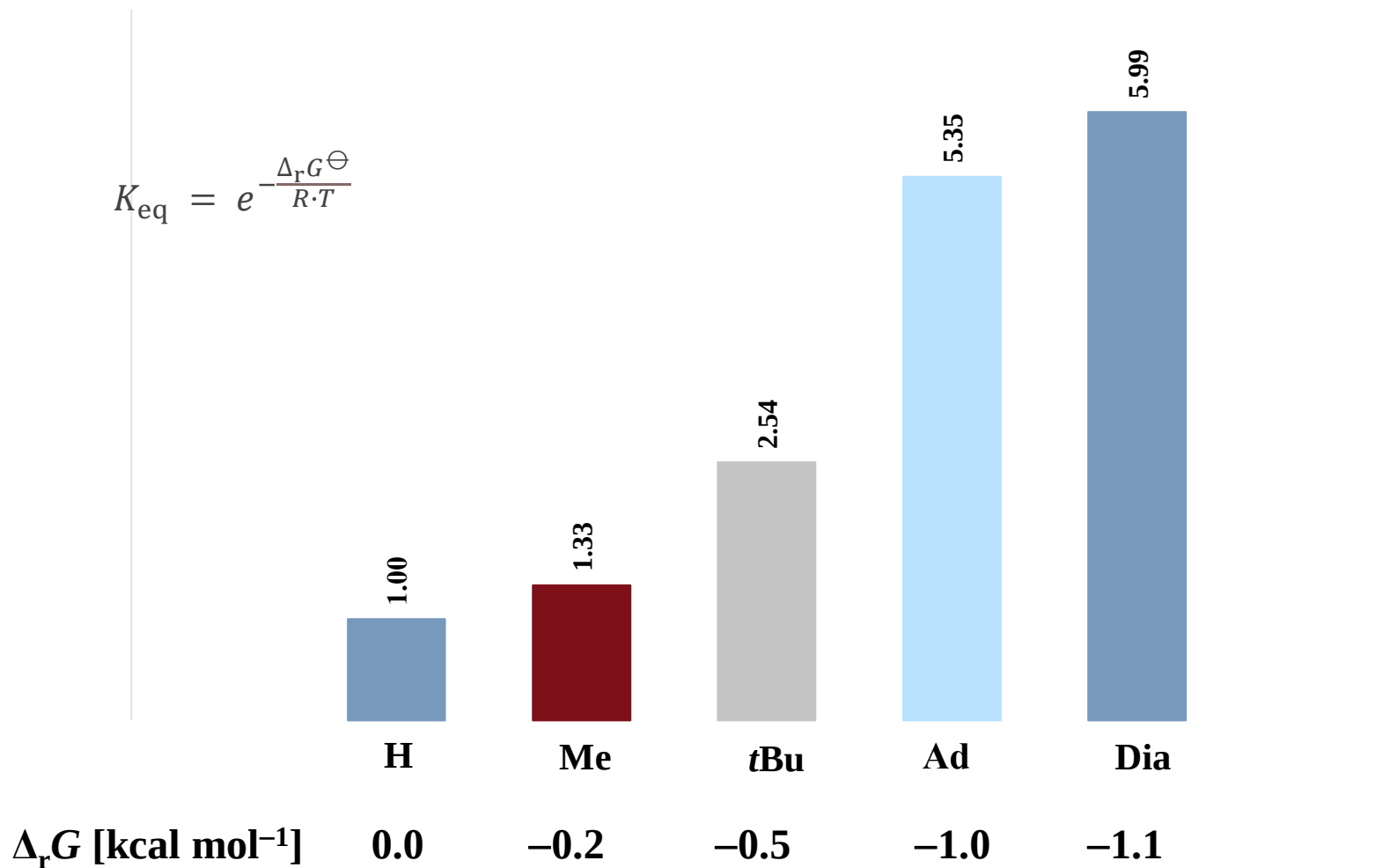
Reference for COT parental system: O. Castaño, R. Palmeiro, L. M. Frutos, J. Luisandrés *J. Comput. Chem.* **2002**, 23, 732-736.

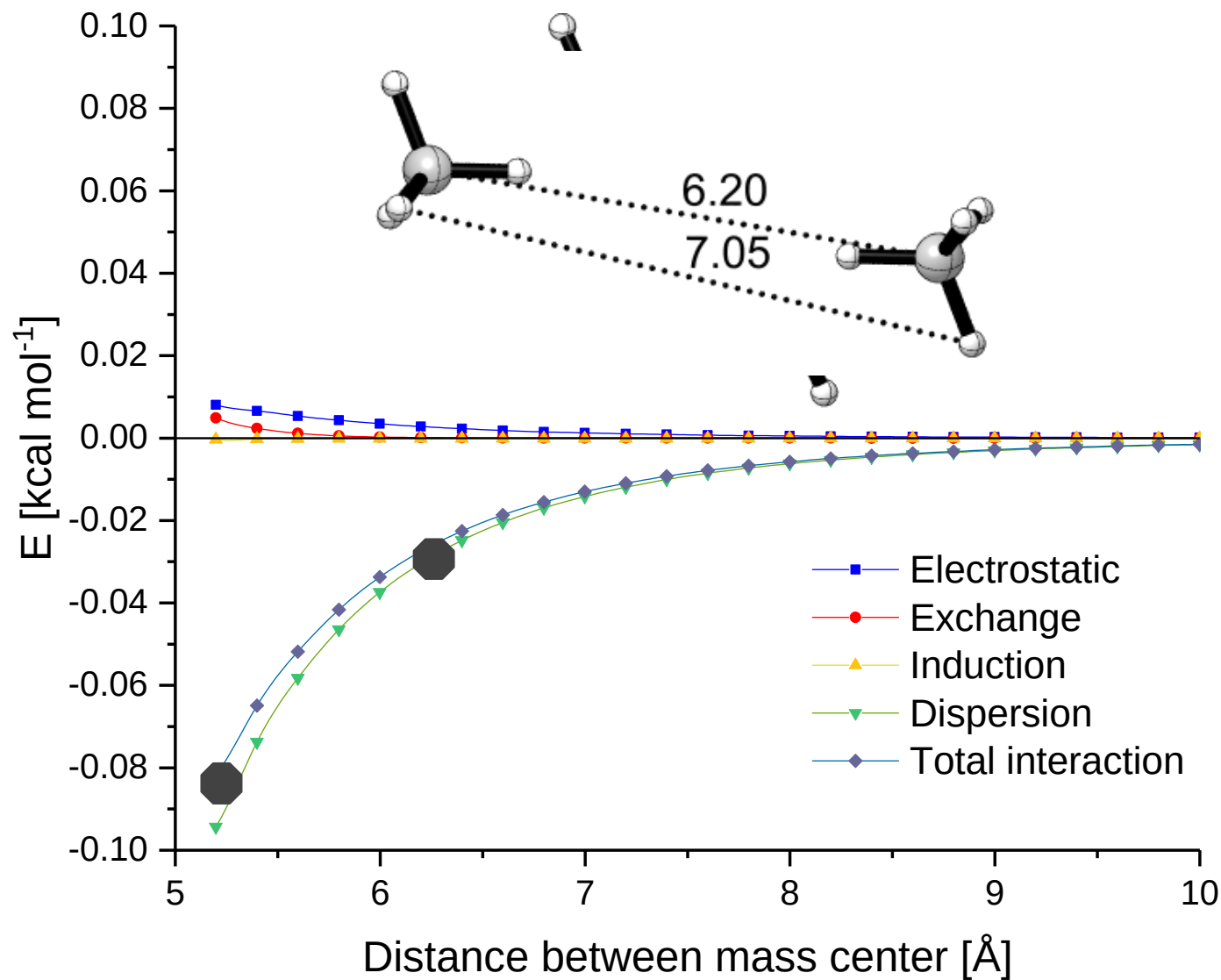
D. A. Hrovat, W. T. Borden, *J. Am. Chem. Soc.* **1992**, 114, 5879-5881. J. E. Anderson, P. A. Kirsch, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1951-1957. J. M. Schumann, J.-P. Wagner, A. K. Eckhardt, H. Quanz and P. R. Schreiner **2020** unpublished results.



R	$\Delta_r G^\ddagger$ [kcal mol⁻¹]	<i>T</i> [K]	<i>T</i> [°C]	<i>k</i> [s⁻¹]	<i>t</i>_{1/2} [s]	<i>t</i>_{1/2} [min]
H	13.7	268	−5	37.58583	0.018	0.00
Me	17.3	325	52	15.75224	0.044	0.00
<i>t</i> Bu	22.6	298	25	0.00016	4188.6	69.81
Ad	?					
Dia	?					







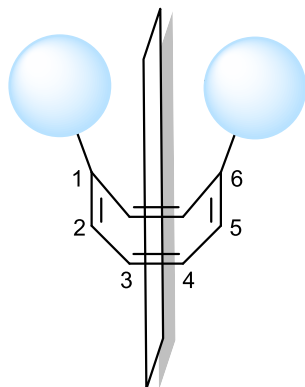


$$K_{\text{eq.}} (298\text{K}) = 1.10$$

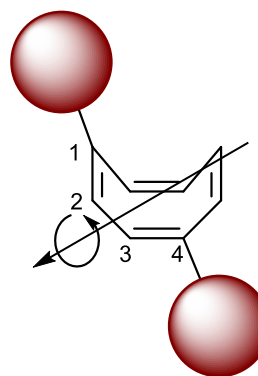
$$\Delta G (298\text{K}) = -0.06 \text{ kcal mol}^{-1}$$

$$\text{exp. } \Delta H_0 = -0.29 \text{ kcal mol}^{-1}$$

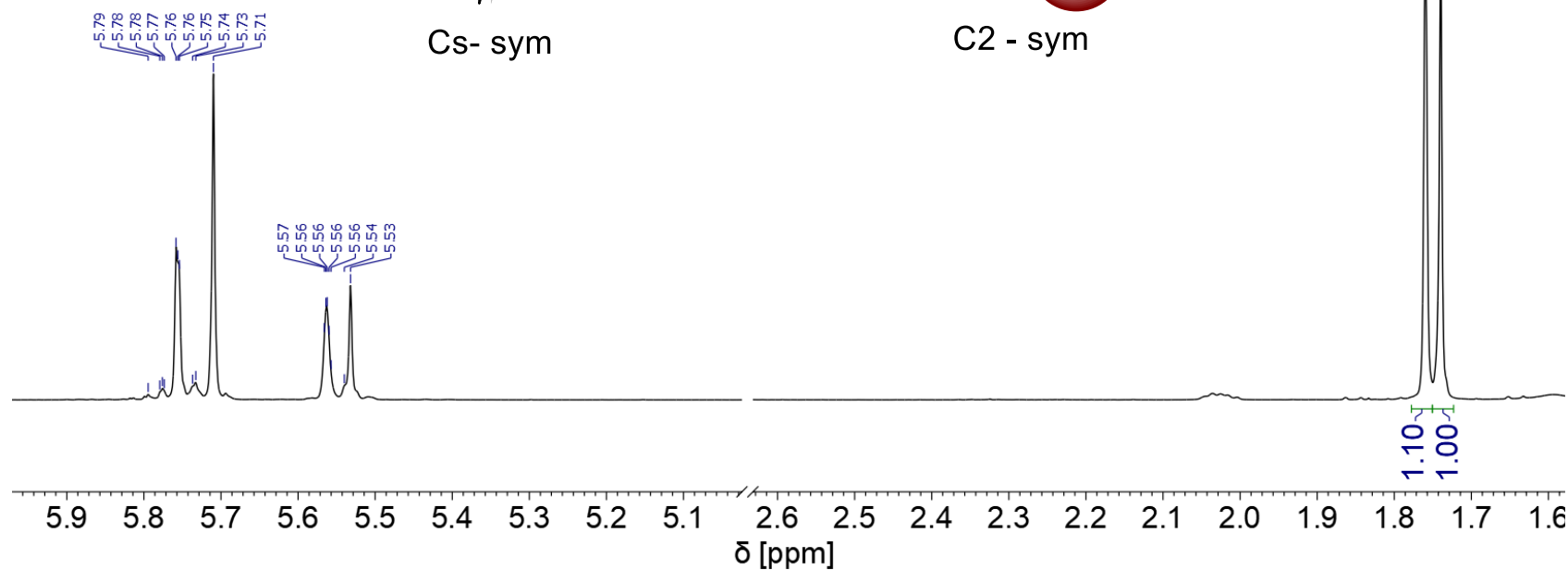
$$\text{Comp. } \Delta H_0 = -0.2 \text{ kcal mol}^{-1}$$

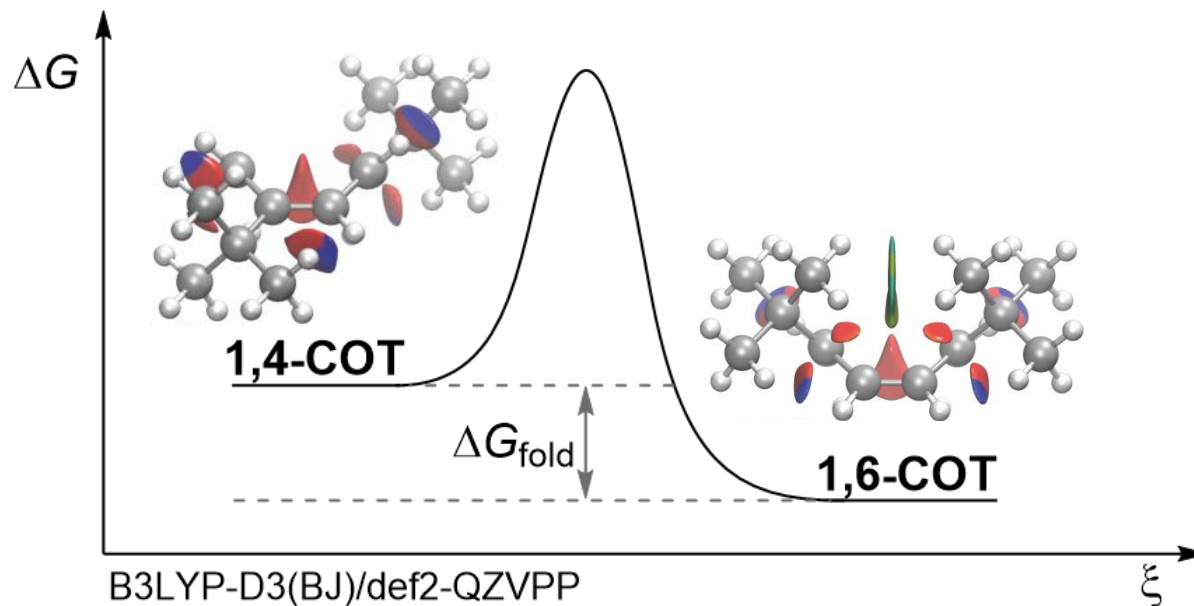


Cs - sym



C2 - sym

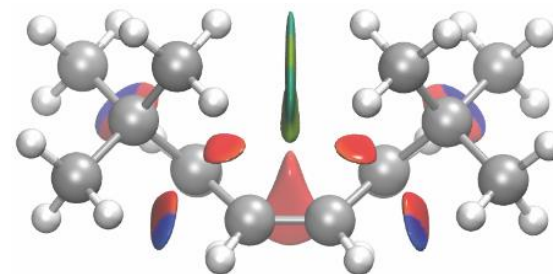
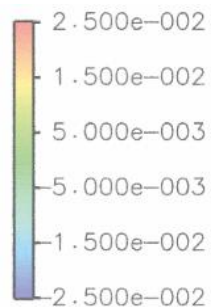
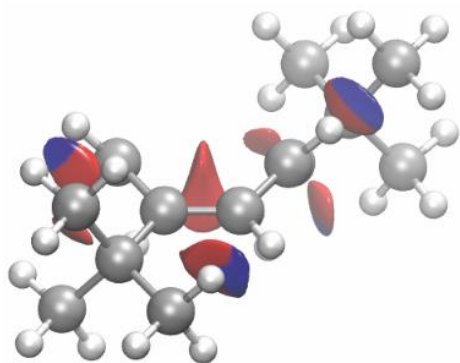
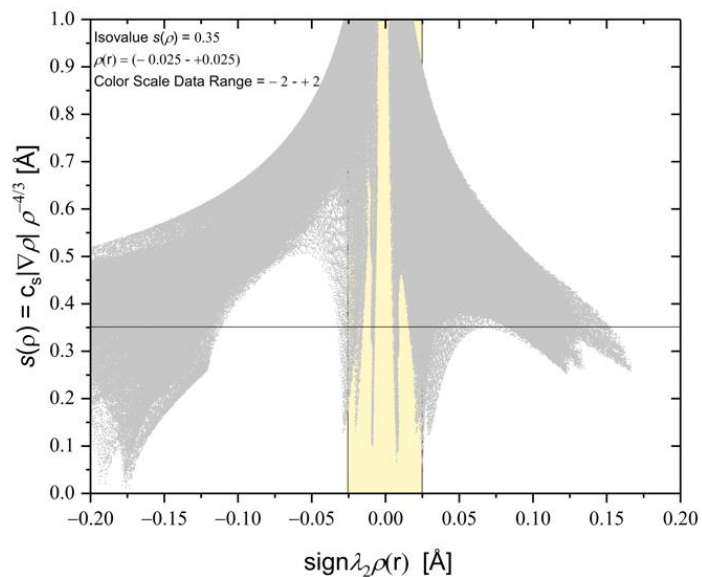
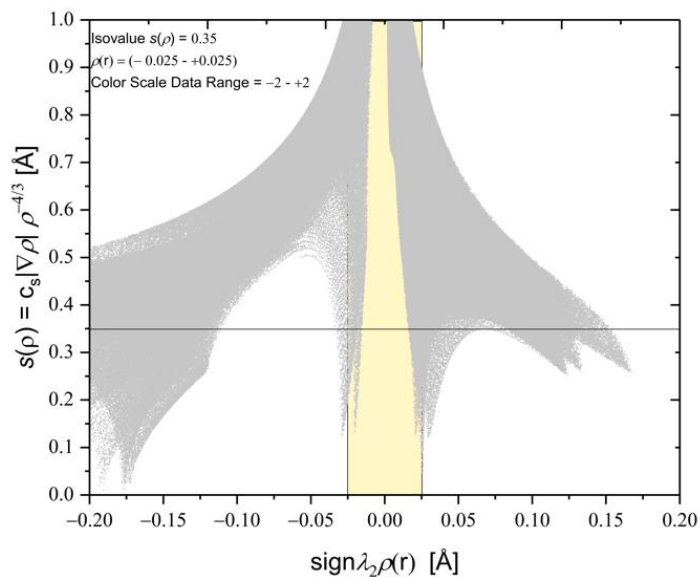


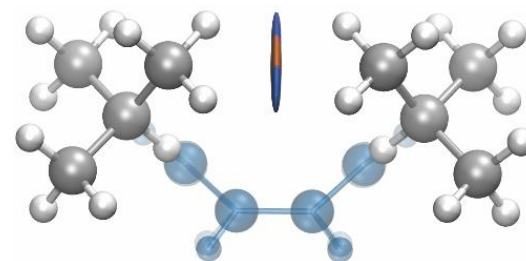
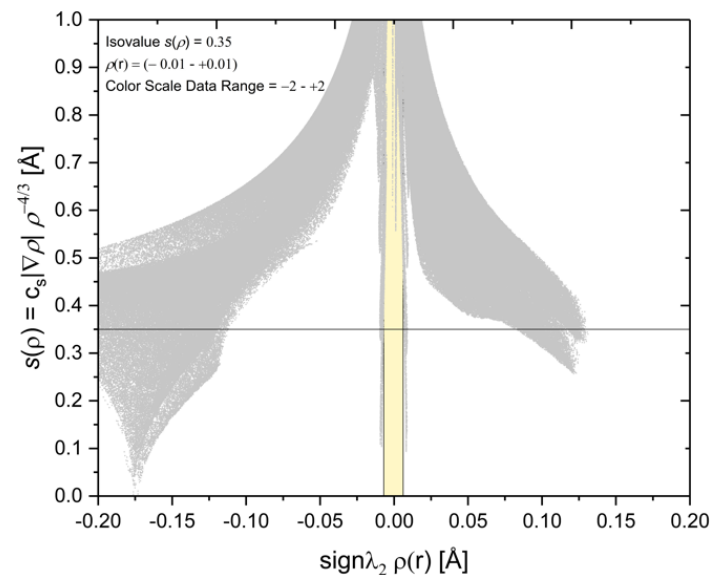
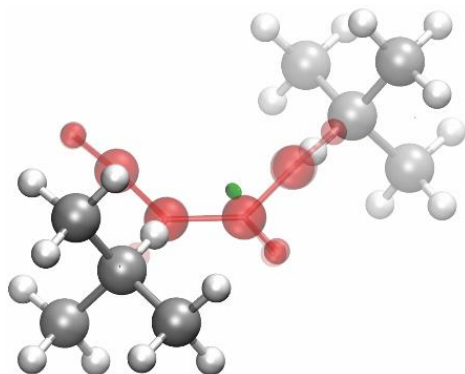
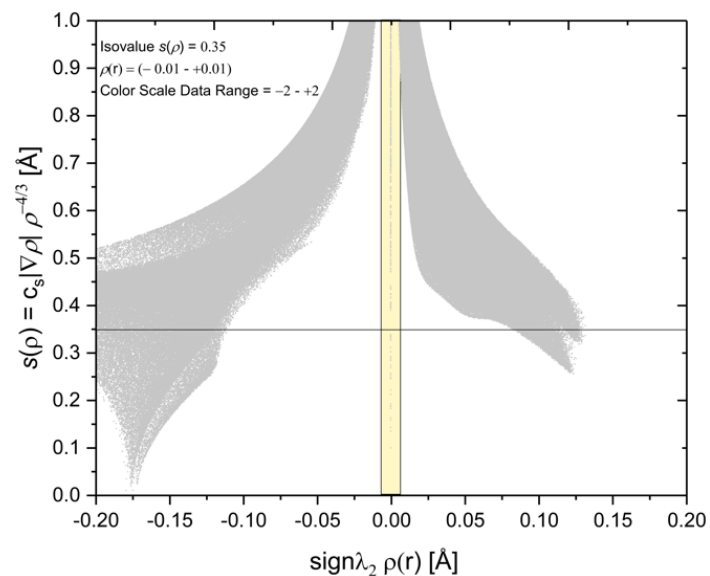


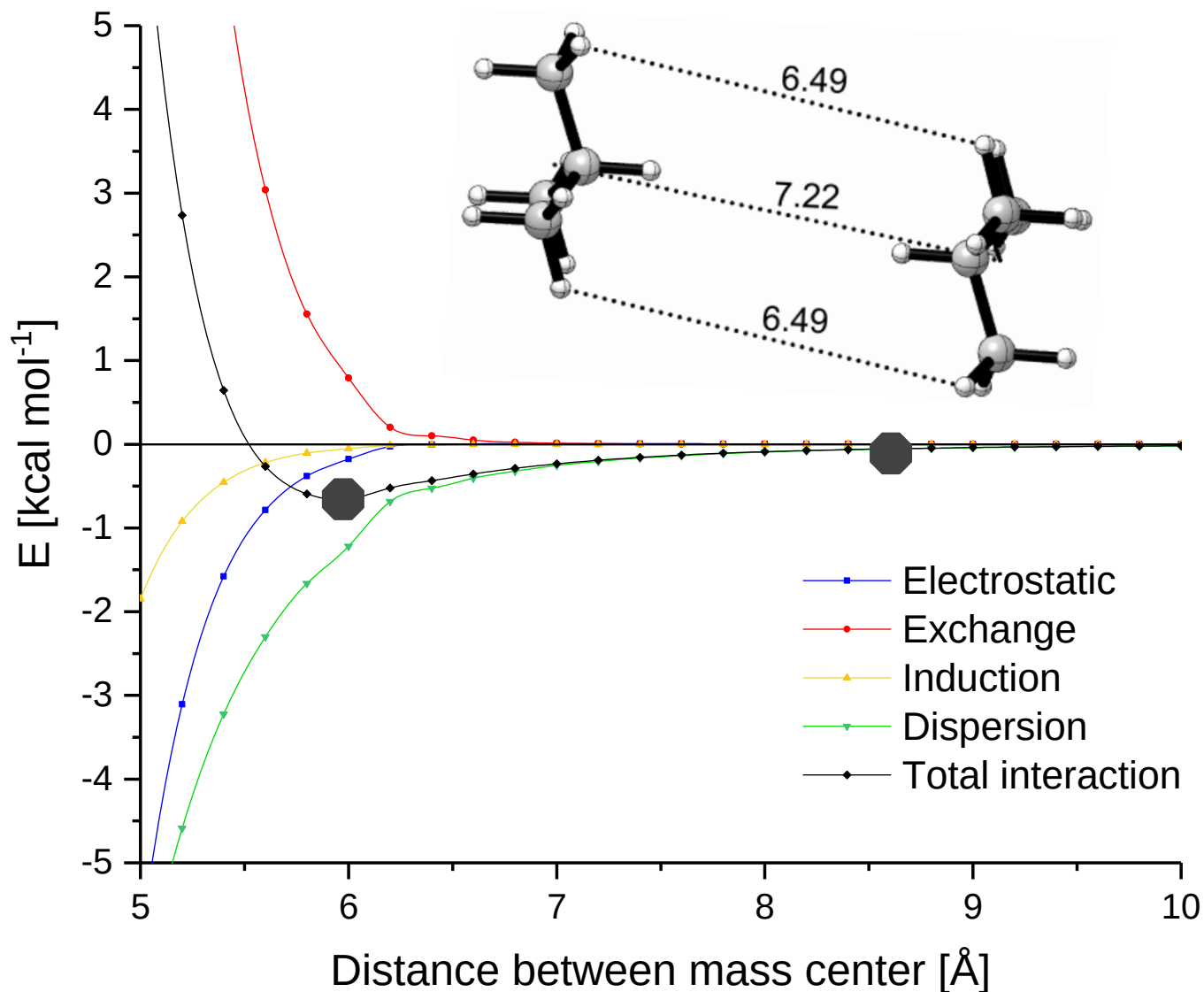
	$\Delta E_e(RHF)$	$\Delta E_e(MP2)$	$\Delta E_e(CCSD)$	$\Delta E_e(CCSD(T))$
<i>cc-pVDZ</i>	+0.25	+0.16	+0.05	−0.02
<i>cc-pVTZ</i>	+0.16	−0.06	−0.15	[−0.23]
<i>cc-pVQZ</i>	+0.12	−0.16	[−0.24]	[−0.32]
<i>cc-pV5Z</i>	+0.08	−0.23	[−0.32]	[−0.39]
<i>CBS LIMIT</i>	[+0.06]	[−0.29]	[−0.38]	[−0.45]
<i>FUNCTION</i>	$a+be^{-cX}$	$a+bX^{-3}$	<i>additivity</i>	<i>additivity</i>
<i>X (Fit points)</i>	(3,4,5)	(4,5)		

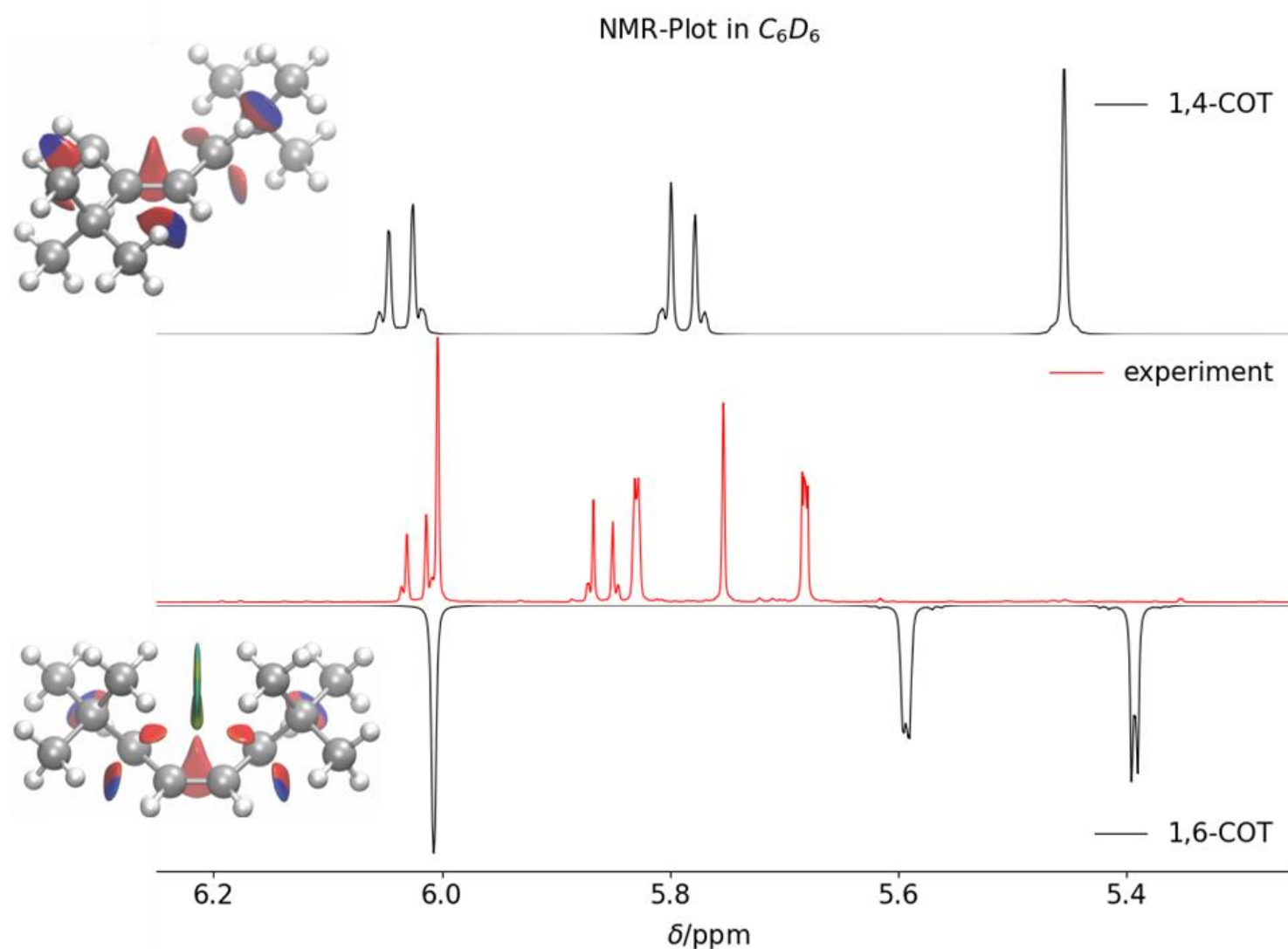
RI-(AE)MP2/cc-pVTZ reference geometries

$\Delta ZPVE$ (harmonic) = 0.20; $\Delta H_0 = (-0.45 + 0.20) \text{ kcal mol}^{-1} = -0.26 \text{ kcal mol}^{-1}$









Extendet tight binding (xTB) energetic sorting (enso) of conformer rotamer ensembles (CRE)
 automated nuclear magnetic resonance (anmr) plotted via python nmrplot.py

S. Grimme, C. Bannwarth, S. Dohm, A. Hansen, J. Pisarek, P. Pracht, J. Seibert, F. Neese, *Angew. Chem. Int. Ed.* **2017**, *56*, 14763-14769.

C. Bannwarth, S. Ehlert, S. Grimme, *J. Chem. Theory Comput.* **2019**, *15*, 1652-1671. C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen,

P. Pracht, J. Seibert, S. Snicher, S. Grimme, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2020**, n/a, 49



$K_{eq.}$ (298K) = 1.46 (15 min equilibration time)

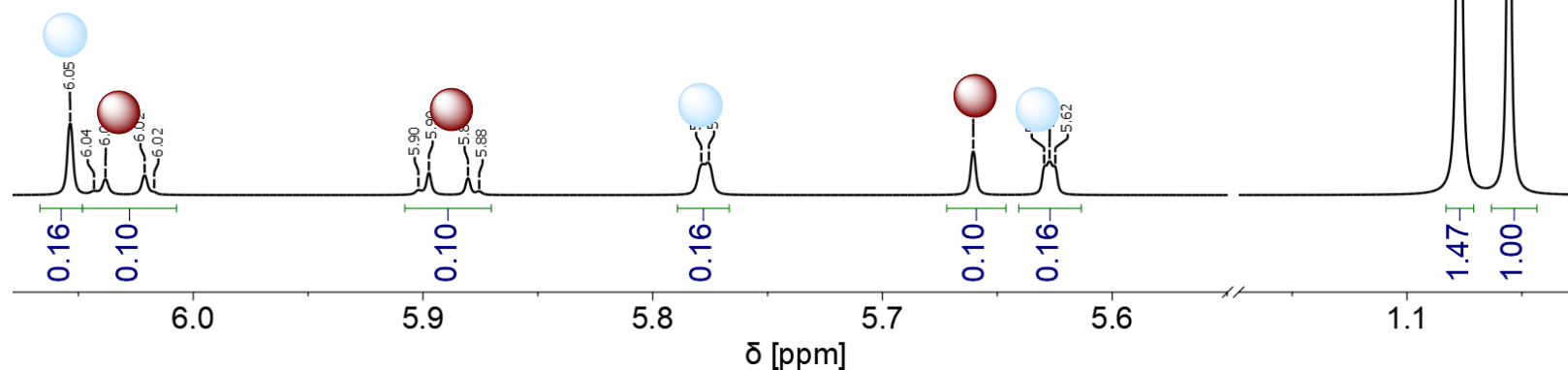
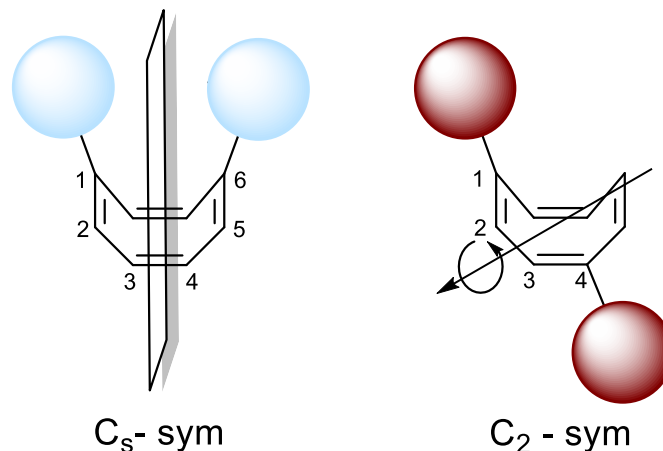
$\Delta G(298K)$ = - 0.22 (15 min equilibration time)

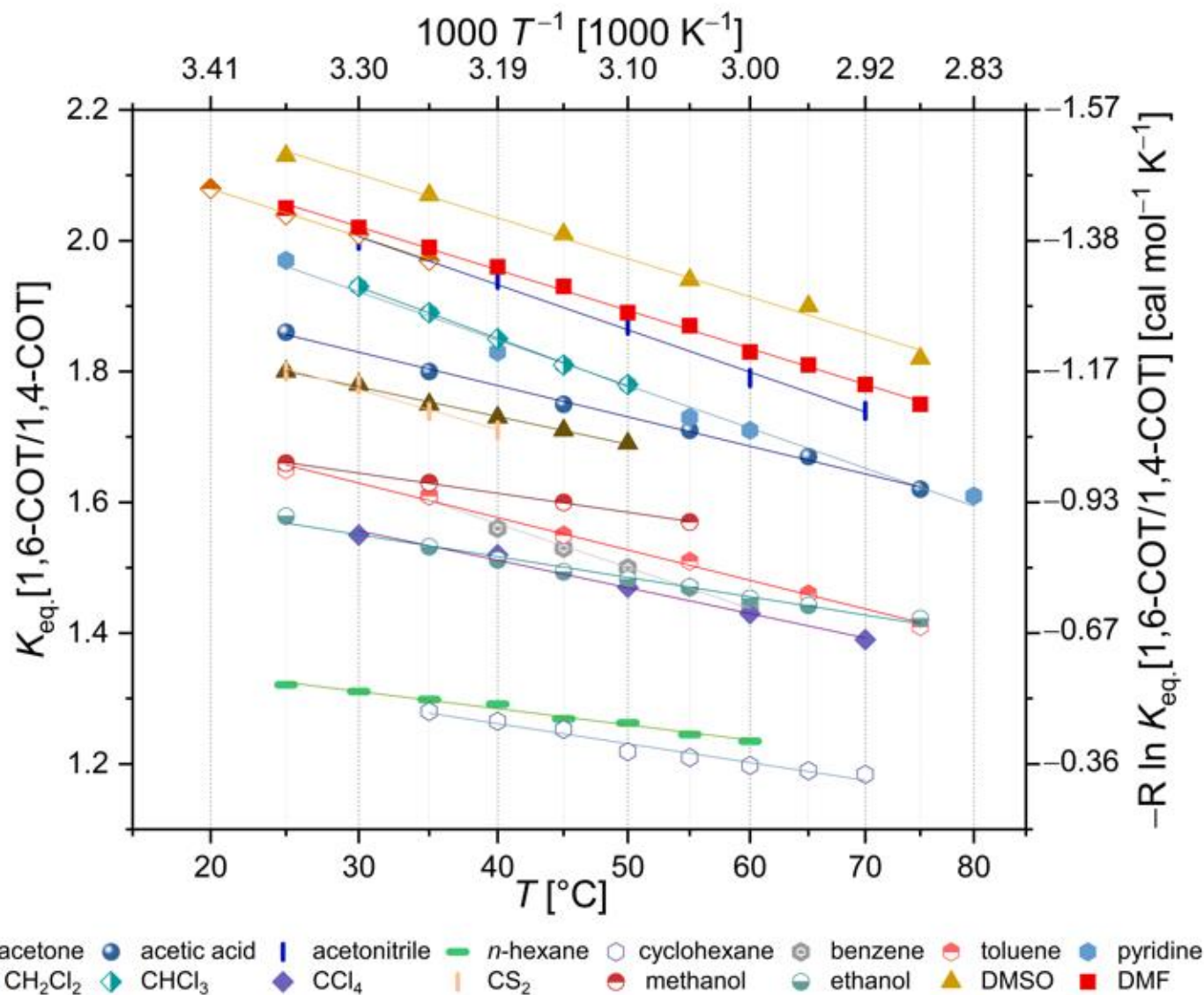
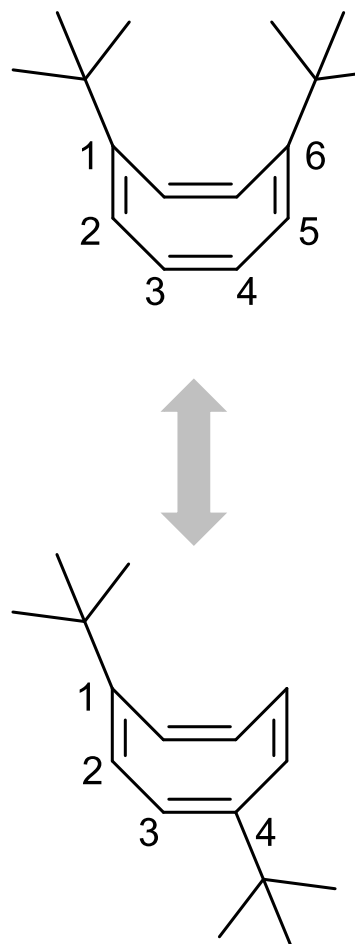
$K_{eq.}$ (298K) = 2.01 (60 min equilibration time)

$\Delta G(298K)$ = - 0.41 (60 min equilibration time)

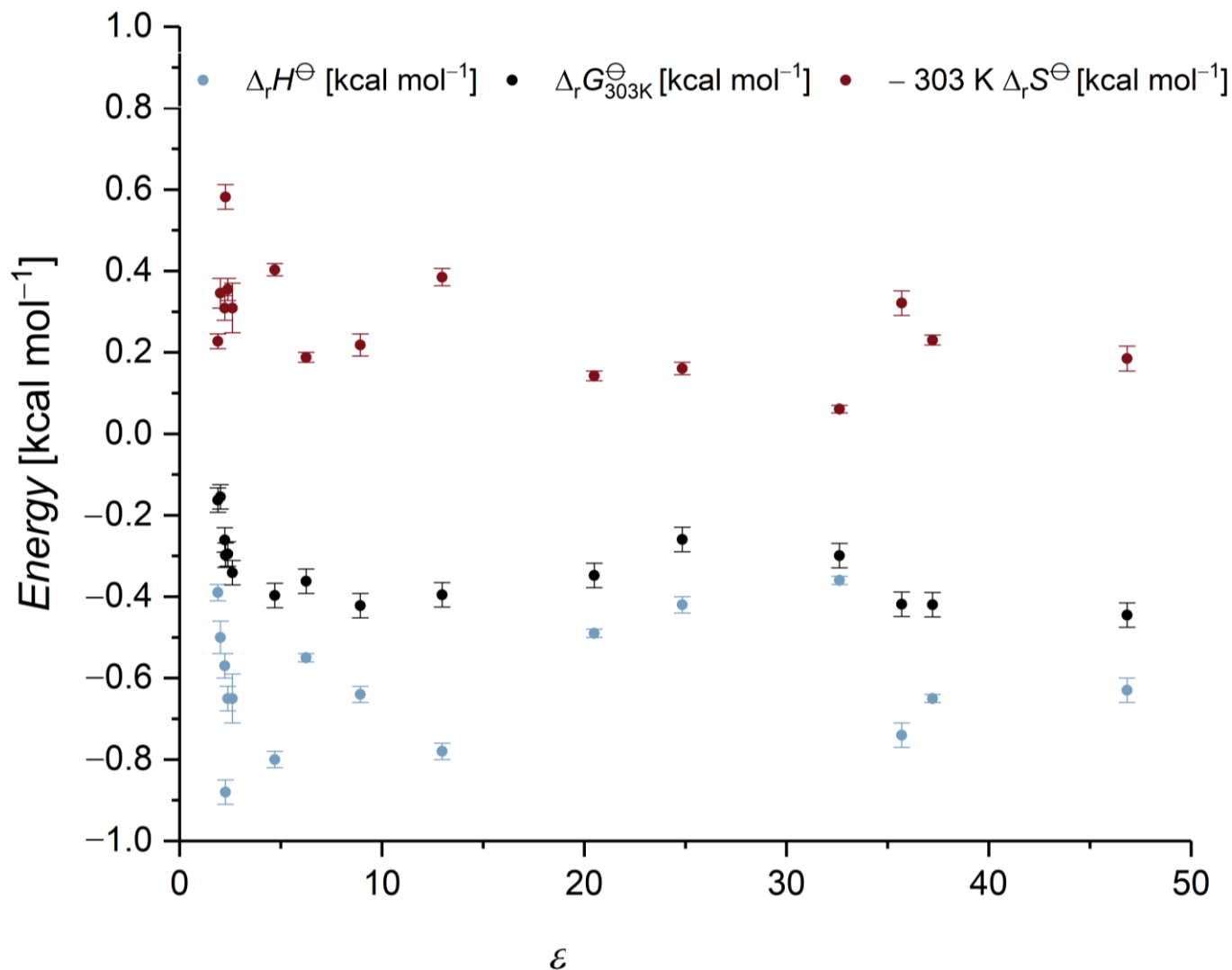
exp. : ΔH_0 = - 1.08 kcal mol⁻¹

comp.: ΔH_0 = - 0.5 kcal mol⁻¹

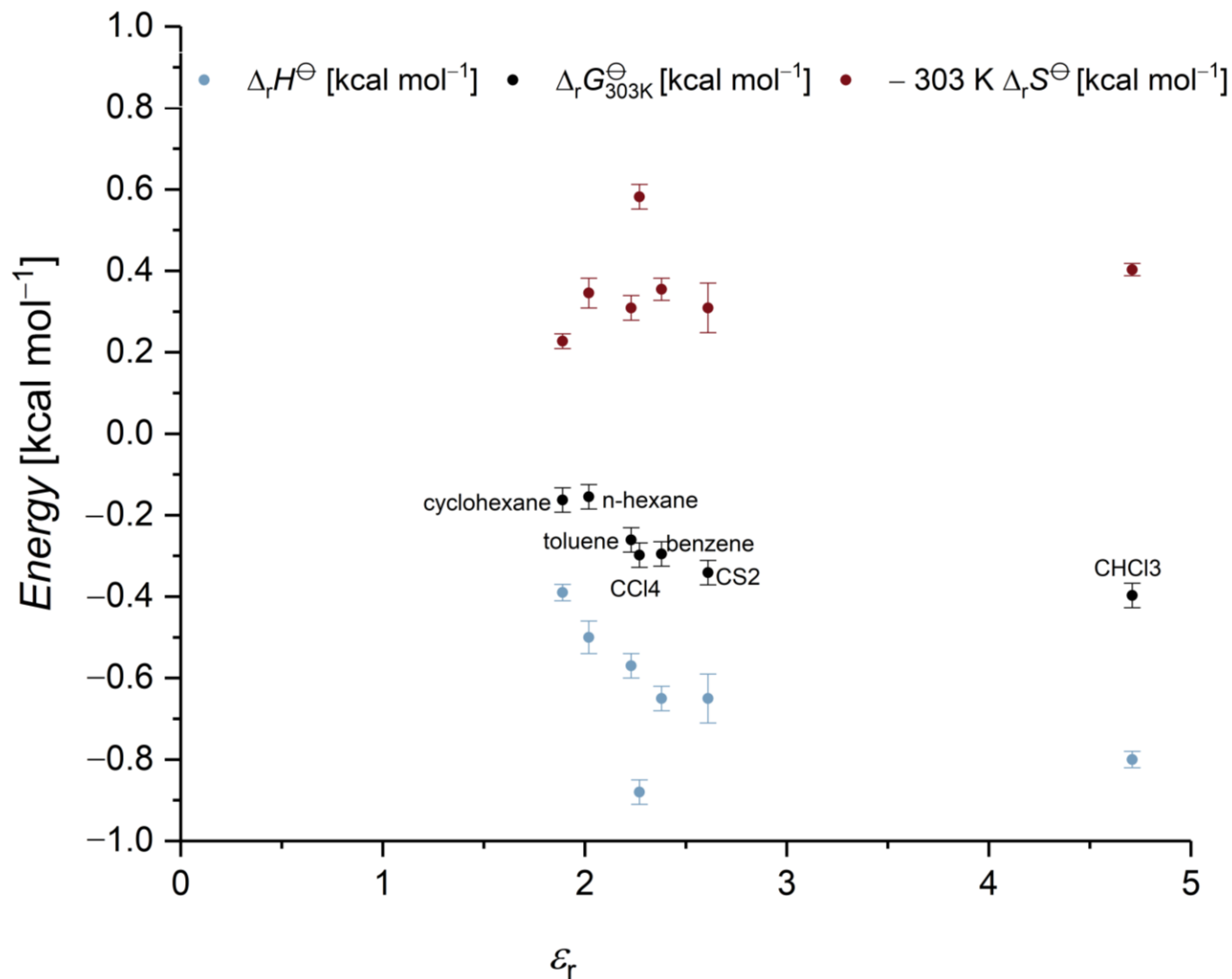




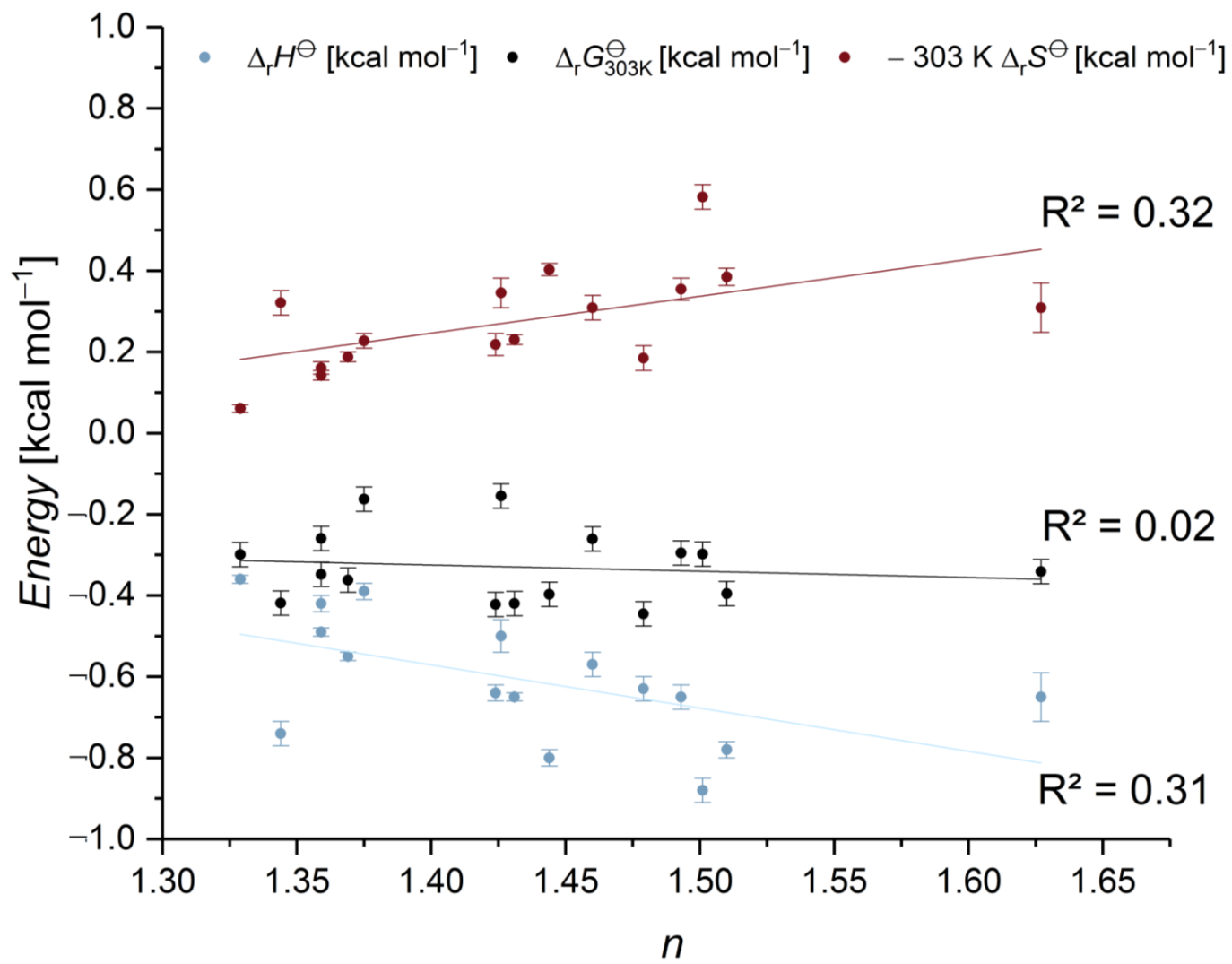
$$-R \cdot \ln K_{eq,1h}^T \left\{ \frac{[\text{folded}]}{[\text{unfolded}]} \right\} [\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] = \Delta H_{\text{fold}}^0 [\text{kcal} \cdot \text{mol}^{-1}] \cdot \frac{1}{T} [\text{K}^{-1}] - \Delta S^0 [\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}]$$

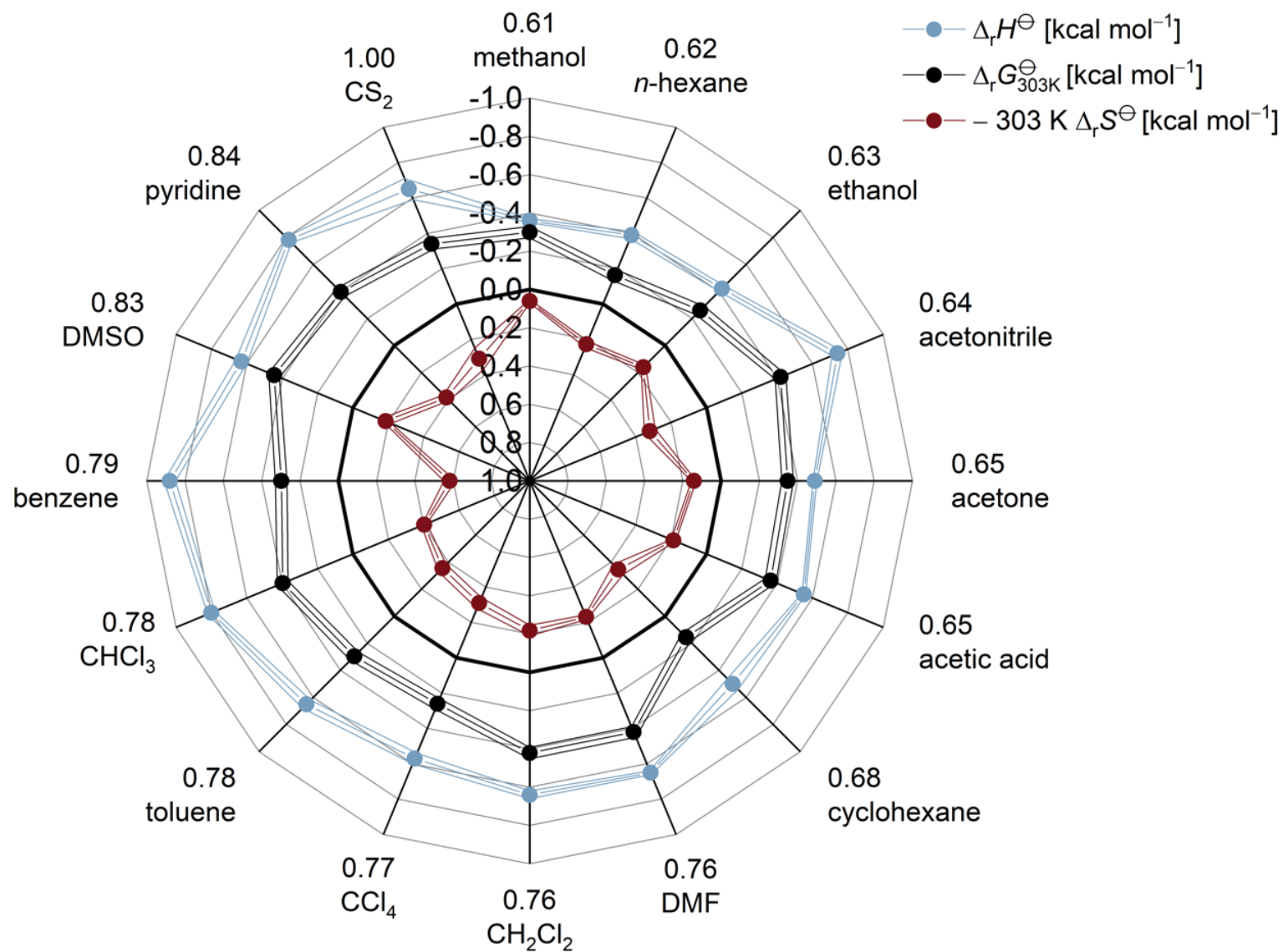


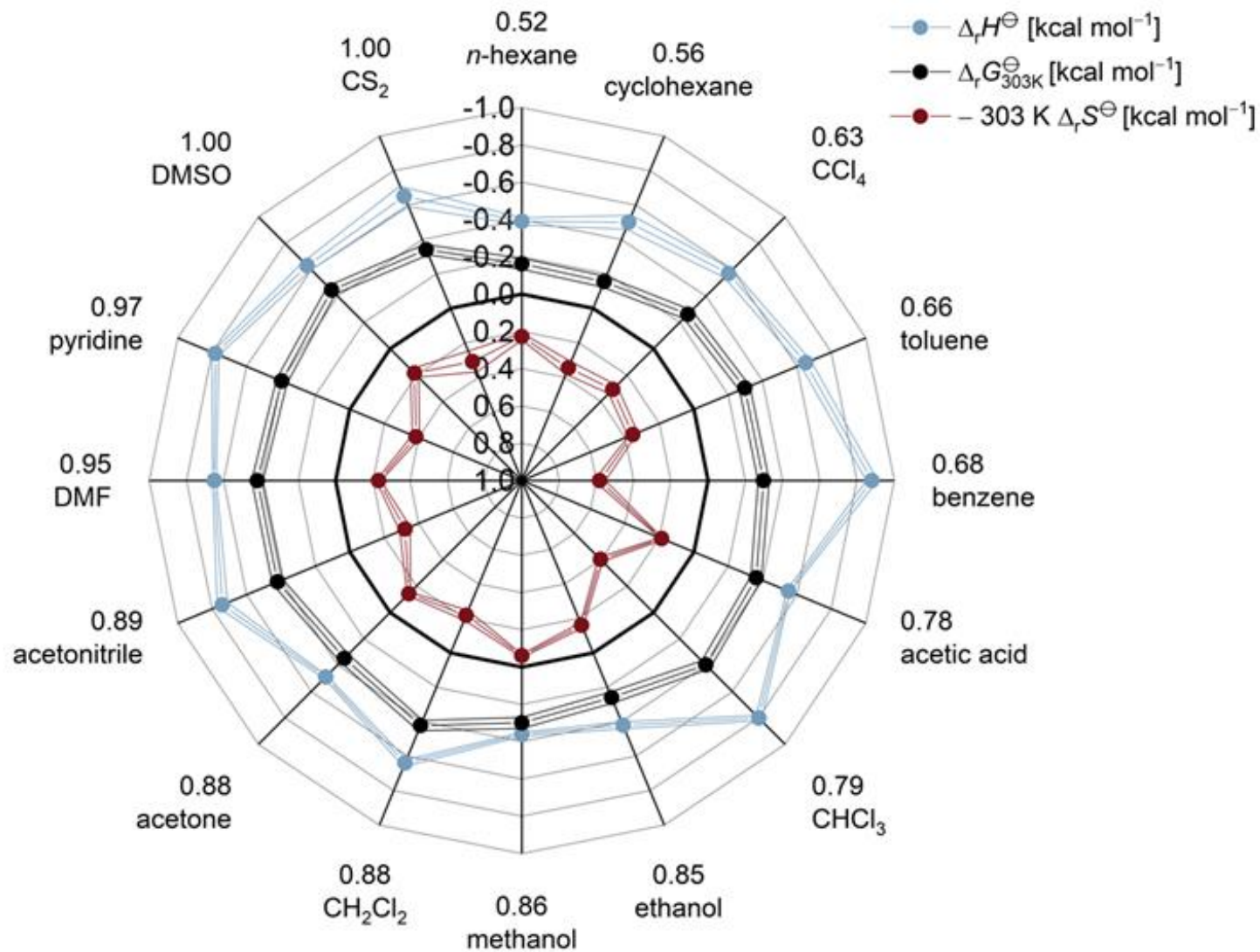
The permittivity of a substance (often called the dielectric constant) is the ratio of the electric displacement D to the electric field strength E when an external field is applied to the substance. The quantity tabulated here is the relative permittivity, which is the ratio of the actual permittivity to the permittivity of a vacuum; it is a dimensionless number.

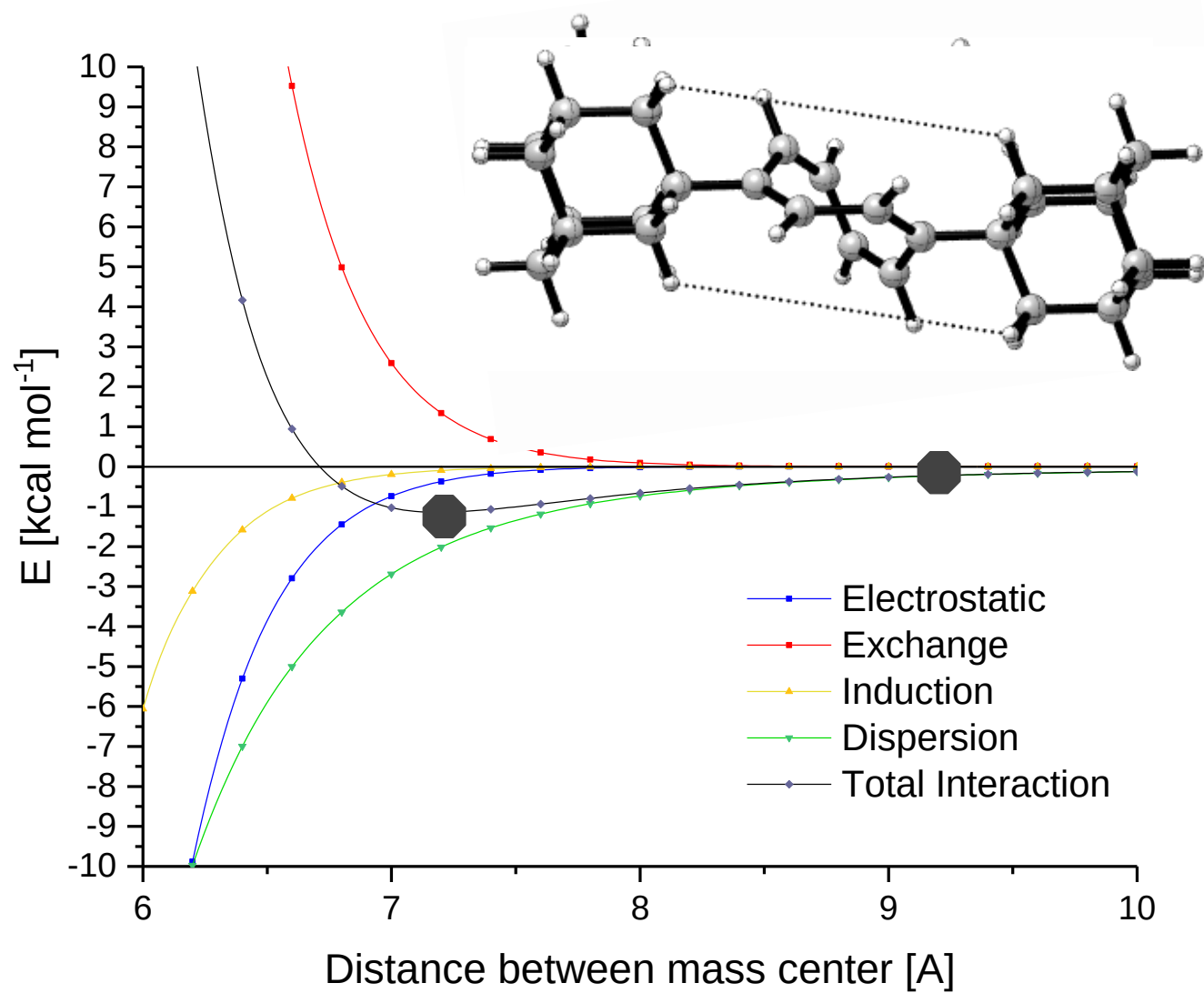


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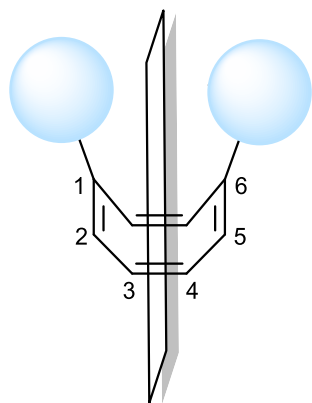




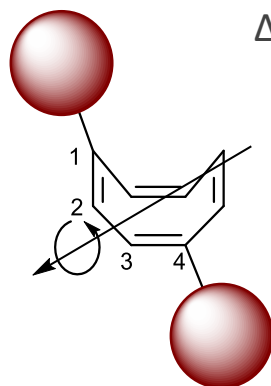


$K_{\text{eq.}}(298\text{K}) = 1.70$ (15 min equilibration time)

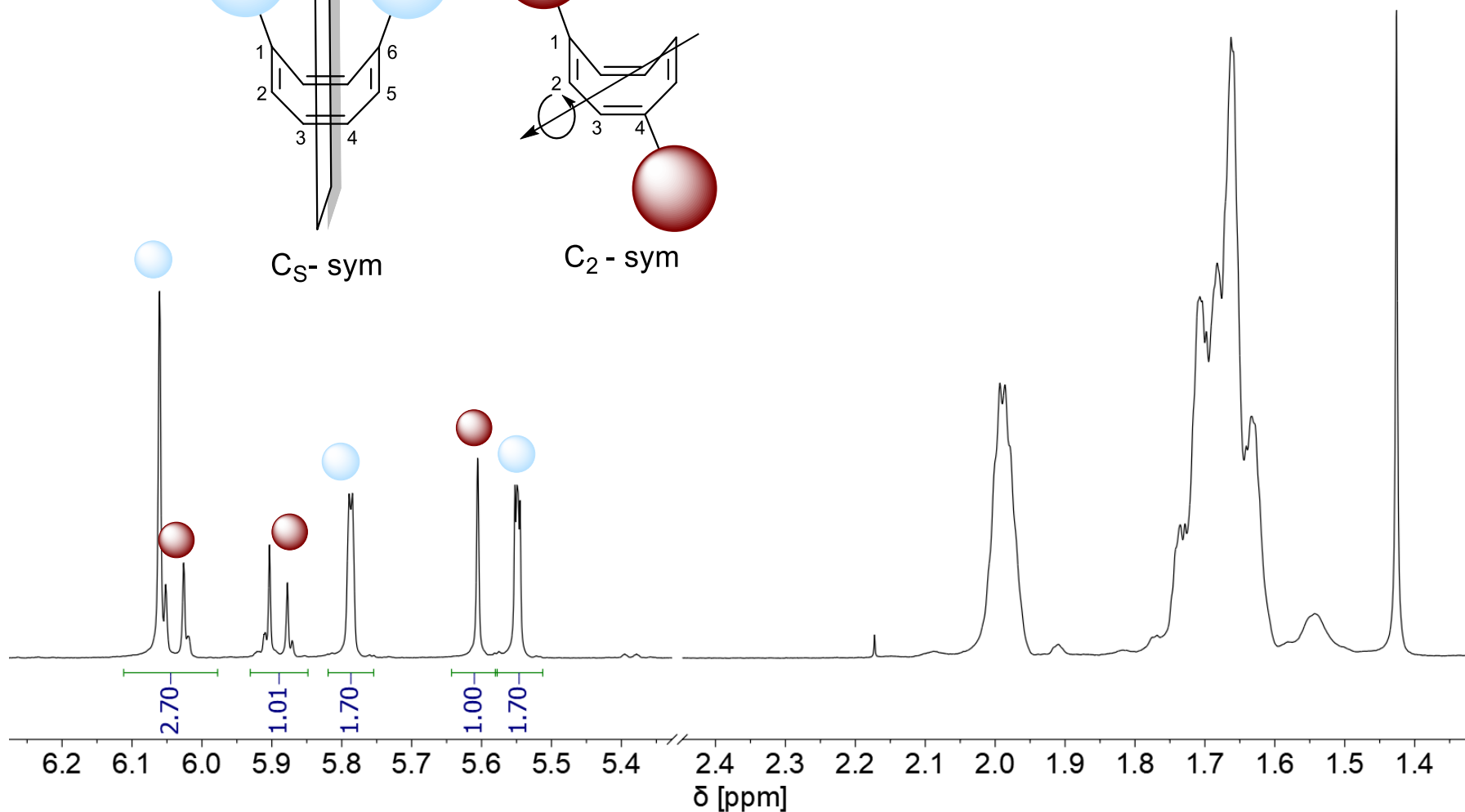
$\Delta G(298\text{K}) = -0.31$ (15 min equilibration time)



C_S -sym

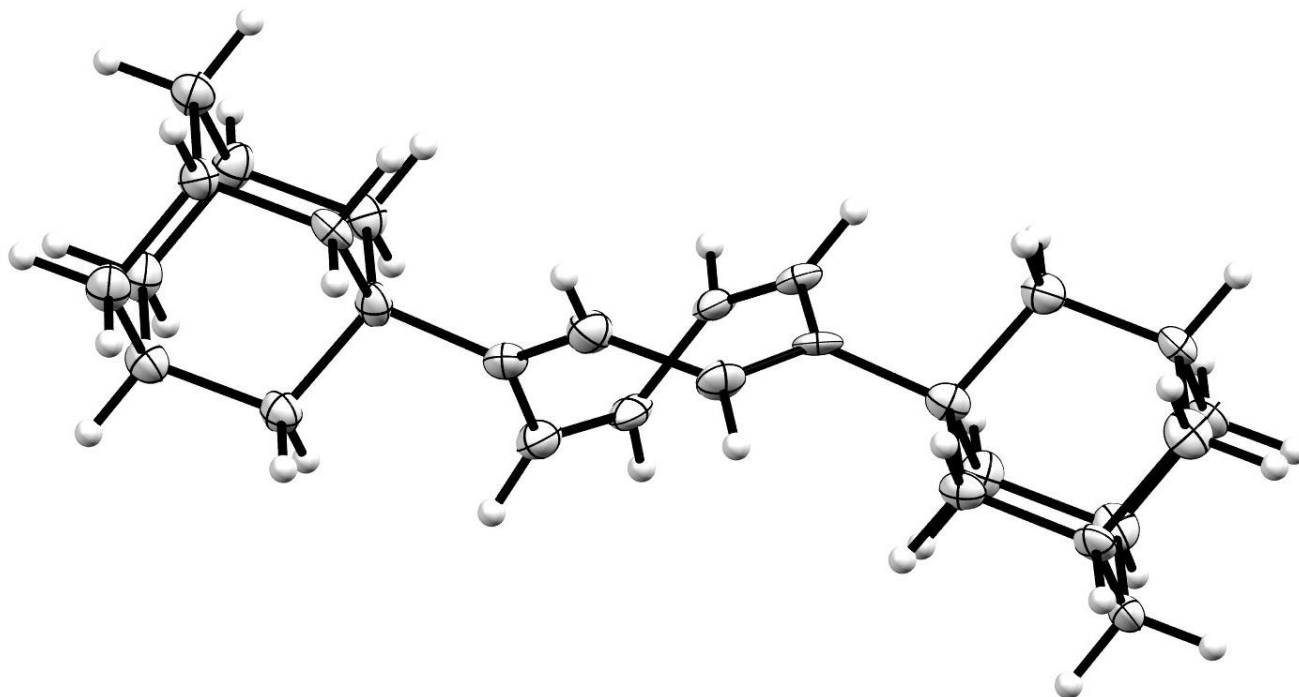


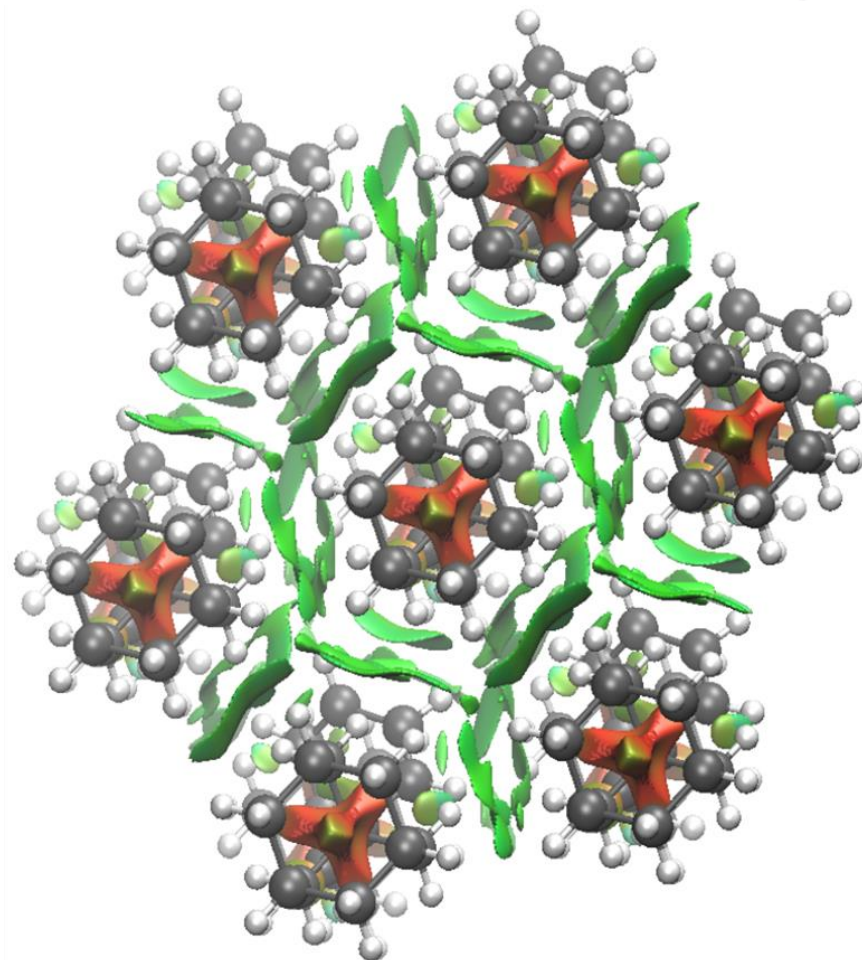
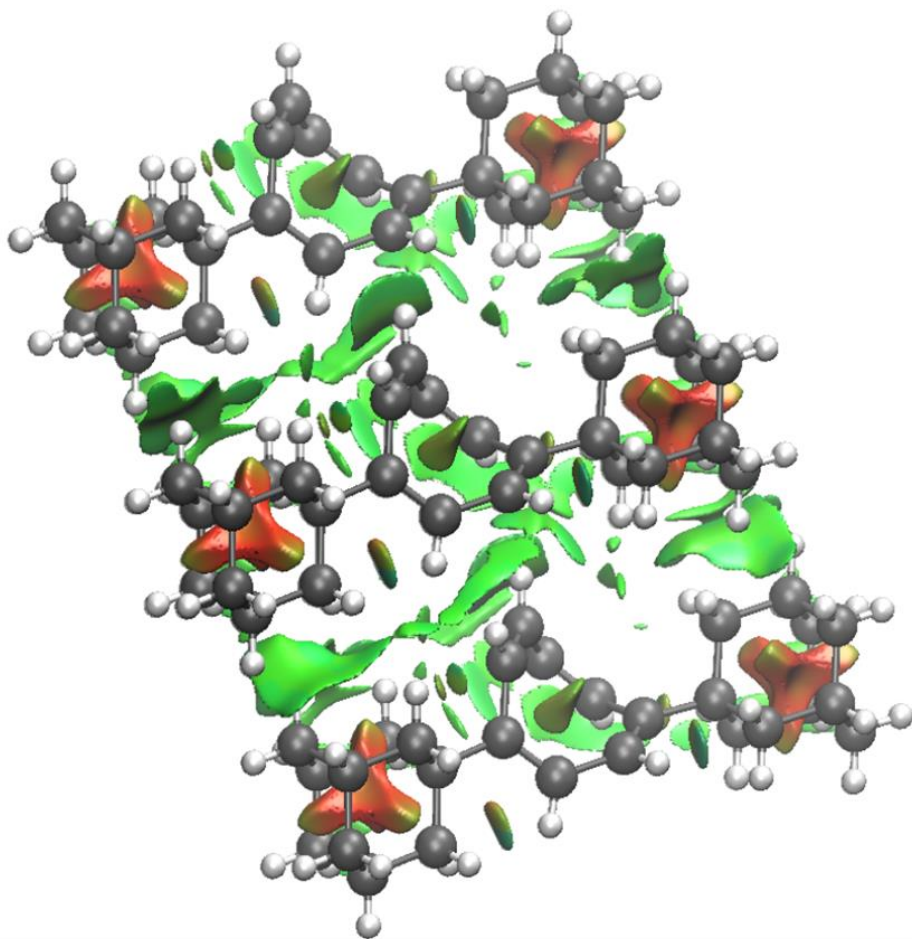
C_2 -sym





First and only crystall structure of a purely hydrocarbon based cyclooctatetraene!!!

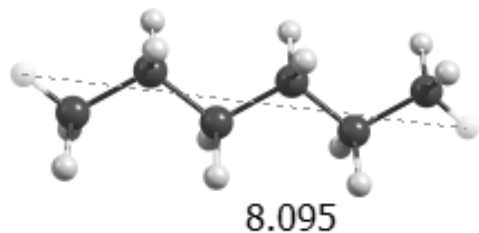
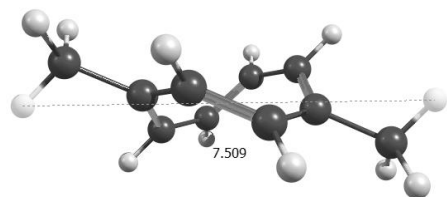




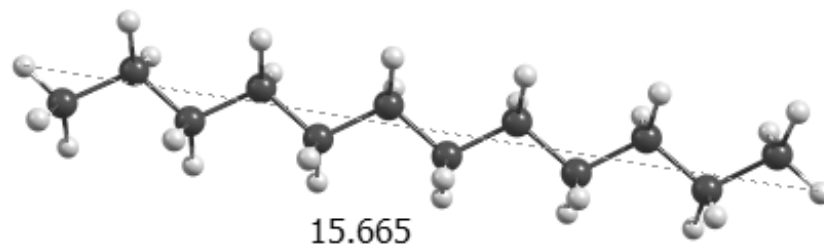
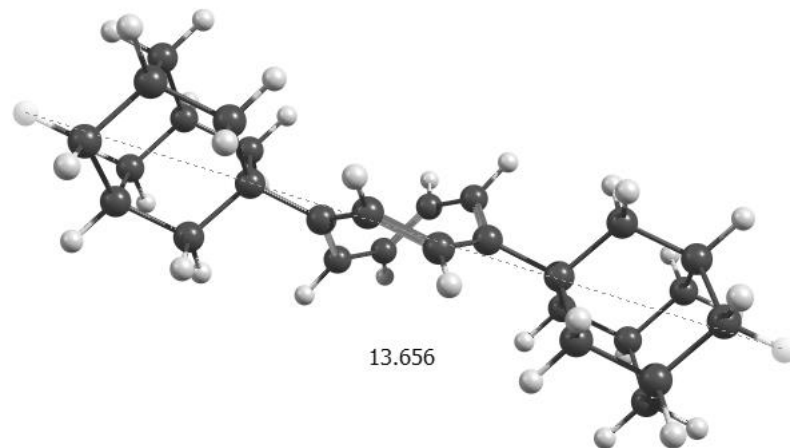
Special recipe for scaled SAPT0 (see Manual):

Electrostatics sSAPT0	-2.22440367	[mEh]
Exchange sSAPT0	7.94806944	[mEh]
Induction sSAPT0	-0.69823215	[mEh]
Dispersion sSAPT0	-19.03812445	[mEh]
Total sSAPT0	-14.01269084	[mEh]

-1.39583438	[kcal/mol]	-5.84017103	[kJ/mol]
4.98748887	[kcal/mol]	20.86765344	[kJ/mol]
-0.43814729	[kcal/mol]	-1.83320826	[kJ/mol]
-11.94660346	[kcal/mol]	-49.98458887	[kJ/mol]
-8.79309625	[kcal/mol]	-36.79031472	[kJ/mol]



Standard vaporisation enthalpy 7.6 kcal/mol



Standard vaporisation enthalpy 14.7 kcal/mol



- **Intramolecular Dispersion** does not cancel in solution
- Know your system! - Beware of the transition state
- Dispersion interactions can be used as a tool to **fine-tune** molecular structures, ...





Current group members:

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M.Sc. Friedemann Dreßler (GER)
M.Sc. Frederick R. Erb (GER)
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Prof. Dr. Andrey A. Fokin (UKR)
Dr. Dennis Gerbig (GER)
Dr. Radim Hrdina (CZE)
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Dr. Gowrisankar Saravanan (IND)
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Prof. Dr. Peter R. Schreiner (GER)
M.Sc. Jan M. Schümann (GER)
M.Sc. Alexander Seitz (GER)
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MSc. Kai Feuer (GER)
MSc. Henrik F. König (GER)
BSc. Kyangzi K. Calderon Cerquera (COL)

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Dr. André K. Eckhardt (GER)
Dr. Dominik Niedek (GER)
Dr. Lijuan Song (CHN)

