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inorganic & structural chemistry

Gas Electron Diffraction
–
Eliminating Ambiguities of Quantum Chemistry

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16th European Symposium on Gas-Phase Electron Diffraction (ESGED16)

Frauenchiemsee, June 23, 2015

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Ferrocenes

Ferrocenes – history

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1966 – gas-phase structure of Ferrocene[1]

1968 – rotational barrier of Ferrocene[2]

1979 – gas-phase structure and rotational barrier of Me_{10}Ferrocene[3]

⋮

2010 – gas-phase structure and rotational barrier of Cl_{10}Ferrocene[4]

2015 – F_5Ferrocene[5]

[1] R. K. Bohn, A. Haaland, *J. Organomet. Chem.* **1966**, *5*, 470.
[2] A. Haaland, J. E. Nilsson, *Acta Chem. Scand.* **1968**, *22*, 17.
[3] A. Almenningen, A. Haaland, S. Samdal, J. Brunvoll, J. L. Robbins, J. C. Smart, *J. Organomet. Chem.* **1979**, *173*, 293.
[4] L. Phillips, M. K. Cooper, A. Haaland, S. Samdal, N. I. Giricheva, G. V. Girichev, *Dalton Trans.* **2010**, *39*, 4631.
[5] K. Sünkel, S. Weigand, A. Hoffmann, S. Blomeyer, C. G. Reuter, Yu. V. Vishnevskiy, N. W. Mitzel, *J. Am. Chem. Soc.* **2015**, *137*, 126-129.

Ferrocenes – GED

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compound (Fc=Ferrocene)	ΔE / kJ mol^{-1}	C_5–X bending (+ towards, – away from Fe)
$H_{10}Fc$[1,2]	–3.8(13)	+3.7(9)°
$Me_{10}Fc$[3]	+4.2(13)	–3.4(5)°
$Cl_{10}Fc$[4]	+0.8(2)	–3.7(3)°

$\Delta E = E_{ecl} - E_{stag}$

1,2,3,4,5-Pentafluoroferrocene:
first “mixed-ligand“ and
first fluorinated metallocene in GED

→hard to predict any structural feature

F_5Ferrocene – QC

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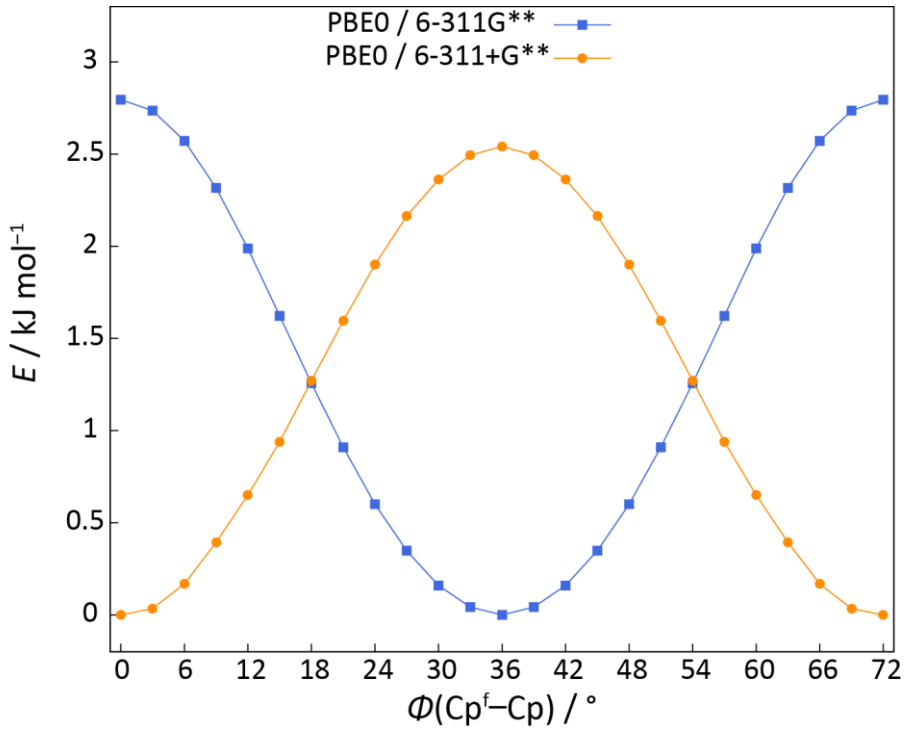

Method		ΔE / kJ mol^{-1}	d(Fe–C_F) / Å
PBE0	6-311G(d,p)	+2.7	1.999
	6-311+G(d,p)	−2.3	2.007
	cc-pVTZ	−2.2	2.013
MP2	6-311G(d,p)	−5.8	1.862
	6-311+G(d,p)	−20.8	1.865
	cc-pVTZ	−17.1	1.856

$\Delta E = E_{ecl} - E_{stag}$

F_5Ferrocene – GED

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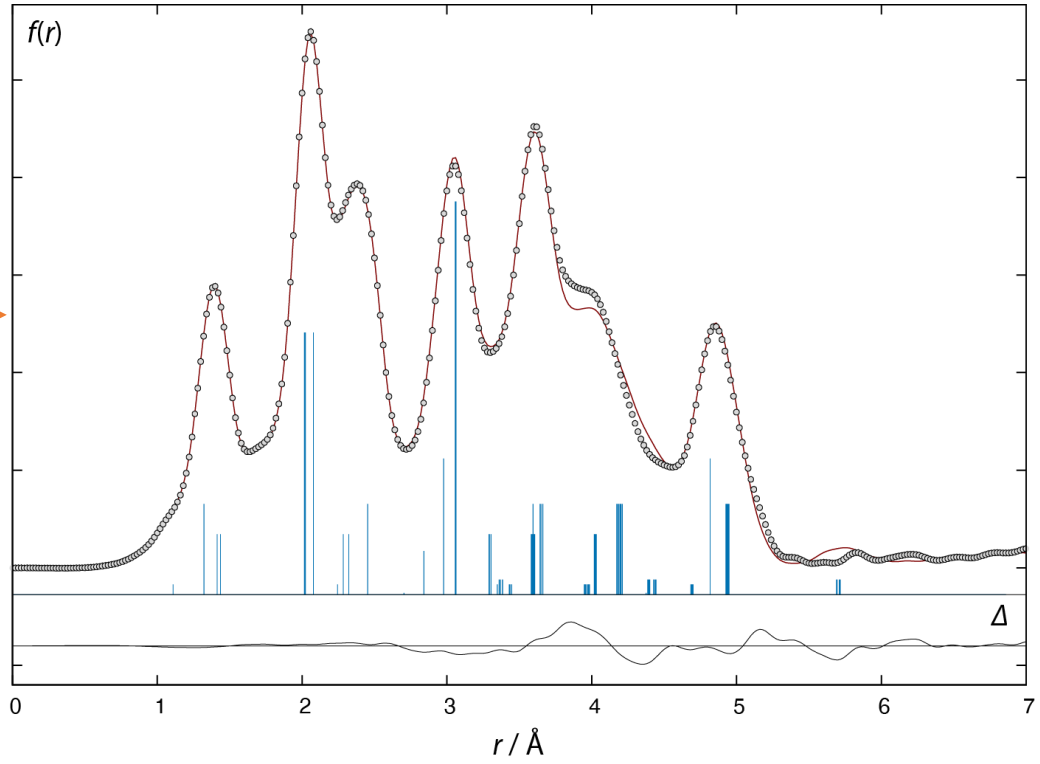
GED models:

- Φ = 0°: R_f = 5.8 %
- Φ = 36°: R_f = 7.8 %
- Φ refined: Φ = 15.5(13)°, R_f = 4.8 %



sample provided by:
Prof. Dr. K. Sünkel, LMU München

F_5Ferrocene – GED

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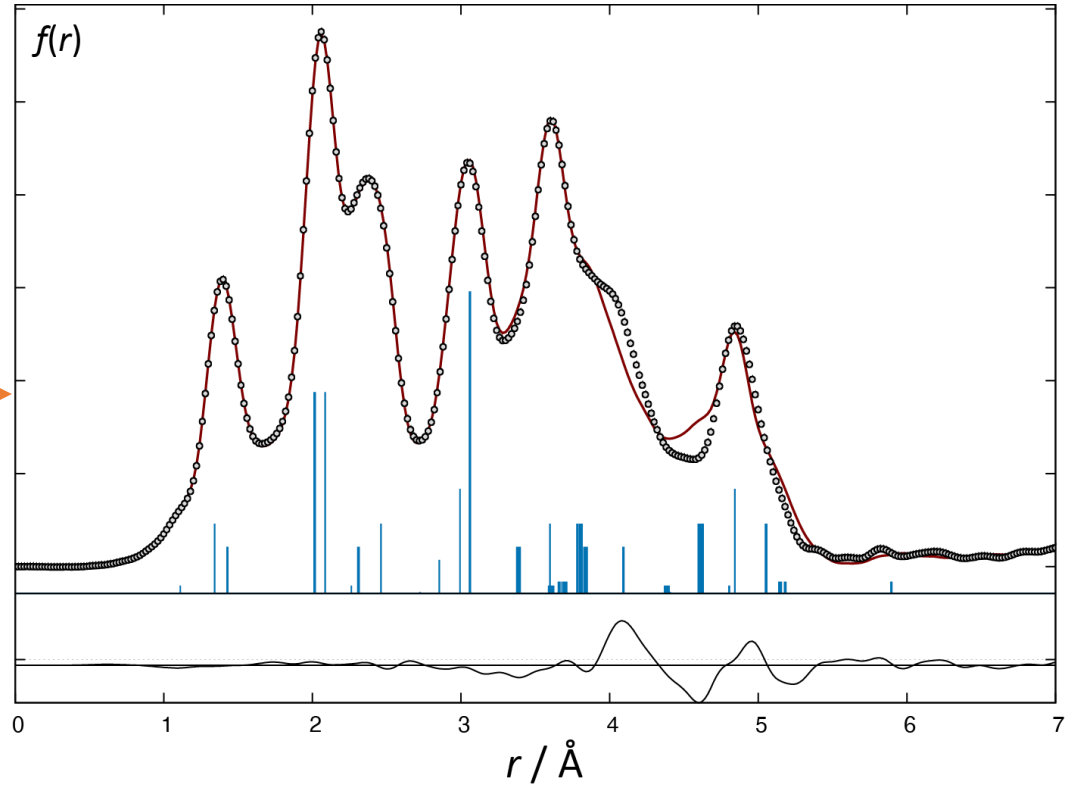

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F_5Ferrocene – GED

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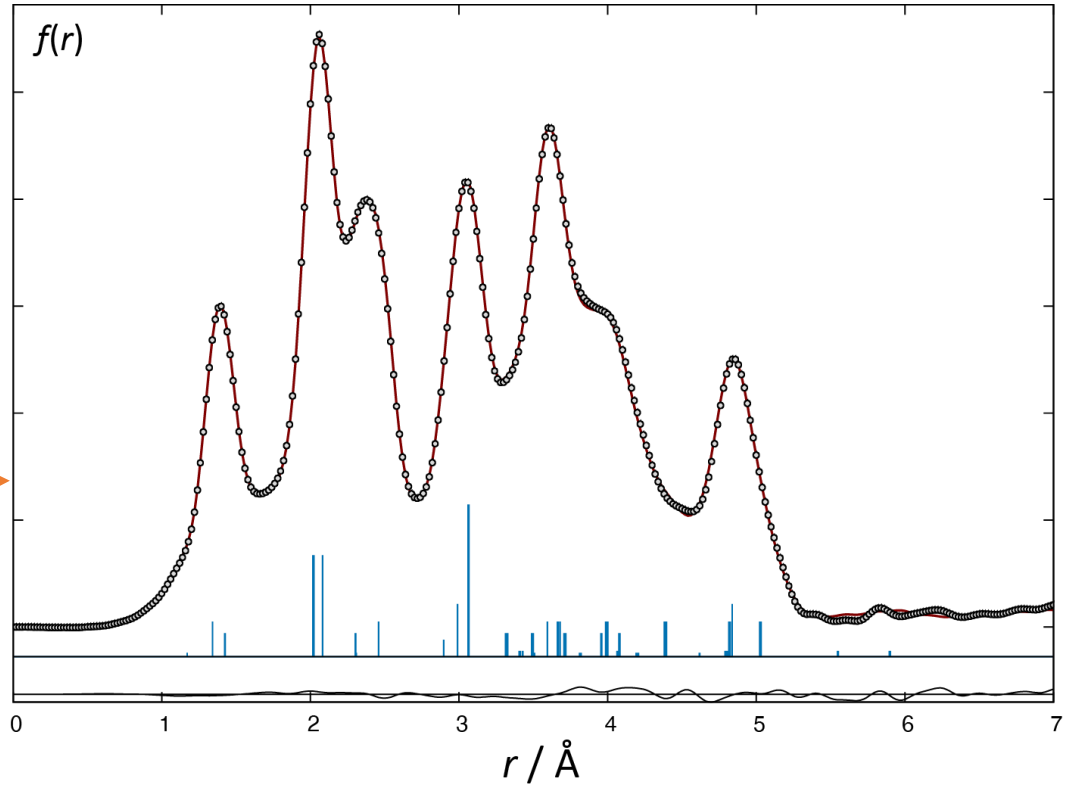

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F_5Ferrocene – GED

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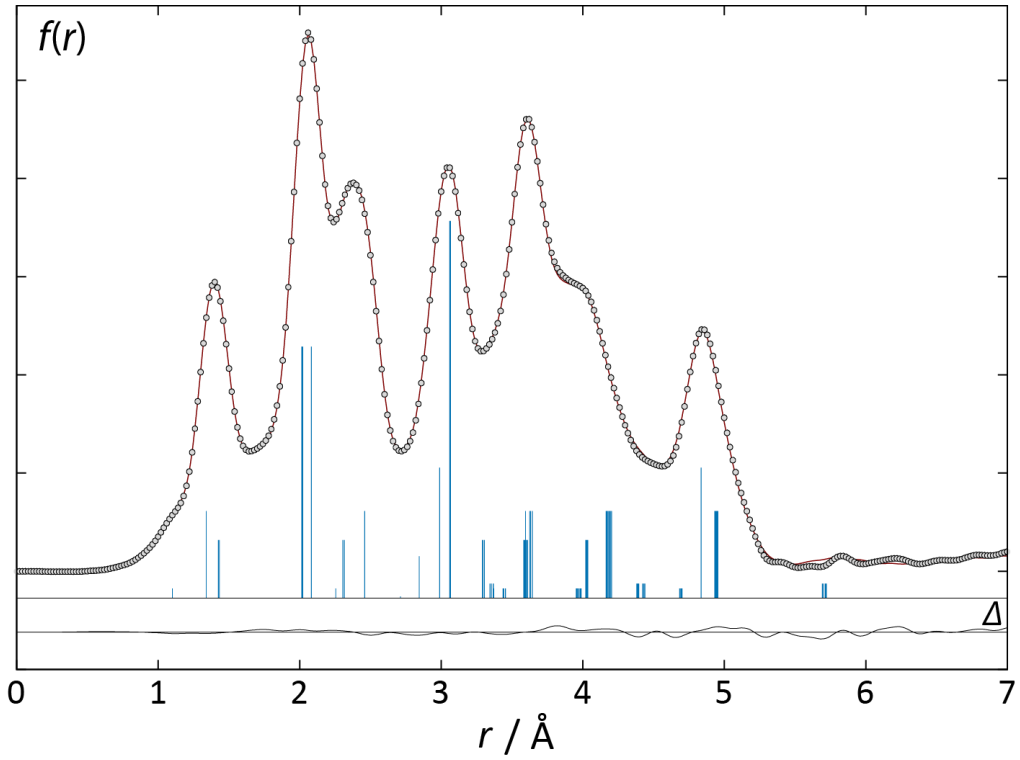
internal rotation

- isolated vibrational mode
  - $\tilde{\nu}$ = 27 cm^{-1} (PBE0/cc-pVTZ)
- external potential
  - $V(\Phi) = V_5\,[(\,1 - \cos(5\Phi)]\,/\,2$

Results[5]:

- eclipsed minimum
- V_5 = 2.4(8) kJ mol^{-1}
- C_5–H bent inwards (+1.6(6)°)
- C_5–F bent outwards (−3.7(3)°)
- d(Fe–(C_5F_5)) < d(Fe–(C_5H_5)):
  - 1.606(5) Å vs. 1.679(4) Å



R_f = 4.4 %

Ferrocenes – structures

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compound (Fc=Ferrocene)	ΔE / kJ mol^{-1}	C_5–X bending (+ towards, – away from Fe)
$H_{10}Fc$[1,2]	–3.8(13)	+3.7(9)°
$Me_{10}Fc$[3]	+4.2(13)	–3.4(5)°
$Cl_{10}Fc$[4]	+0.8(2)	–3.7(3)°
F_5Fc[5]	–2.4(8)	C_5–H: +1.6(6)°, C_5–F: –3.7(3)°
Cl_5Fc (PBE0/cc-pVTZ)	–1.3	C_5–H: +2.9°, C_5–Cl: –4.4°
Br_5Fc (PBE0/cc-pVTZ)	–0.8	C_5–H: +3.1°, C_5–Br: –4.3°
$F_{10}Fc$ (PBE0/cc-pVTZ)	–3.2	–2.7°

$\Delta E = E_{ecl} - E_{stag}$

→ equilibrium structure: interplay of steric repulsion and dispersive attraction
→ bending: ligand-specific and -intrinsic effect

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1-(1-Diamantyl)diamantane

Bis-diamantane – QC

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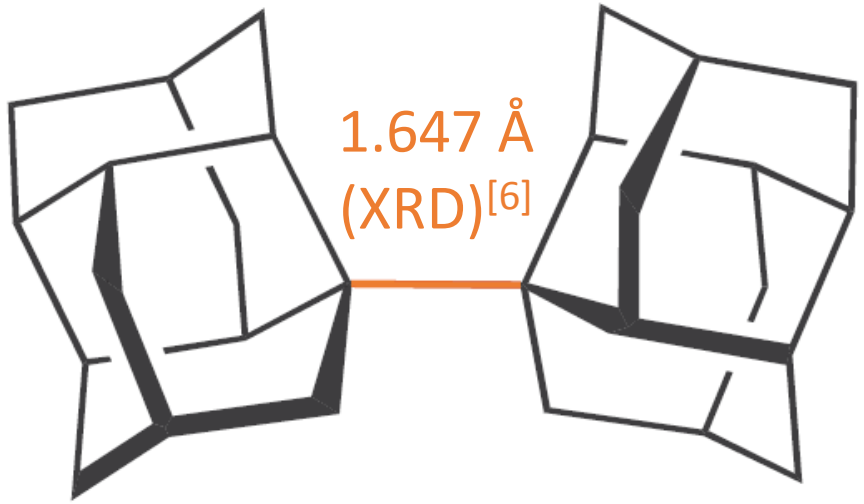

QC method	$d(C–C)_{long}$ / Å
B3LYP/6-31G(d,p)	1.674[6]
B3LYP-D/6-31G(d,p)	1.648[6]
B3LYP-D3/6-31G(d,p)	1.665
B3LYP-D3/cc-pVTZ	1.664
MP2/6-311G(d,p)	1.636

"…we estimate that a value of 1.655 Å would be the most realistic approximation of the central bond length […] in the gas phase."[7]

[6] P. R. Schreiner, L. V. Chernish, P. A. Gunchenko, E. Yu. Tikhonchuk, H. Hausmann, M. Serafin, S. Schlecht, J. E. P. Dahl, R. M. K. Carlson, A. A. Fokin, *Nature* **2011**, *477*, 308.
[7] A. A. Fokin, L. V. Chernish, P. A. Gunchenko, E. Yu. Tikhonchuk, H. Hausmann, M. Serafin, J. E. P. Dahl, R. M. K. Carlson, P. R. Schreiner, *J. Am. Chem. Soc.* **2012**, *134*, 13641.

Bis-diamantane – QC

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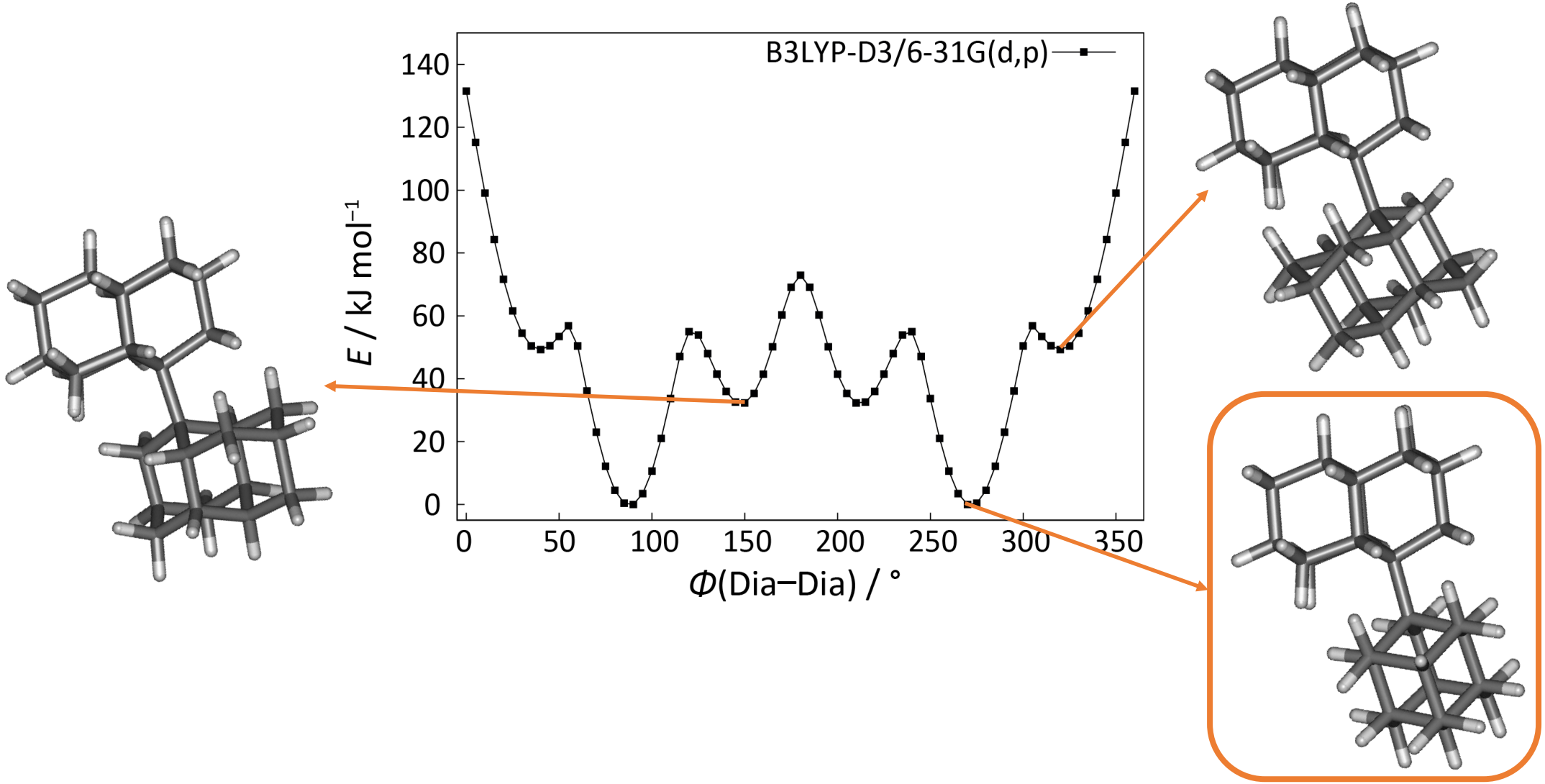

Bis-diamantane – GED

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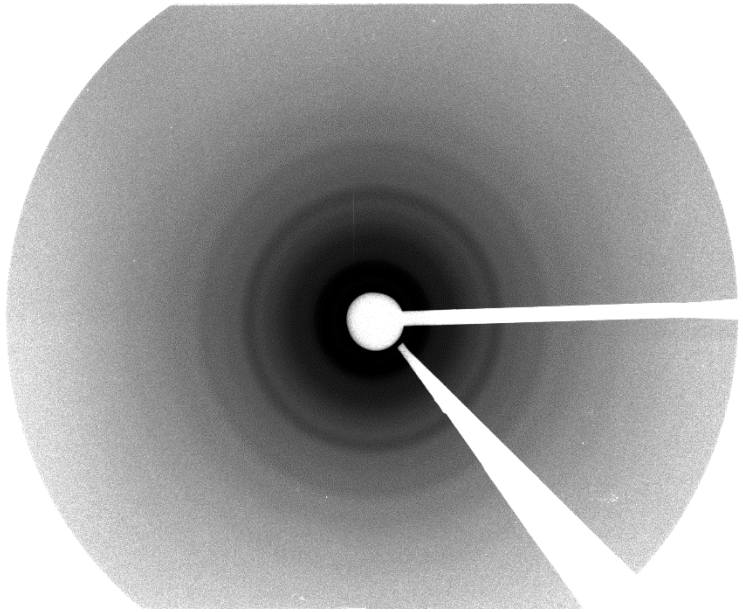
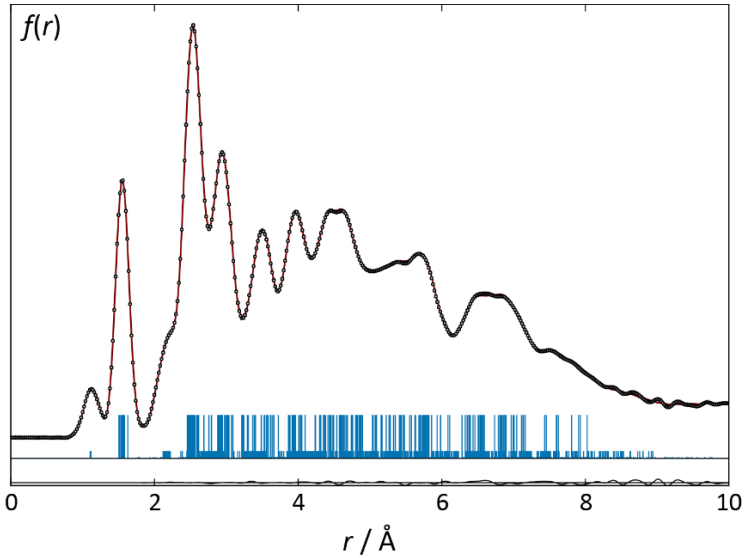
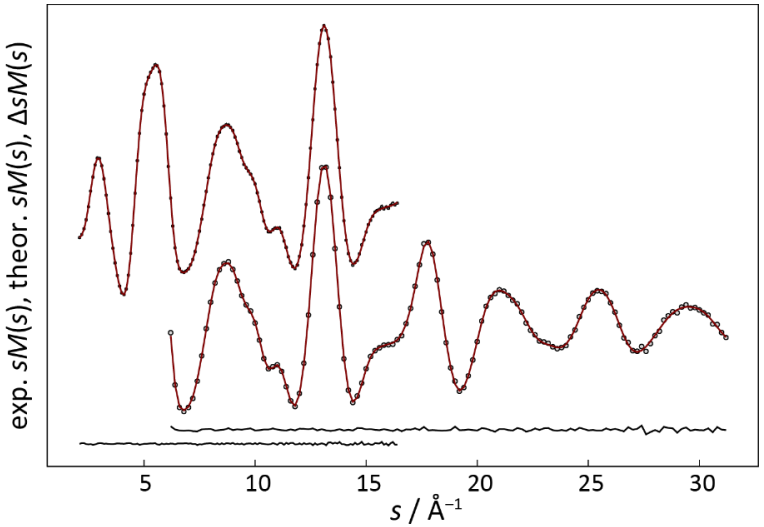
GED experiments at 310 °C:

- very intense diffraction



sample provided by:
Prof. Dr. P. R. Schreiner, JLU Gießen





R_f = 1.68 %

$\Phi \approx 40° \rightarrow R_f = 3.9$ %
$\Phi \approx 150° \rightarrow R_f = 4.5$ %

atom-richest compound @ BI

Bis-diamantane – GED

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distance/angle [Å/°]	r_e / Φ_e (GED)
d(C–C)$_{long}$	1.603(12)
d(C–C)$_{other}$	1.524(5)–1.567(5)
Φ(Dia-Dia)	92.3(15)

d(C–C)$_{long}$ significantly shorter than:

- all calculations (shortest: 1.636 Å)
- XRD (1.647 Å)
- “estimated” value (1.655 Å)

→ calculations: underestimate strength of dispersion forces

→ GED structures: benchmarks for improvements?

Summary

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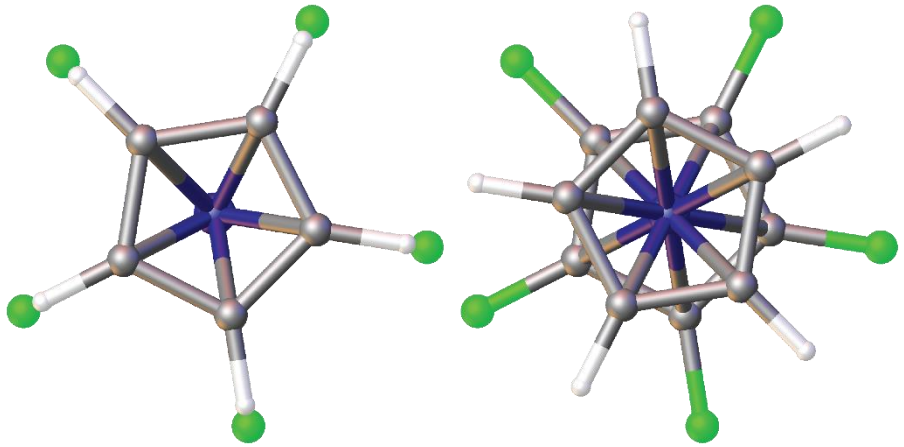
Flexiblity in 1,2,3,4,5-Pentafluoroferrocene



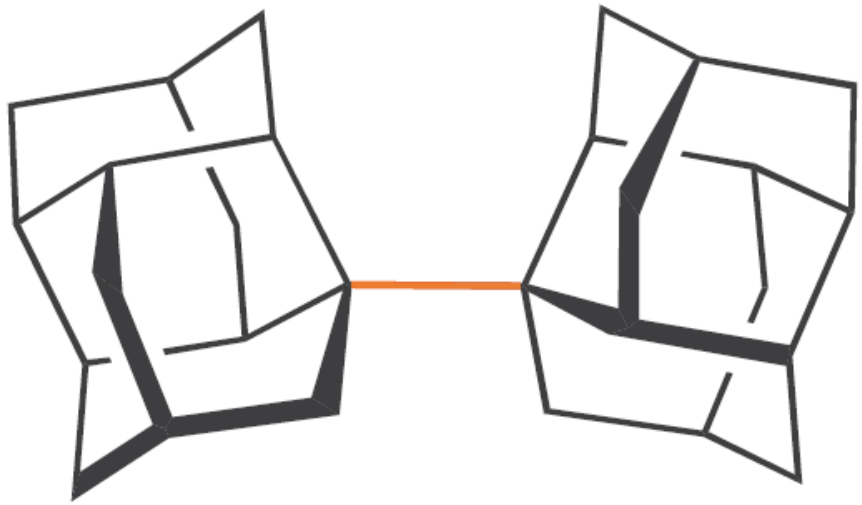
eclipsed equilibrium

ΔE = 2.4(8) kJ mol^{-1}

H atoms bent inwards

F atoms bent outwards

Dispersion Forces in 1-(1-Diamantyl)diamantane



1.636–1.674 Å (QC)

vs.

1.603(12) Å (GED)