Mitzel Group
inorganic & structural chemistry

structural chemistry in the gas-phase

group seminar – 08.02.2016

Sebastian Blomeyer

retrospect – talk 05/15

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Rückblick – Vortrag 02/15

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GED – weitere Projekte

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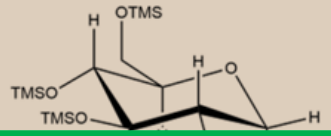
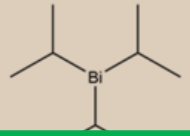
Altabef (ARG):

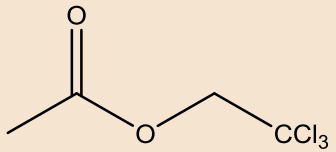
Schreiner (Gießen):

Pietschnig (Kassel):



Schulz (Essen):





12

3

retrospect – talk 05/15

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$Cl_3CC(O)OEt$

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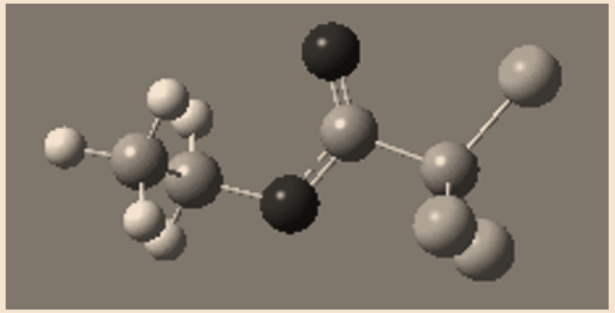
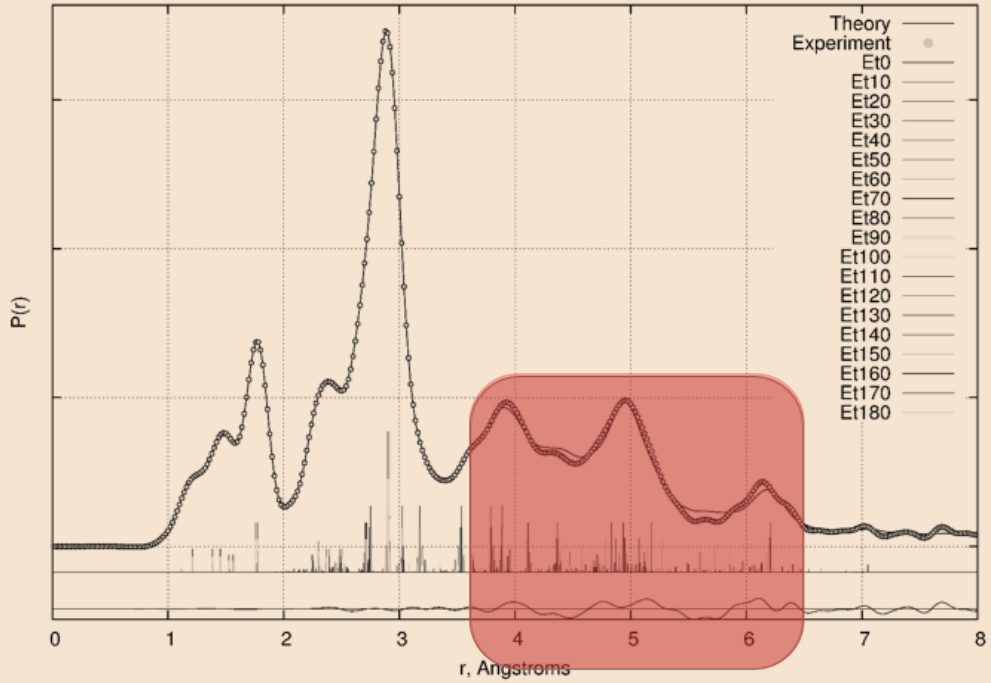
dynamisch (häufigstes Pseudokonformer Φ = 170°, 20 %):



R_f = 6.1 %



$H_3CC(O)OCH_2CCl_3$

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…what next?

GED data

calculations

results

„manuscript“

$H_3CC(O)OCH_2CCl_3$ – QC

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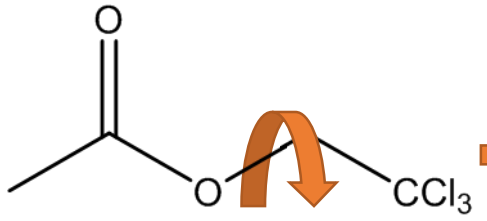
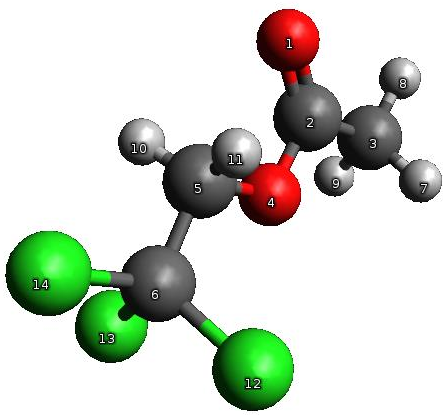
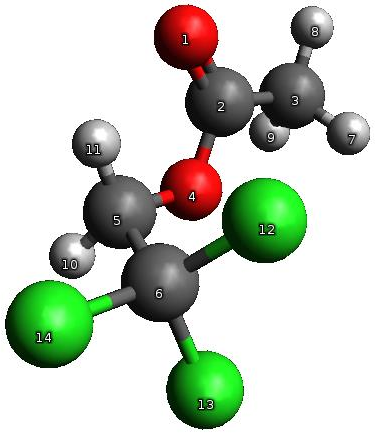
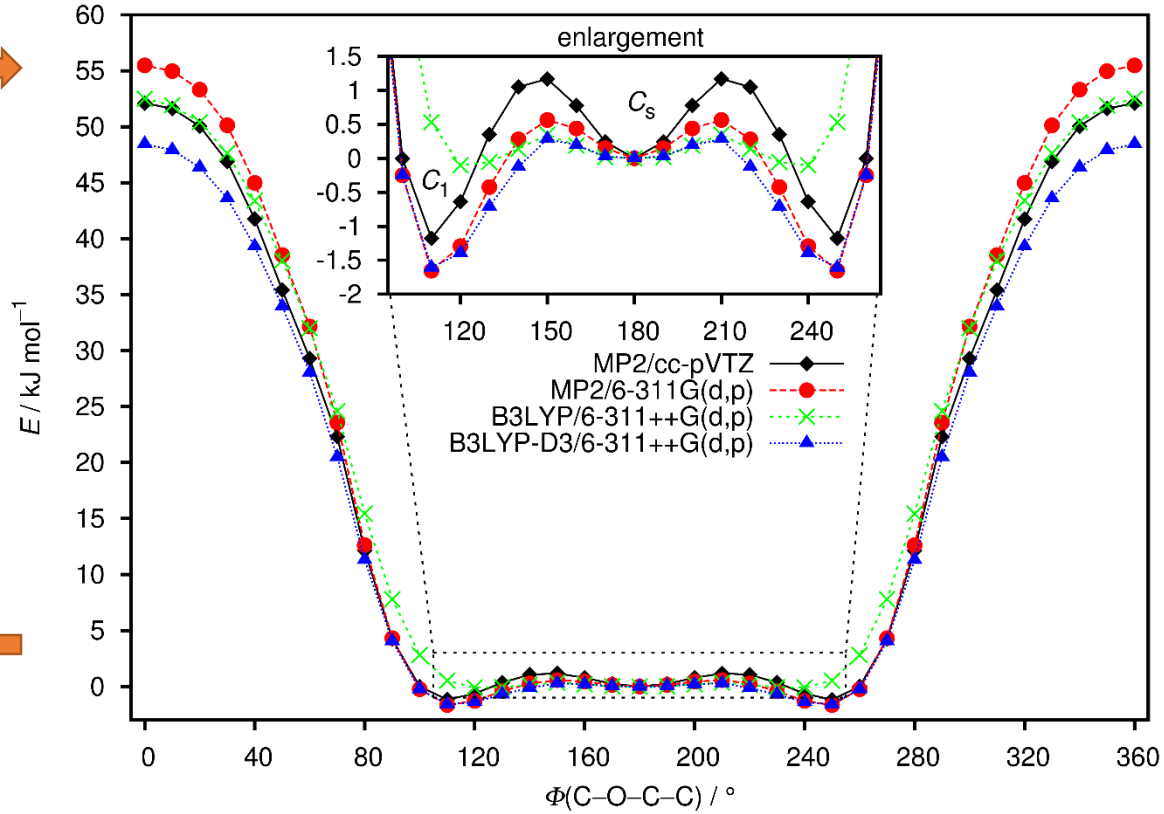




syn–anti



syn–gauche



$H_3CC(O)OCH_2CCl_3$ – QC

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	ΔE / kJ mol^{-1}	$E_{barrier}$ / kJ mol^{-1}	$\Delta G_{323\ K}$ / kJ mol^{-1}	C_s:C_1 ratio
B3LYP/6-311++G(d,p)	−0.1	+0.3	+1.8	0.66:0.34
B3LYP-D3/6-311++G(d,p)	−1.7	+0.3	+1.2	0.61:0.39
MP2/6-311G(d,p)	−1.8	+0.6	+0.9	0.58:0.42
MP2/6-311++G(d,p)	−1.5	+0.2	+1.5	0.64:0.36
MP2/cc-pVTZ	−1.2	+1.2	+0.4	0.54:0.46

$\Delta E = E(syn–gauche) - E(syn–anti)$

$E_{barrier} = E(syn–anti) - E(\mathrm{TS})$

$\Delta G_{323\ K} = G_{323\ K}(syn–gauche) - G_{323\ K}(syn–anti)$

C_s:C_1 ratio: based on $\Delta G_{323\ K}$

$H_3CC(O)OCH_2CCl_3$ – QC

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stability of *syn–gauche*?

→ IQA analysis (**I**nteracting **Q**uantum **A**toms)

→ I-SAPT analysis (**I**ntramolecular **S**ymmetry **A**dapted **P**erturbation **T**heory)

$H_3CC(O)OCH_2CCl_3$ – IQA

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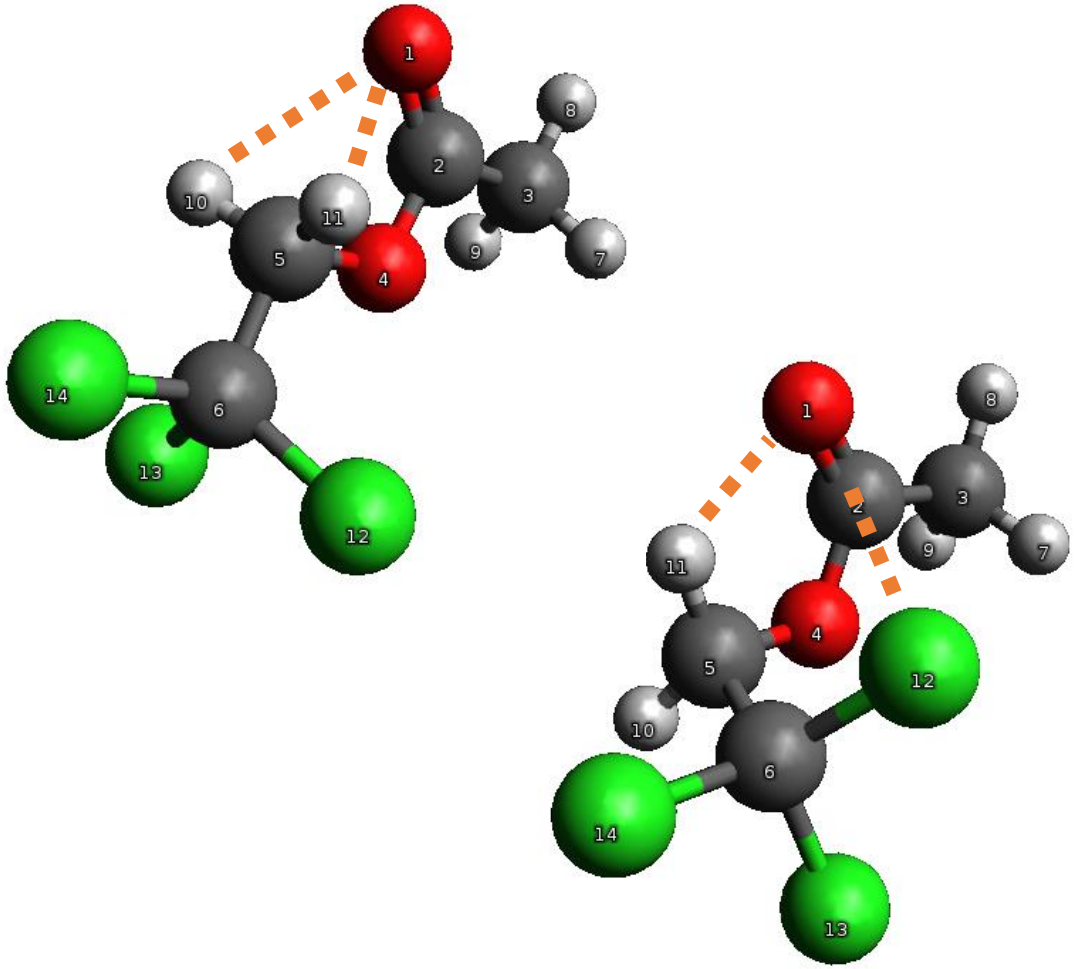
interatomic interaction energies



atom pair	ΔE_{inter} / kJ mol^{-1}
O(1)···H(11)	−41.1
C(2)···Cl(12)	−27.4
O(1)–C(2)	−18.5
O(4)···H(11)	−18.2
C(2)···C(5)	−17.4
C(2)···H(10)	−16.4
C(3)–H(8)	+12.1
O(1)···C(5)	+12.2
C(5)–H(11)	+16.4
O(1)···Cl(12)	+16.7
O(1)···H(10)	+19.5
C(2)···H(11)	+28.2
C(2)–O(4)	+74.0

$H_3CC(O)OCH_2CCl_3$ – QC

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stability of *syn–gauche*?

→ IQA analysis (**I**nteracting **Q**uantum **A**toms)

→ I-SAPT analysis (**I**ntramolecular **S**ymmetry **A**dapted **P**erturbation **T**heory)

$H_3CC(O)OCH_2CCl_3$ – I-SAPT

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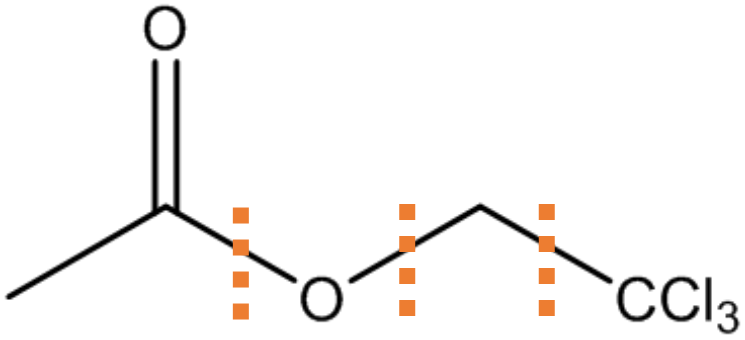
- interactions between fragments of molecules
  - electrostatic
  - exchange (steric)
  - induction
  - dispersion



fragmentation	$\Delta E_{electrostatic}$	$\Delta E_{exchange}$	$\Delta E_{induction}$	$\Delta E_{dispersion}$	$\Delta E_{I\text{-}SAPT0}$
$H_3CC(O)–OCH_2CCl_3$	−11.7	+4.0	+2.3	−2.9	−8.3
$H_3CC(O)O–CH_2CCl_3$	−13.2	+20.3	−5.1	−3.6	−1.6
$H_3CC(O)OCH_2–CCl_3$	−20.5	+7.8	−0.1	−2.8	−15.6

$\Delta E = E(syn–gauche) – E(syn–anti)$

$H_3CC(O)OCH_2CCl_3$ – GED

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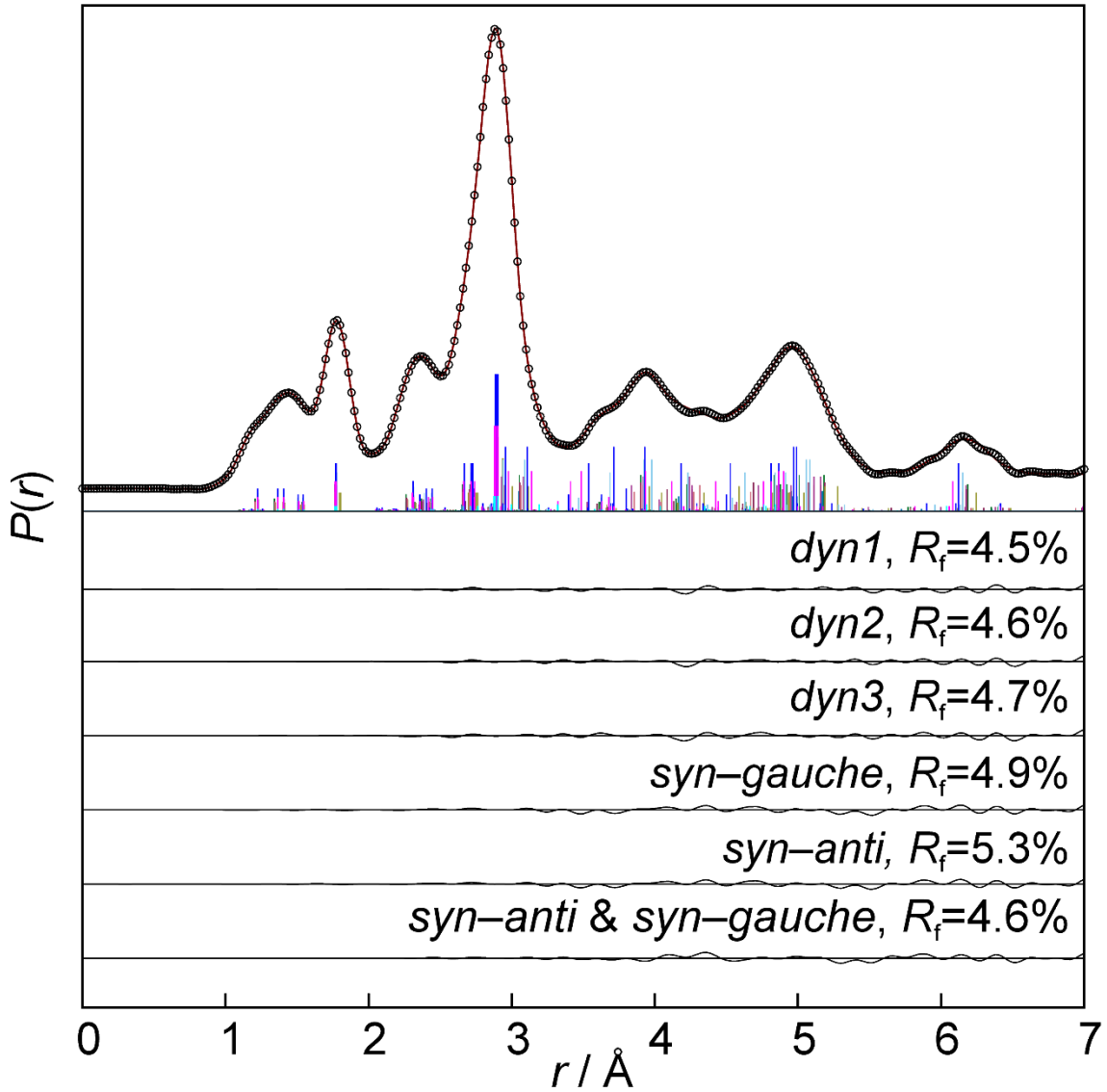
vapour composition in the gas-phase?

→ single-conformer models ☹

→ two-conformer model 😐

→ dynamic models, starting parameters from:

- MP2 → *dyn1* 🙂
- B3LYP-D3 → *dyn2* 🙂
- B3LYP → *dyn3* 🙂



$H_3CC(O)OCH_2CCl_3$ – GED

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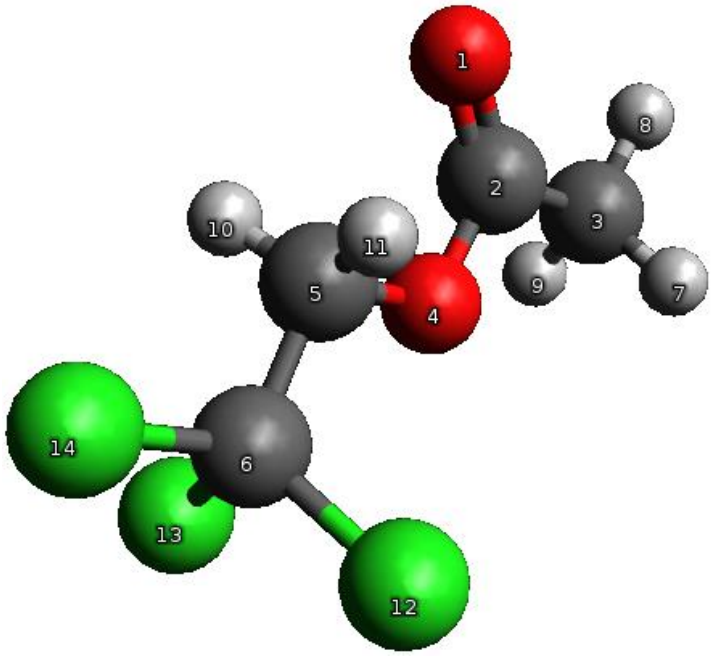

parameter / Å, °	*syn–anti* (r_e)			
	B3LYP	B3LYP-D3	MP2	GED
d(O(1)=C(2))	1.204	1.203	1.205	1.214(5)
d(C(2)–C(3))	1.503	1.503	1.490	1.499(3)
d(C(2)–O(4))	1.362	1.361	1.355	1.338(5)
d(O(4)–C(5))	1.425	1.425	1.414	1.401(5)
d(C(5)–C(6))	1.527	1.527	1.510	1.522(4)
$d(C(6)–Cl)_{mean}$	1.798	1.800	1.766	1.765(1)
α(O(1)–C(2)–C(3))	126.6	126.8	126.7	126.6(27)
α(O(1)–C(2)–O(4))	122.7	122.7	122.8	125.5(23)
α(C(2)–O(4)–C(5))	115.7	115.6	113.6	113.0(19)
α(O(4)–C(5)–C(6))	108.4	108.3	107.6	105.6(8)
Φ(O(4)–C(5)–C(6)–Cl(14))	180.0	180.0	180.0	173.4(15)

$H_3CC(O)OCH_2CCl_3$

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<u>stability of *syn–gauche* conformer</u>

O(1)···H(10/11)
C(2)···Cl(12)

electrostatics (& dispersion)

O(1)···Cl(12)
C(2)···H(10/11)

exchange

<u>vapour composition in the gas-phase</u>

MP2/cc-pVTZ dynamic model

ENDE