Universität Bielefeld

Bielefeld – La Plata Collaboration: Recent GED Results

Yury V. Vishnevskiy

La Plata, 20 March 2013

Overview

Objects:

ClF_2C-C(O)-X: X=CN (published), NCO (published), NCS (in preparation)

X-C(O)-NCS, **X-C(O)-SCN**: X=Cl (in press), F (to be measured)

R-SCN: R=CCl_3, CCl_2F, CH_2Cl (all in preparation)

R-SNO: R=CH_3-CH_2, CF_3-CH_2, $(CH_3)_3C$ (all in progress)

H_3CO-C(S)-SCH_3: (in progress)

CF_3-CF_2-C(O)-X: X=F, Cl, I (all three refined), O-C(O)-CF_2-CF_3 (in progress)

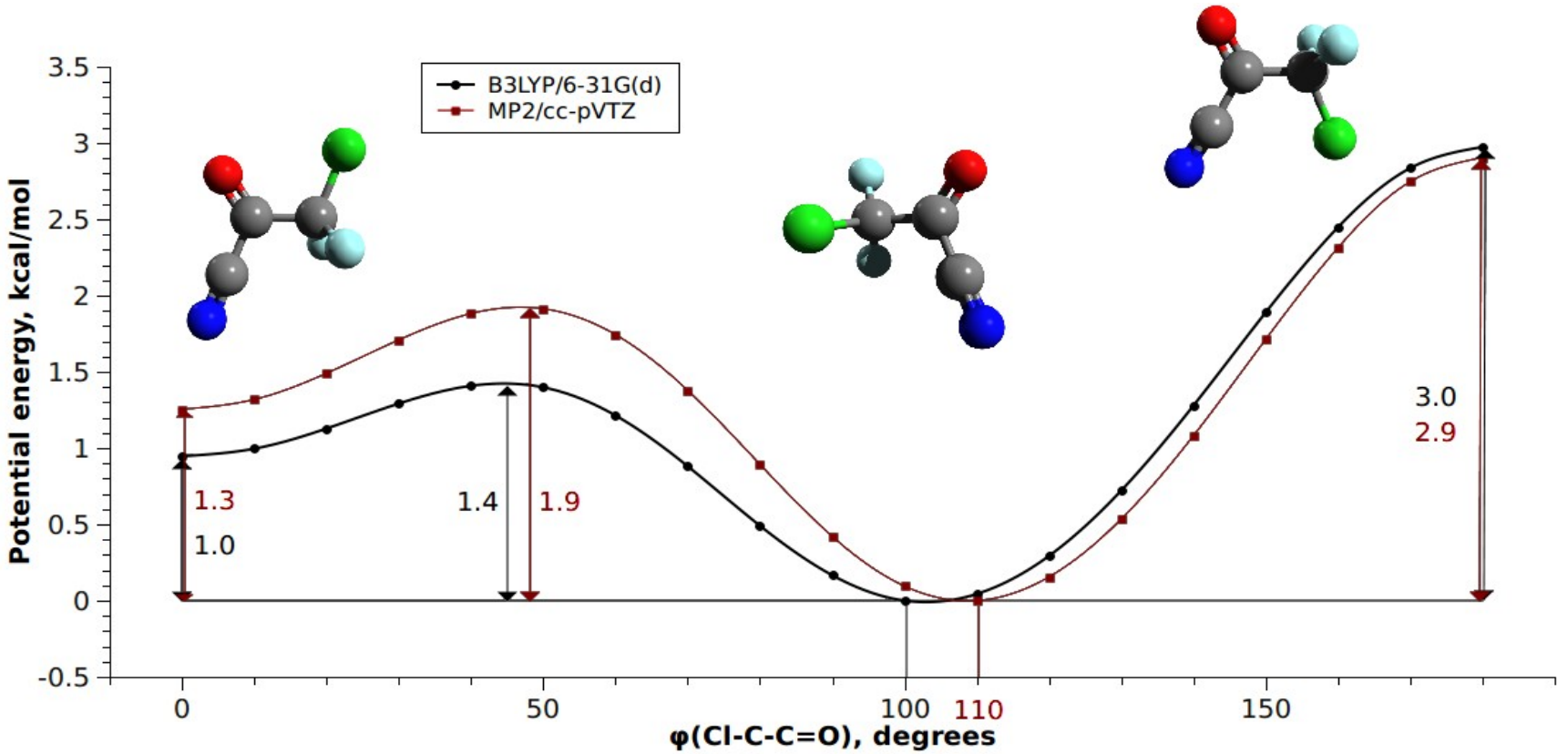
Problems:

Molecular structure, conformational properties, dynamics.

$ClF_2C\text{-}C(O)\text{-}X$

X=CN, NCO, NCS

ClF_2C-C(O)-CN

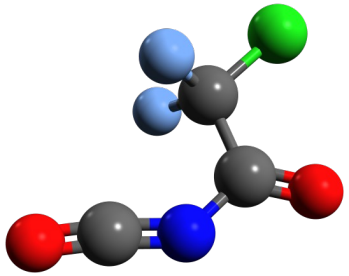


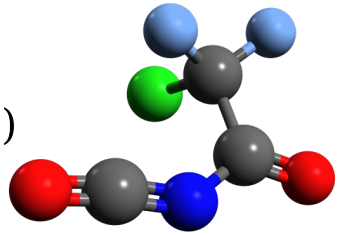
Method	*X* (gauche), %
QC	85-95
IR	88
GED	90(5)

[1] L. A. Ramos, S. E. Ulic, R. M. Romano, S. Tong, M. Ge, Yu. V. Vishnevskiy, R. J. Berger, N. W. Mitzel, H. Beckers, H. Willner, C. O. Della Védova, *Inorg. Chem.*, 50 (2011) 9650.

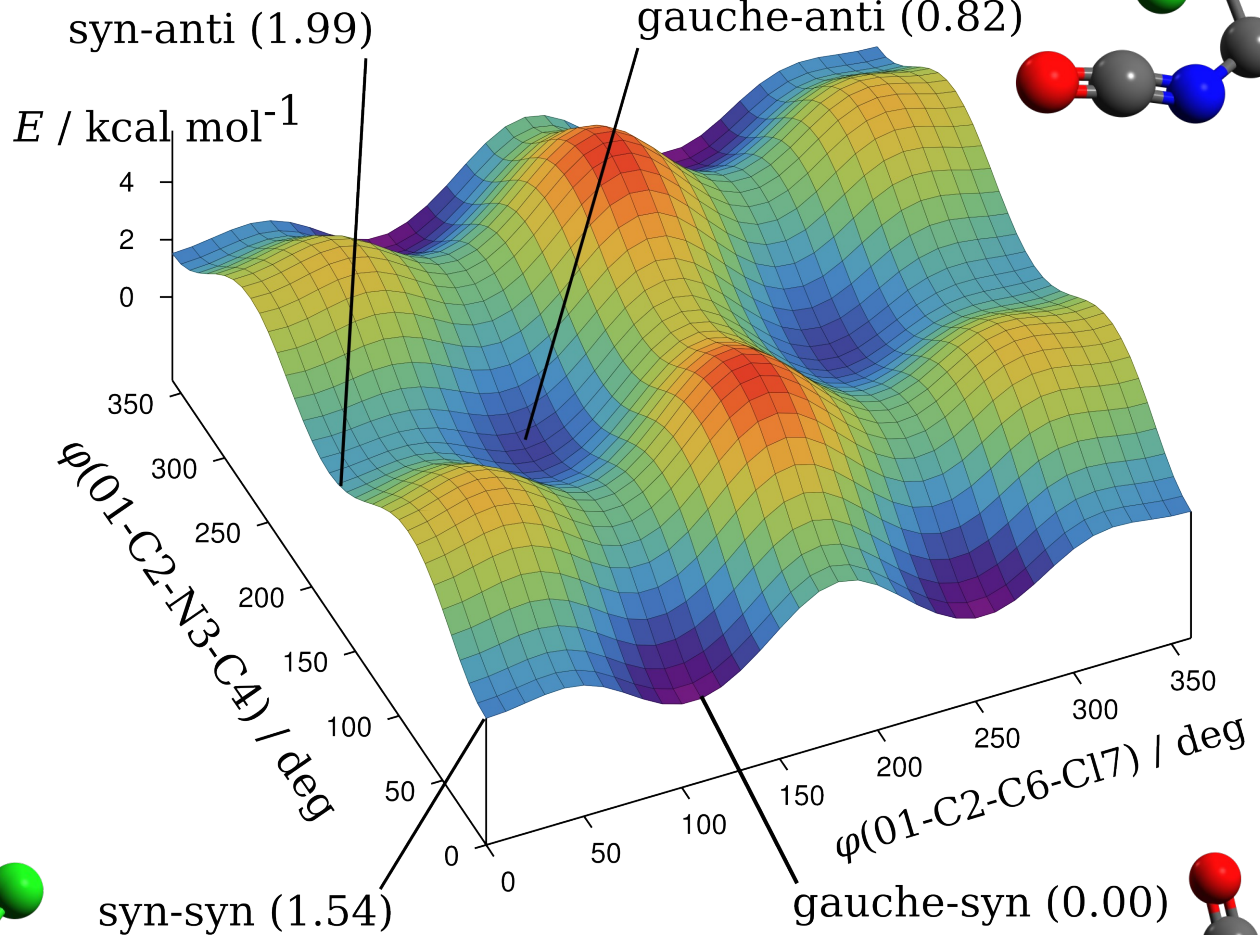
Universität Bielefeld

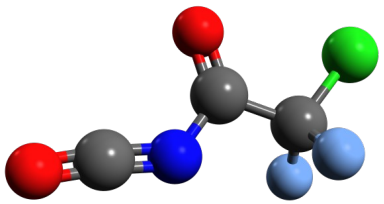
ClF_2C-C(O)-NCO

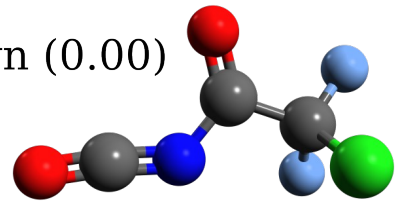




GED: 28(7)%
QC: 19-46%





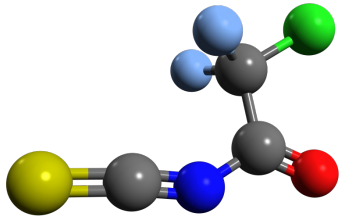


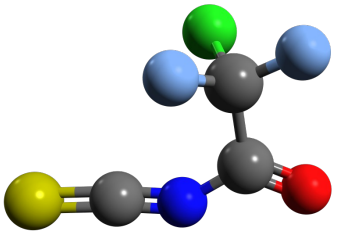
GED: 72(7)%
QC: 54-81%

[1] L. A. Ramos, S. E. Ulic, R. M. Romano, Yu. V. Vishnevskiy, R. J. F. Berger, N. W. Mitzel, H. Beckers, H. Willner, S. Tong, M. Ge, C. O. Della Védova, *J. Phys. Chem. A*, 116 (2012) 11586.

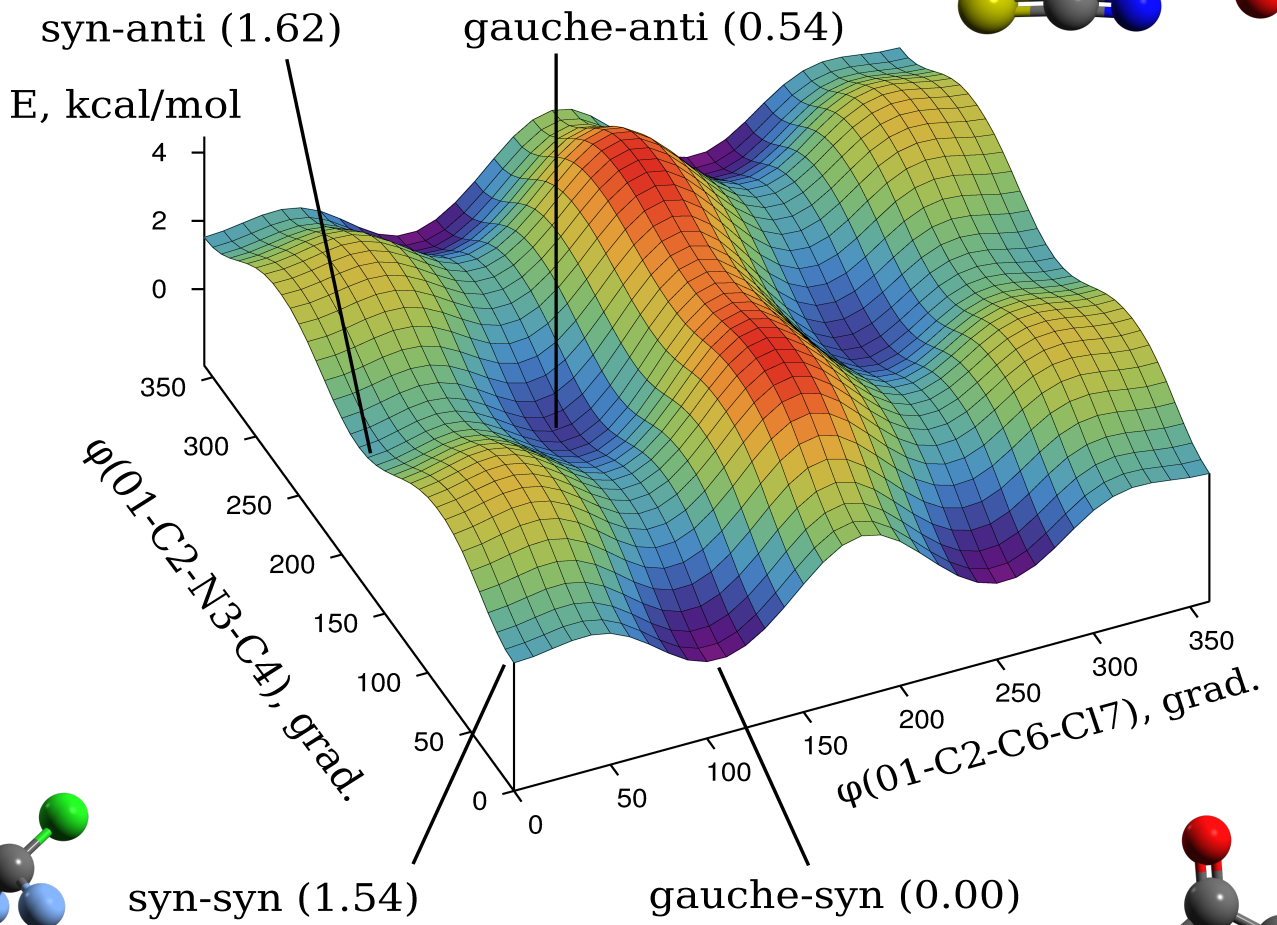
Universität Bielefeld

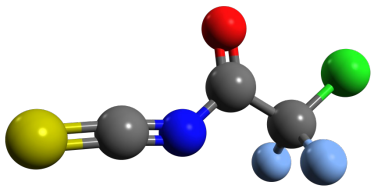
ClF_2C-C(O)-NCS

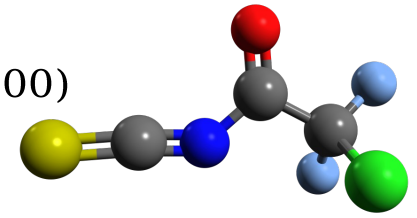




GED: 58(10)%
QC: 25-71%





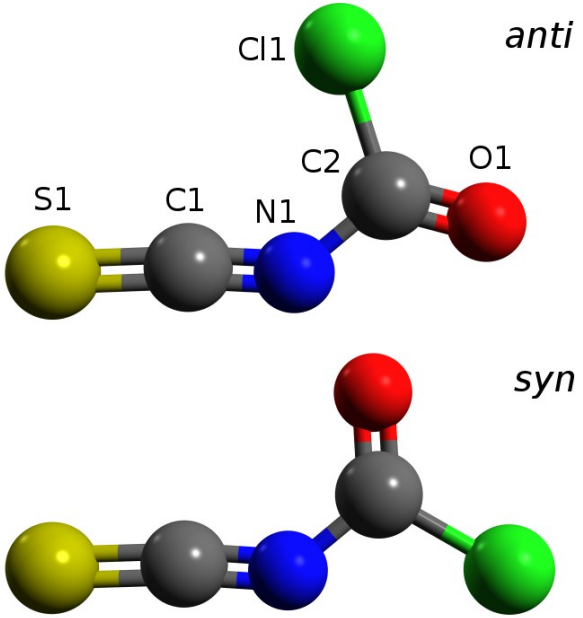


GED: 42(10)%
QC: 29-75%

X-C(O)-R

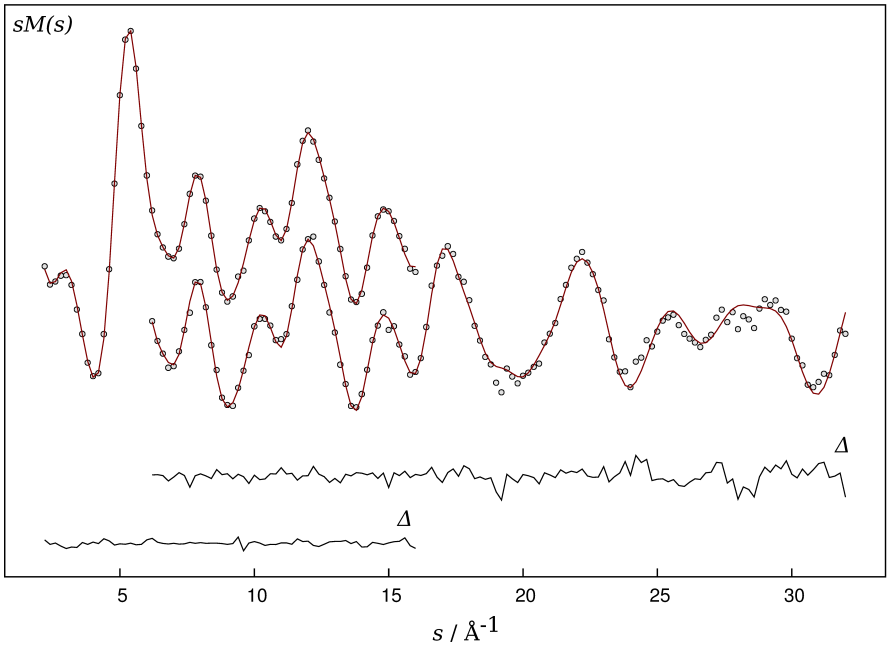
X=F, Cl; R=SCN, NCS

F-, Cl-C(O)-R (R=SCN, NCS)



84(6) %

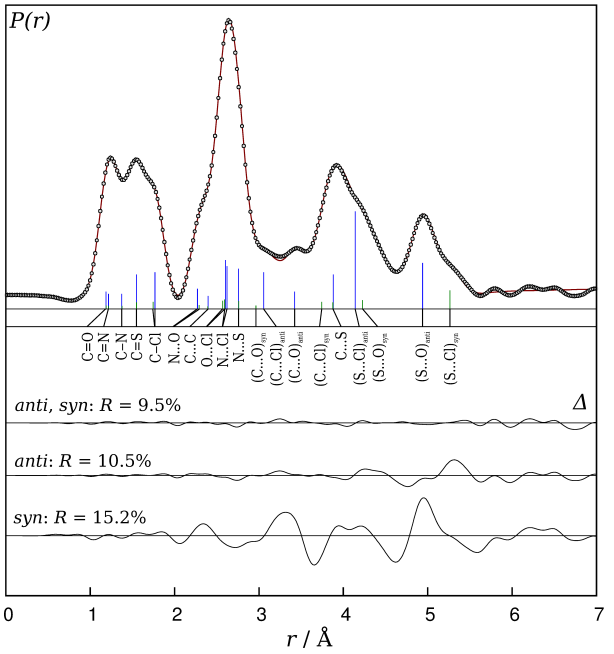
16(6) %



Cl-C(O)-NCS: **in press.**

Cl-C(O)-SCN: **failed.**

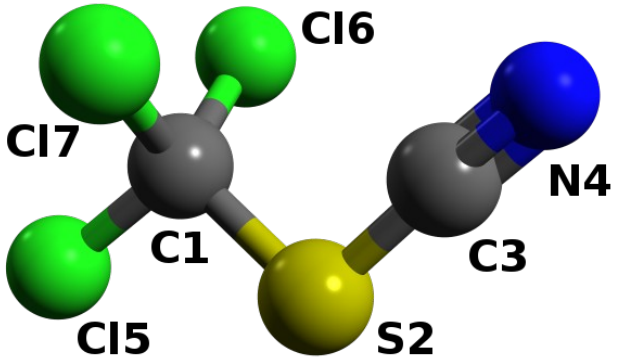
F-C(O)-SCN, -NCS: **to be measured.**

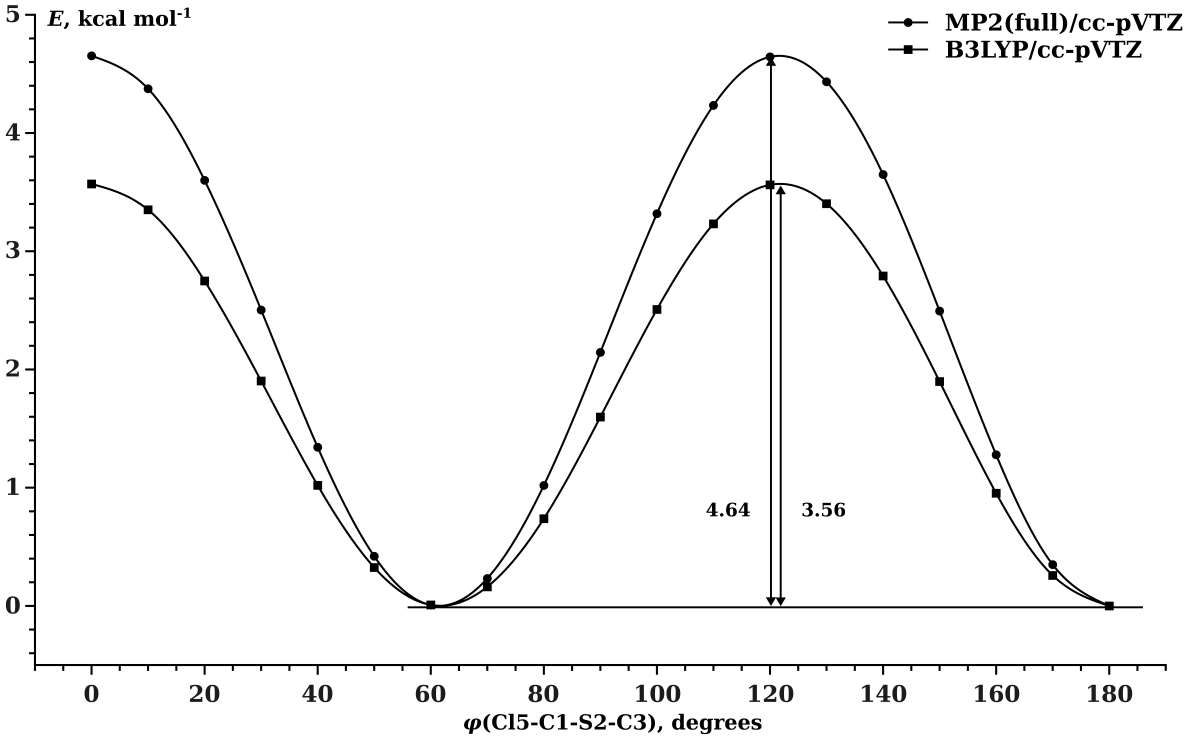


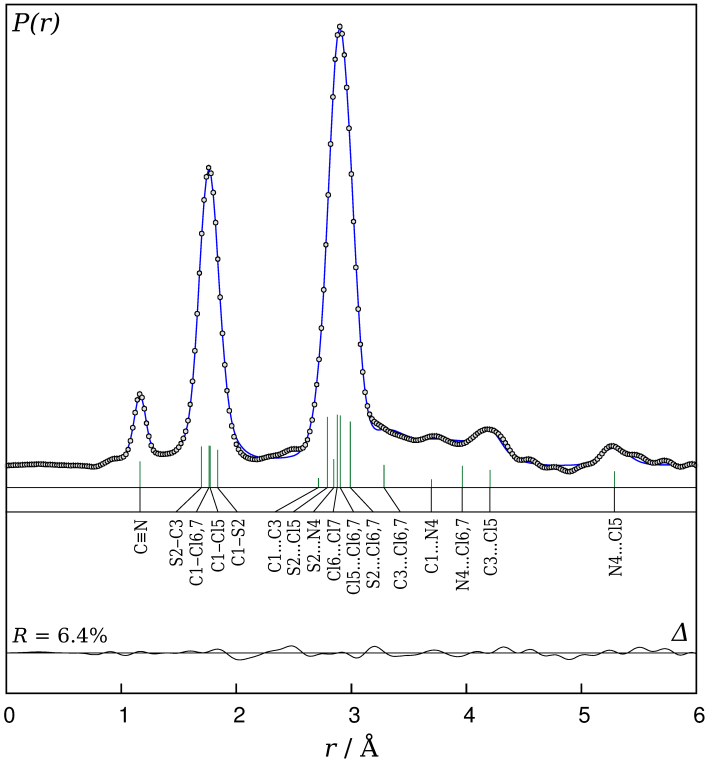
R-SCN

R=CCl_3, CCl_2F, CH_2Cl

CCl_3-SCN

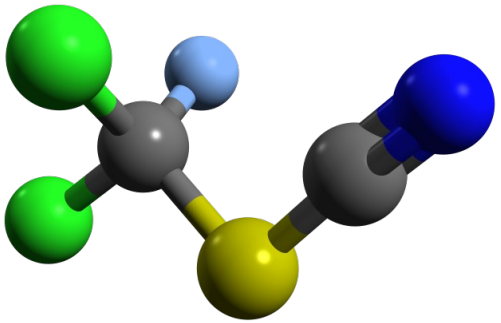

Cl6
Cl7
N4
C1
C3
Cl5
S2


E, kcal mol-1
MP2(full)/cc-pVTZ
B3LYP/cc-pVTZ
4.64
3.56
φ(Cl5-C1-S2-C3), degrees


P(r)
C≡N
S2–C3
C1–Cl6,7
C1–Cl5
C1–S2
C1...C3
S2...Cl5
S2...N4
Cl6...Cl7
Cl5...Cl6,7
S2...Cl6,7
C3...Cl6,7
C1...N4
N4...Cl6,7
C3...Cl5
N4...Cl5
R = 6.4%
Δ
r / Å

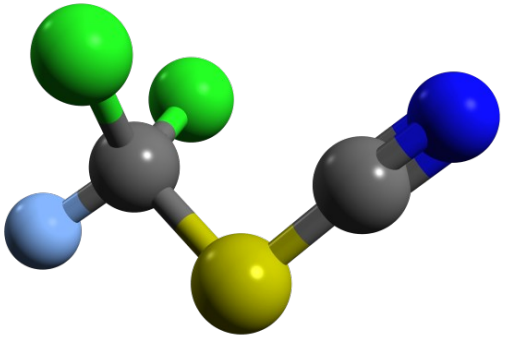
Universität Bielefeld

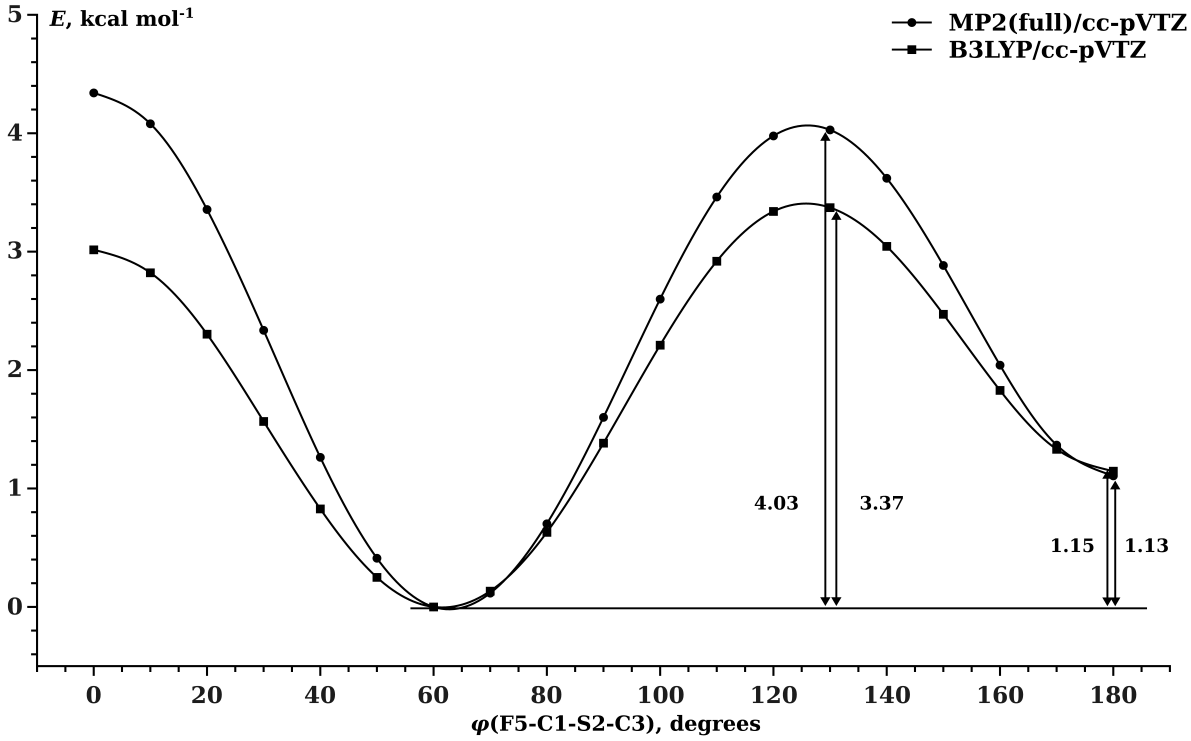
CCl_2F-SCN

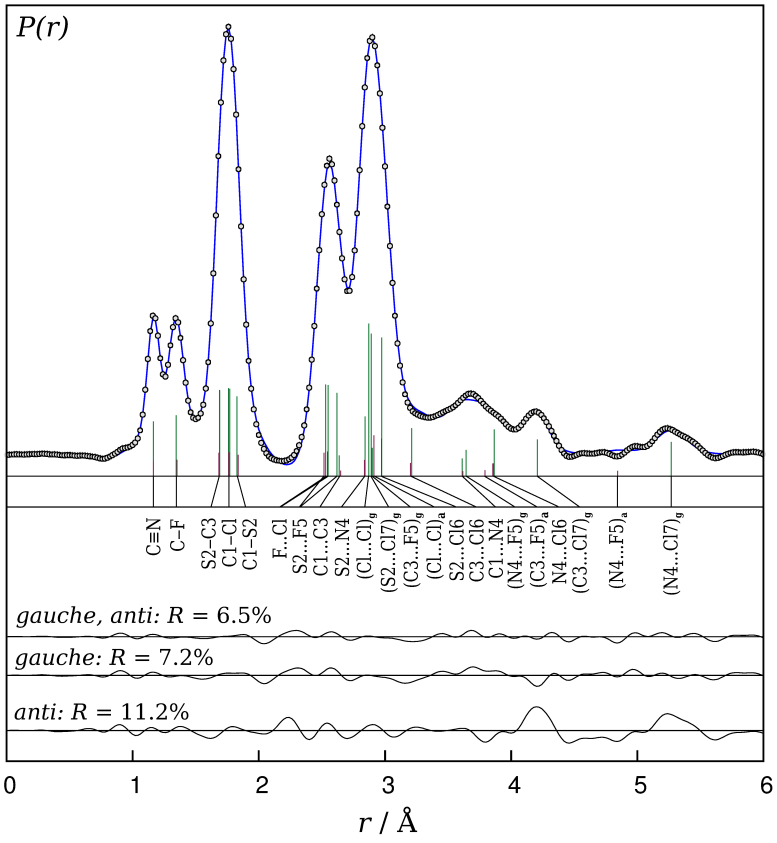


GED: 79(11)%
QC: 93%

GED: 21(11)%
QC: 7%

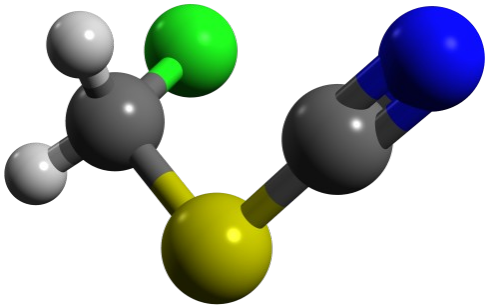






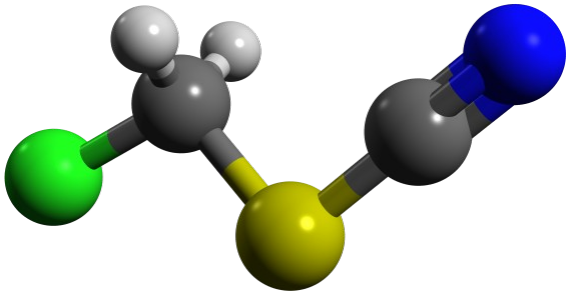
Universität Bielefeld

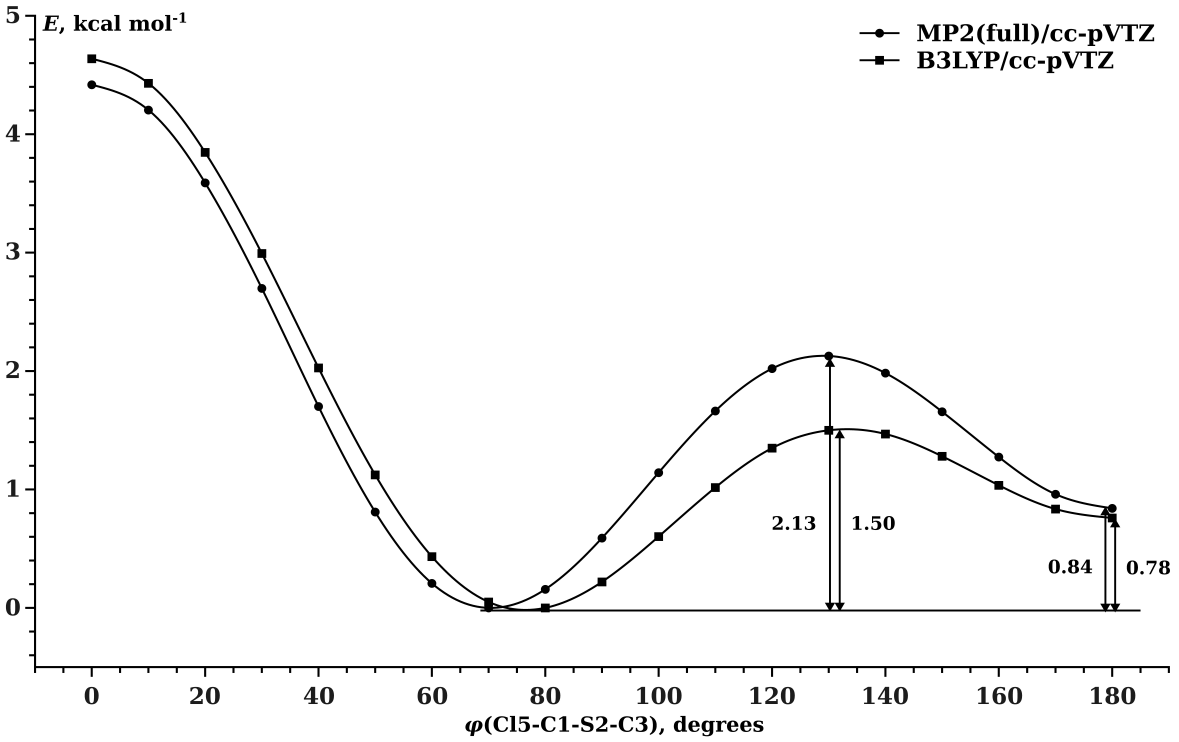
CH_2Cl-SCN

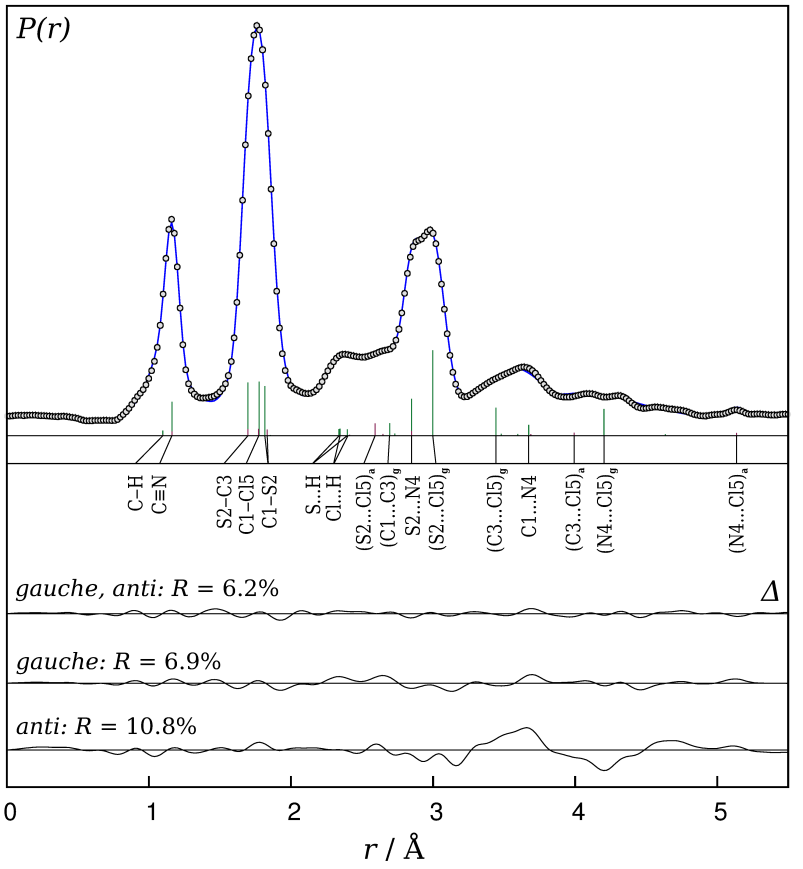


GED: 89(3)%
QC: 82-85%

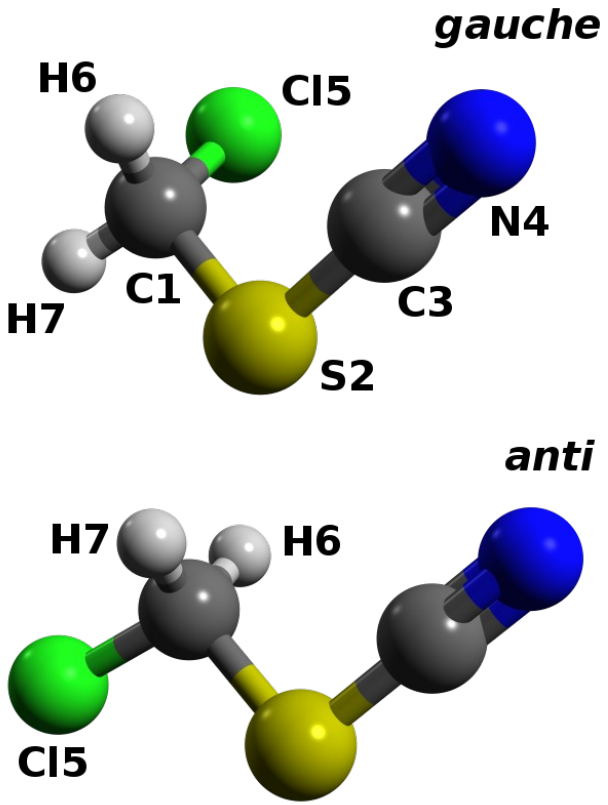
GED: 11(3)%
QC: 15-18%

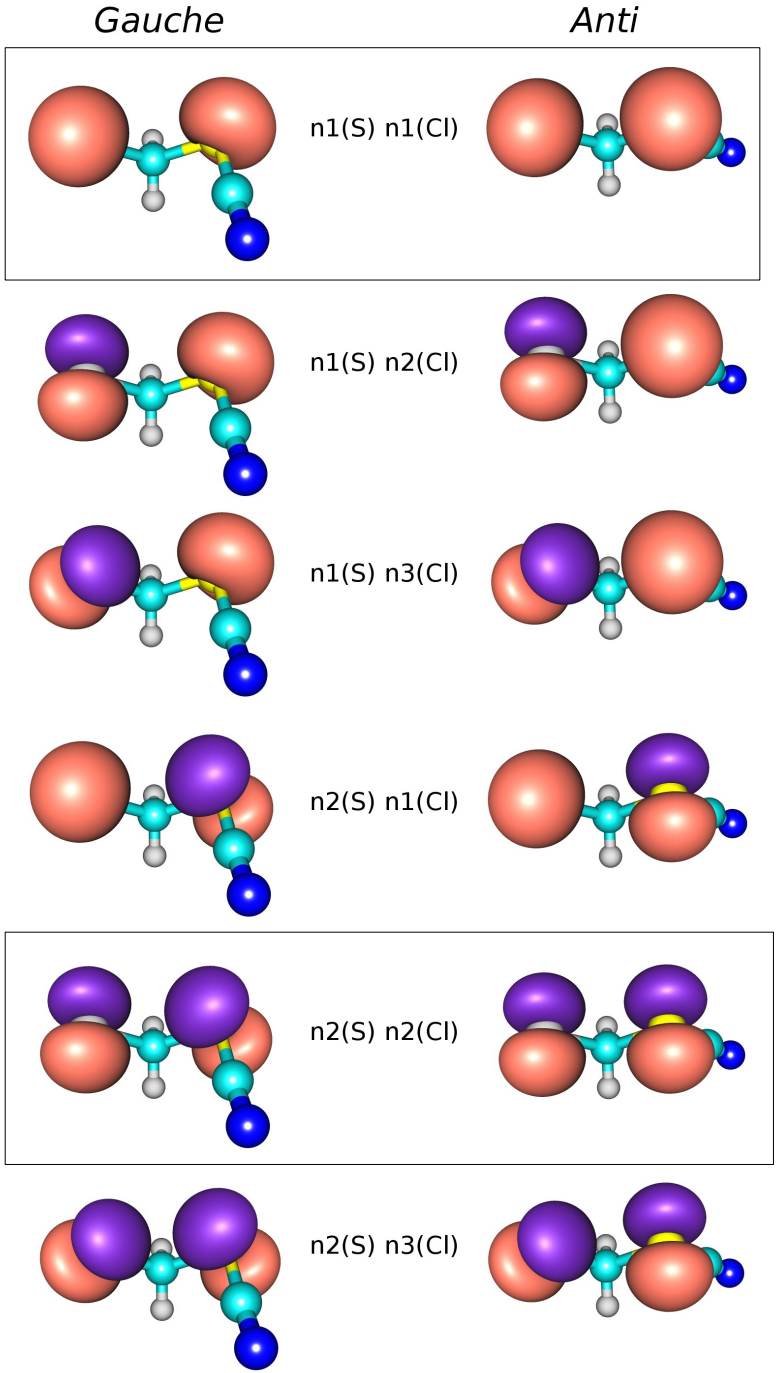






CH_2Cl-SCN





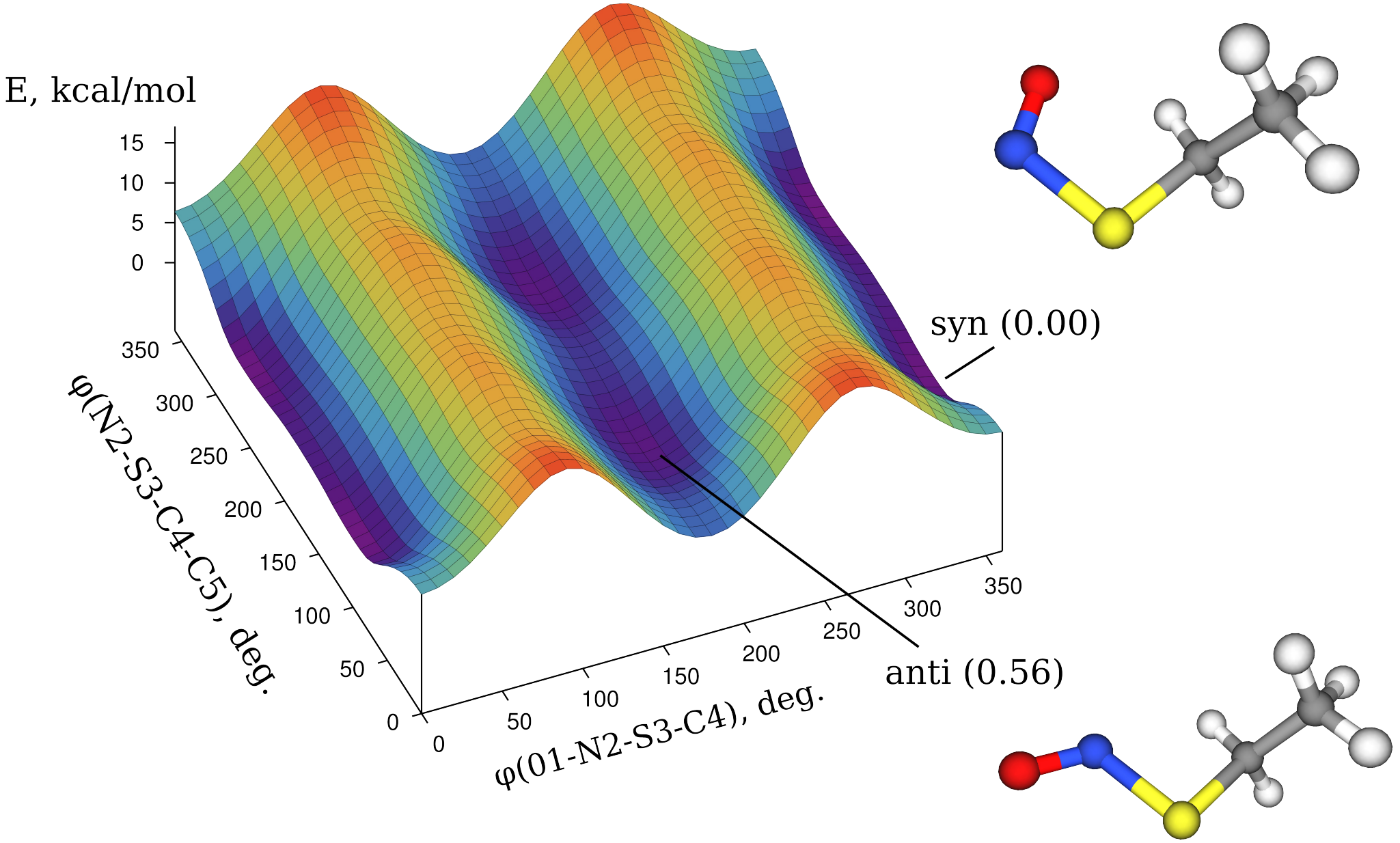
Gauche	vs. Anti
XRD	vs. GED
Electronic	vs. Steric Effects

R-SNO

R=CH_3-CH_2, CF_3-CH_2, $(CH_3)_3C$

Universität Bielefeld

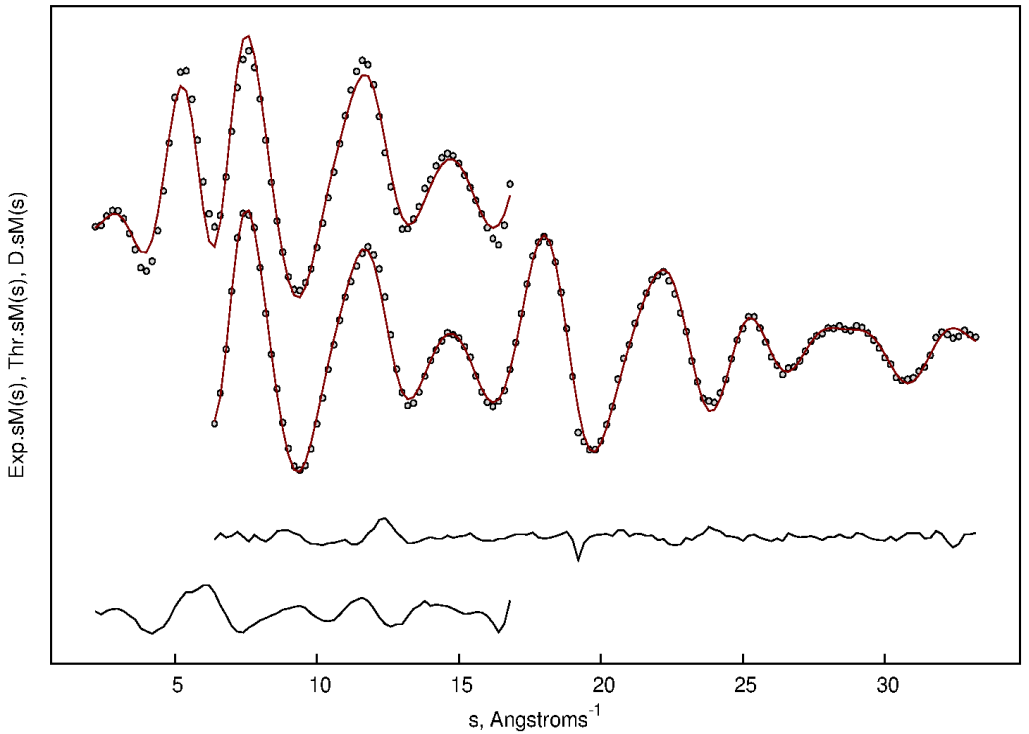
CH_3-CH_2-SNO

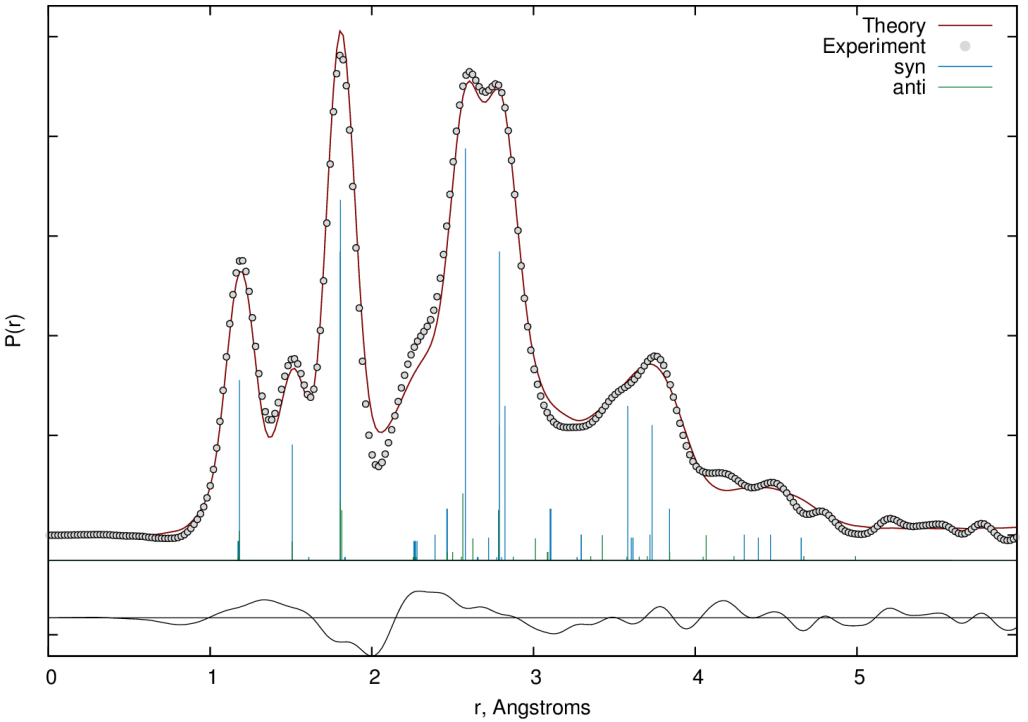


B3LYP/cc-pVTZ; CCSD(T)/cc-pVTZ

Universität Bielefeld

CH_3-CH_2-SNO



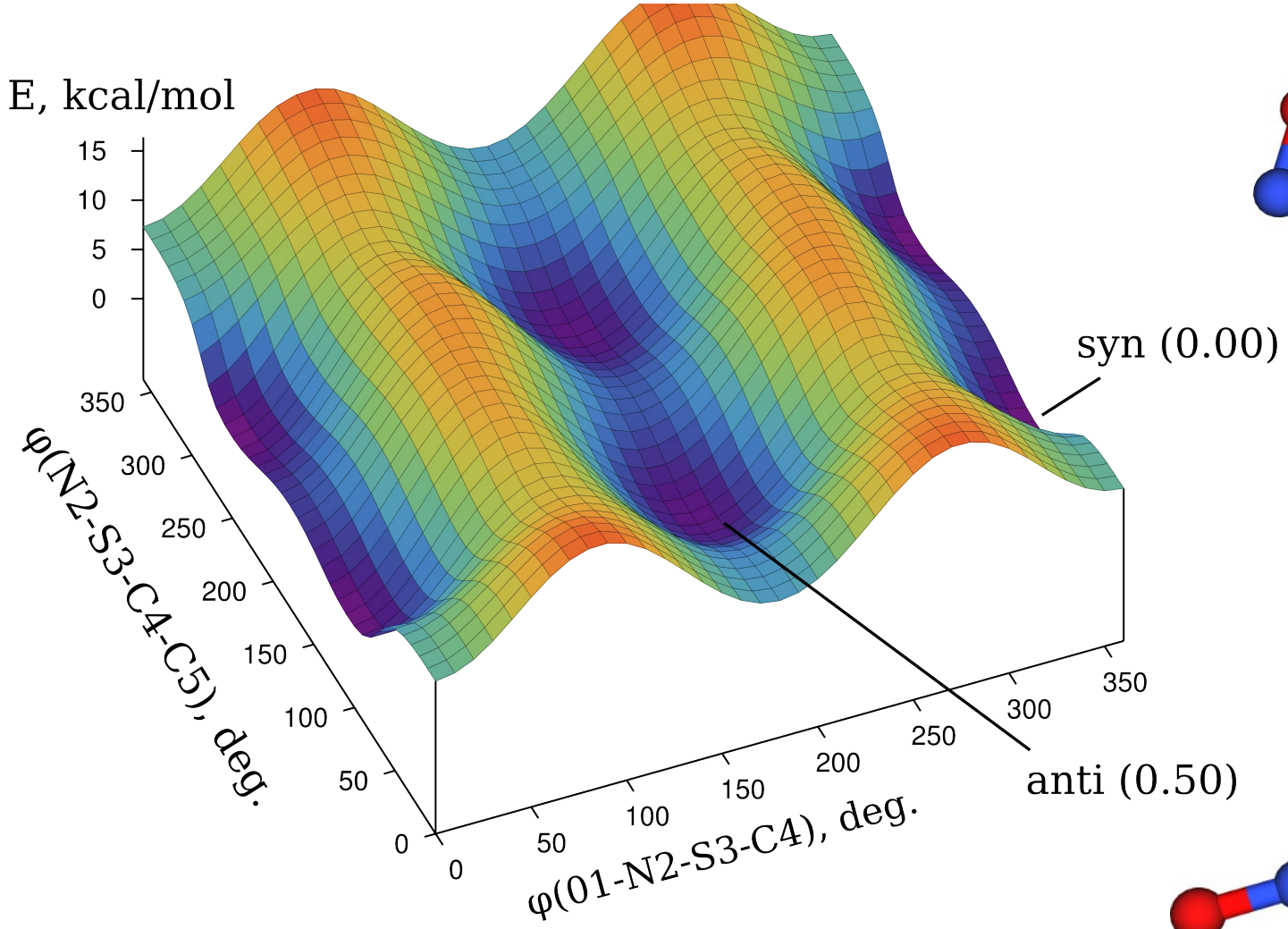


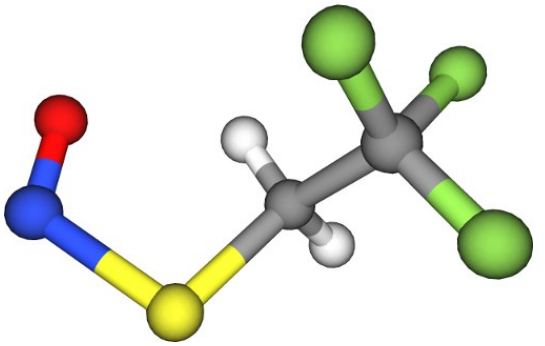
There are problems because of decomposition of substance.

in progress

Universität Bielefeld

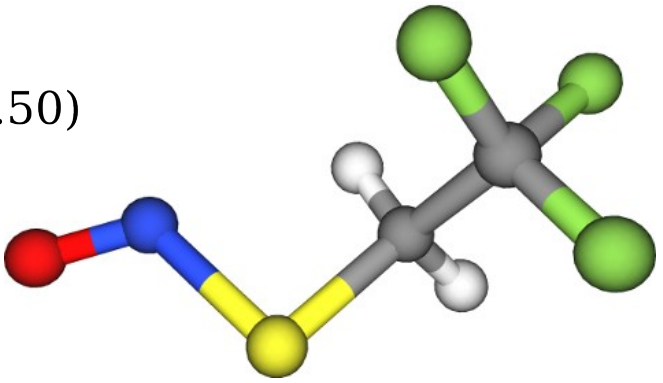
CF_3-CH_2-SNO





syn (0.00)

anti (0.50)

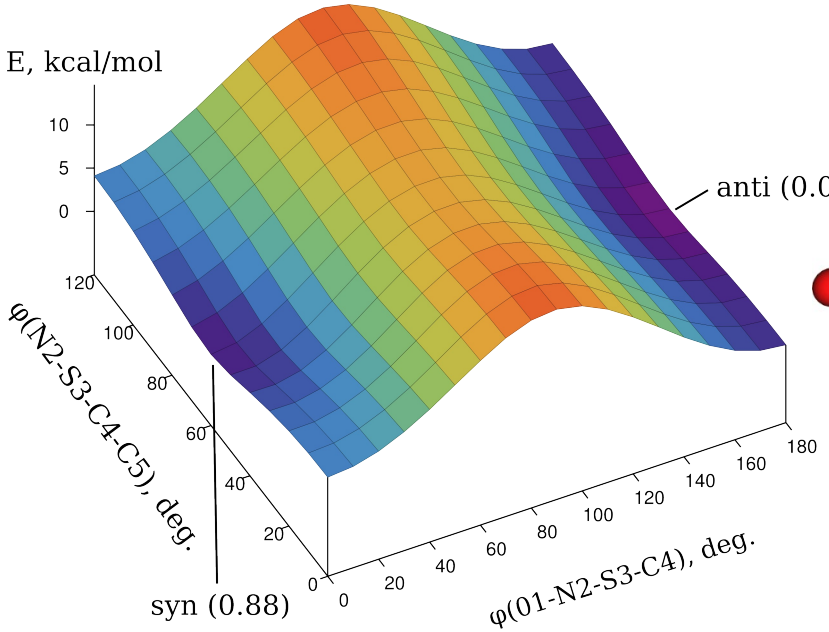


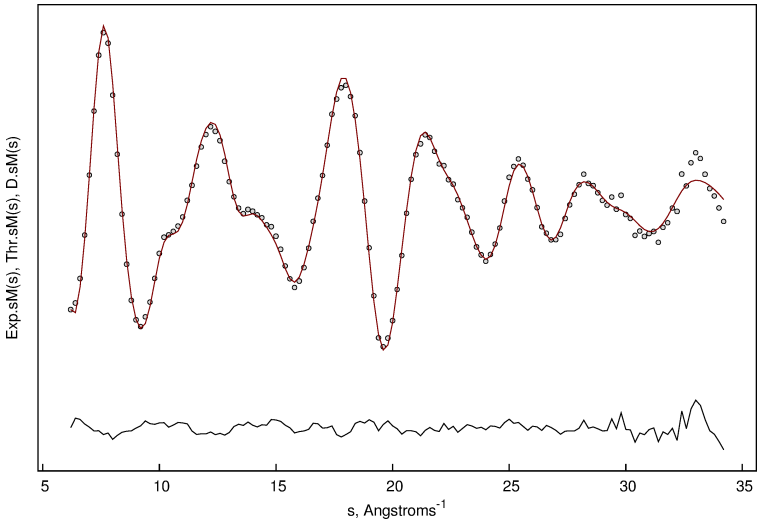
B3LYP/cc-pVTZ; CCSD(T)/cc-pVTZ

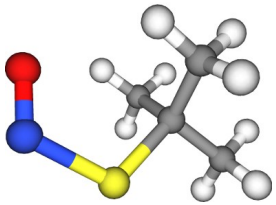
Substance decomposes during measurements.

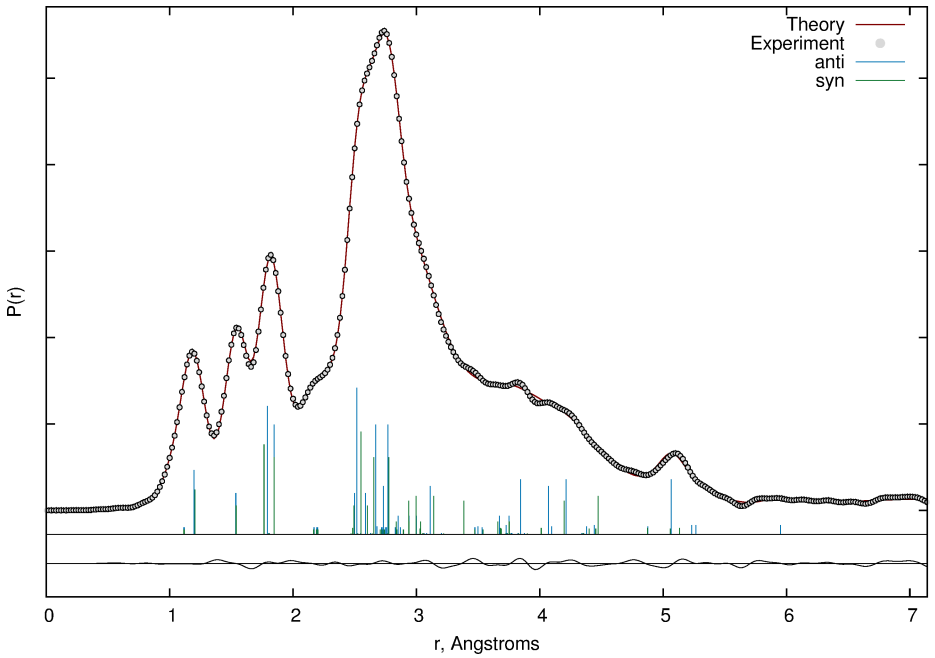
Universität Bielefeld

$(CH_3)_3C\text{-}SNO$









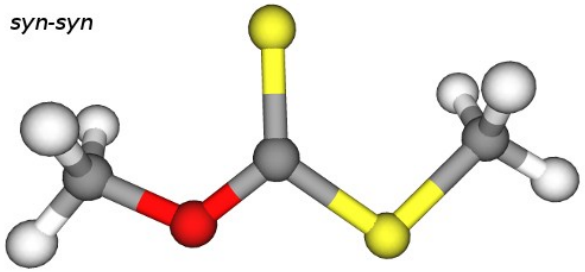
Preliminary results

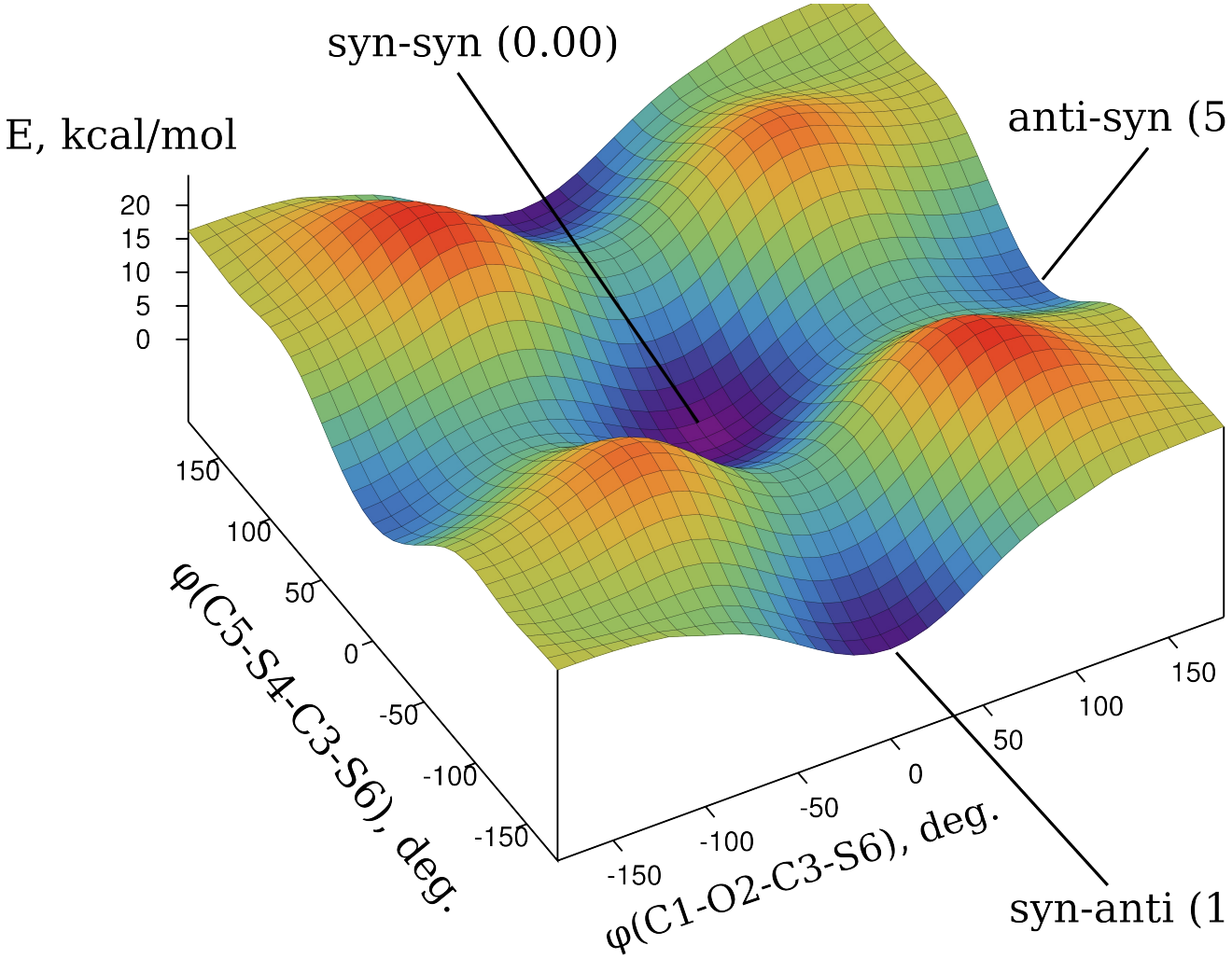
	Anti	**Syn**
GED	59(20) %	41(20) %
QC	81-88 %	12-19 %

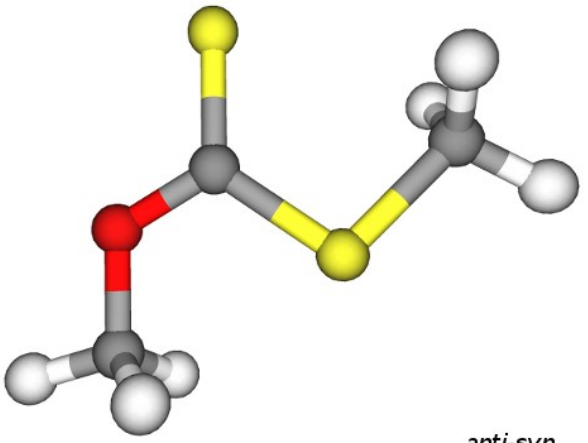
Substance decomposes during measurements.

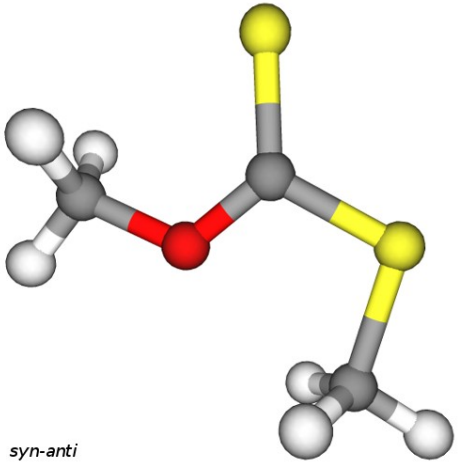

H3CO-C(S)-SCH3

$H_3CO\text{-}C(S)\text{-}SCH_3$

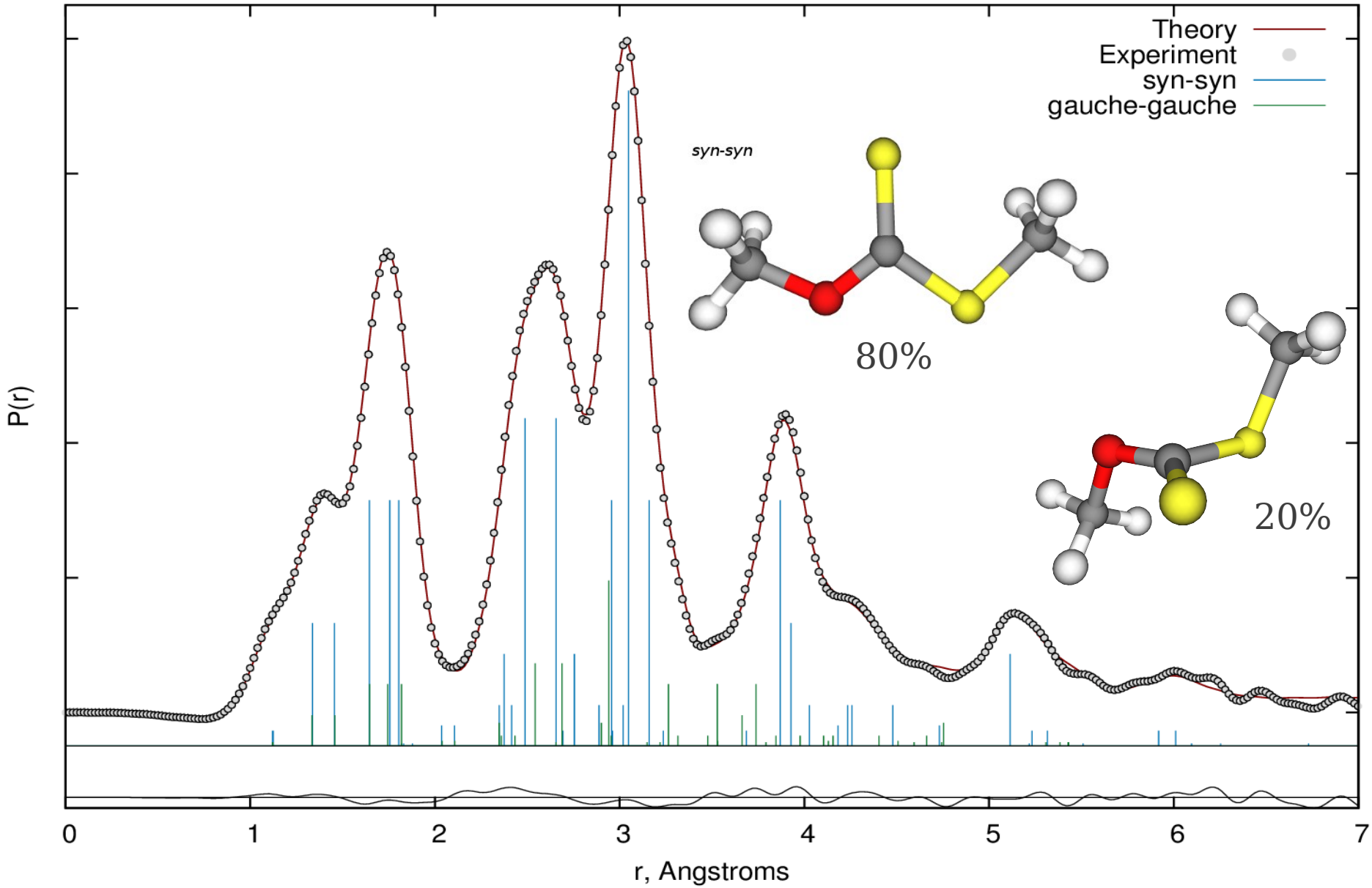








$H_3CO\text{-}C(S)\text{-}SCH_3$



in progress

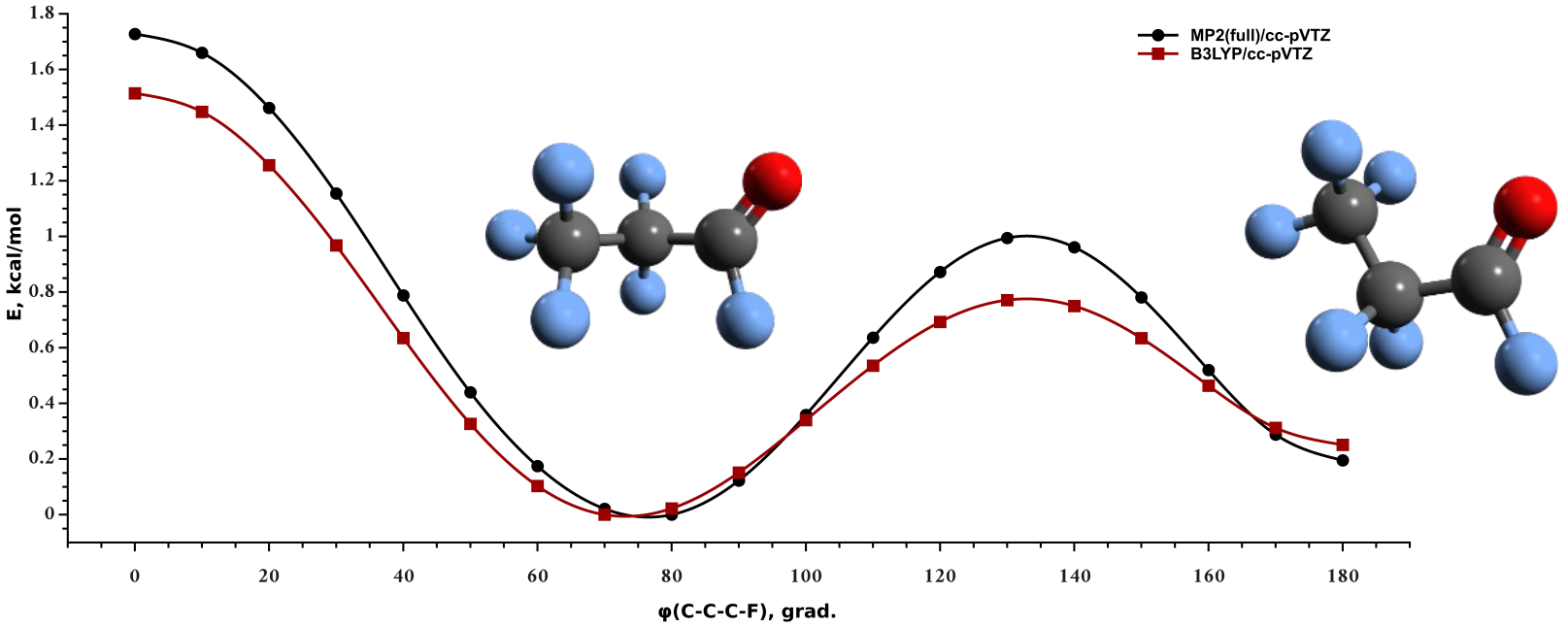
Additional <u>non-planar</u> conformer in gas phase?

$$CF_3\text{-}CF_2\text{-}C(O)\text{-}X$$

$$X=F,\ Cl,\ I,\ O\text{-}C(O)\text{-}CF_2\text{-}CF_3$$

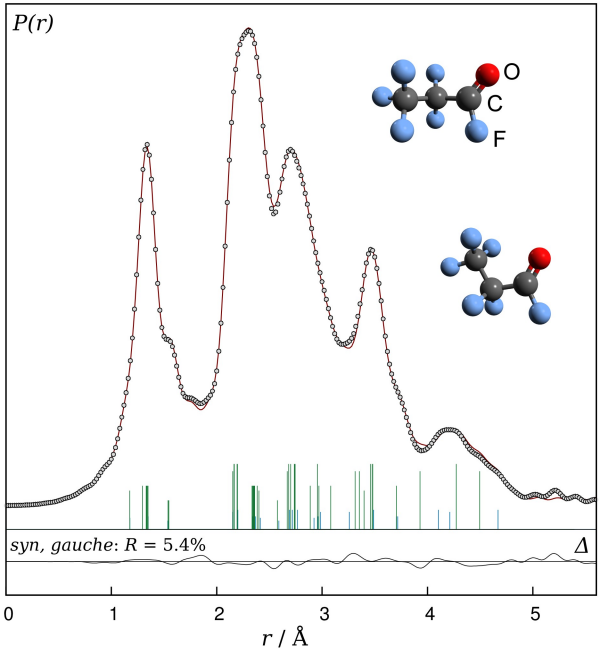
Universität Bielefeld

CF_3CF_2-C(O)-F



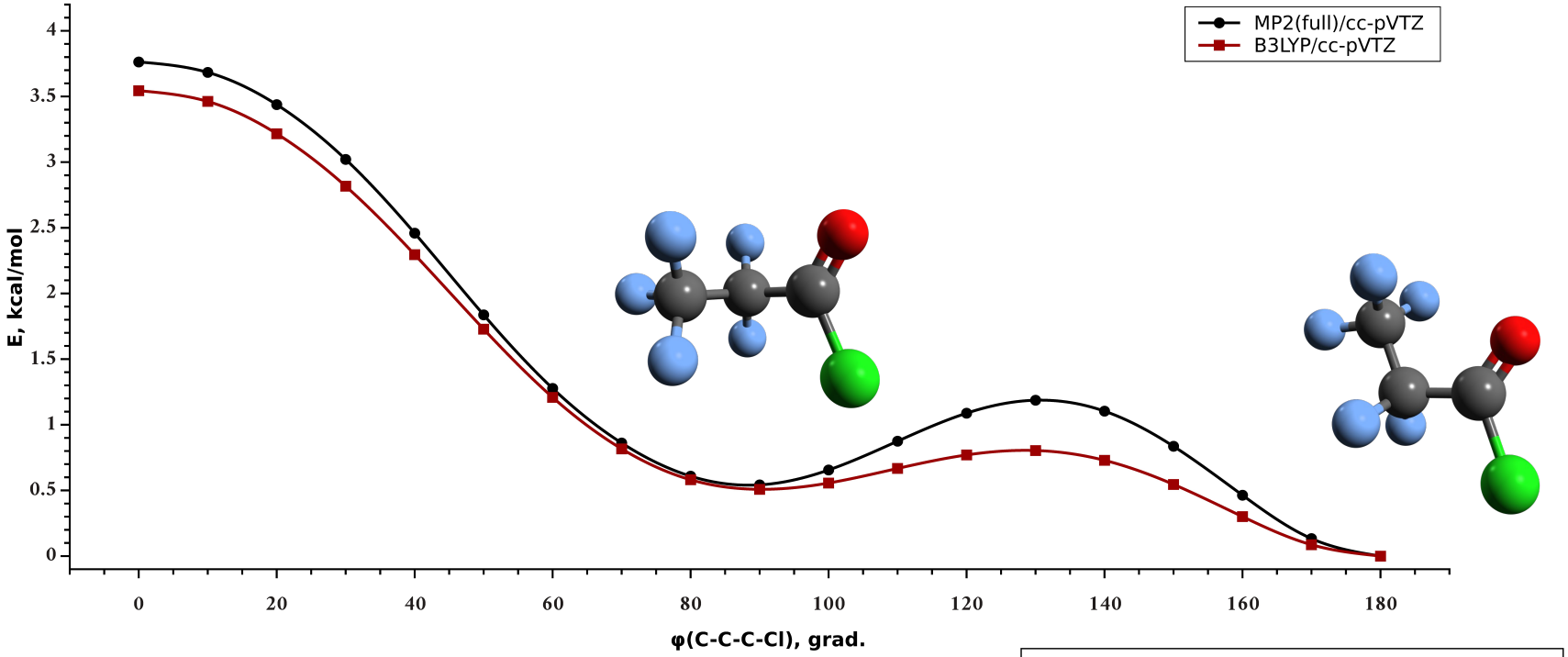
Conformational composition, %:

	Gauche	Syn
GED	77(14)	23(14)
QC	83	17



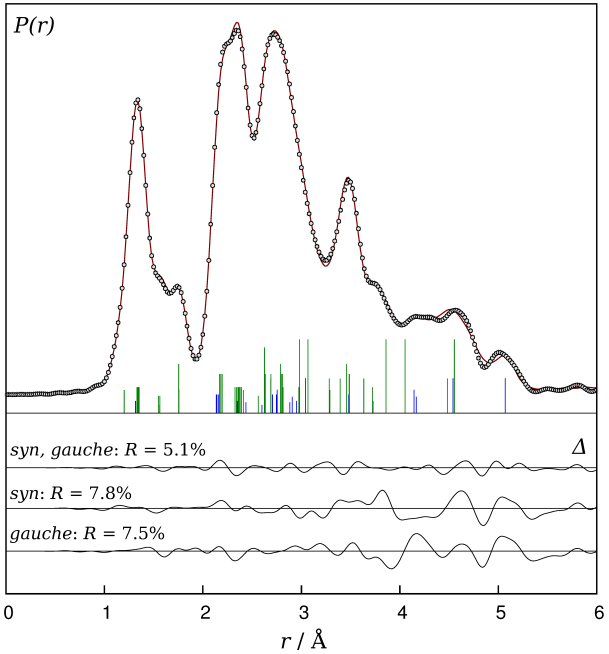
Universität Bielefeld

CF_3CF_2-C(O)-Cl

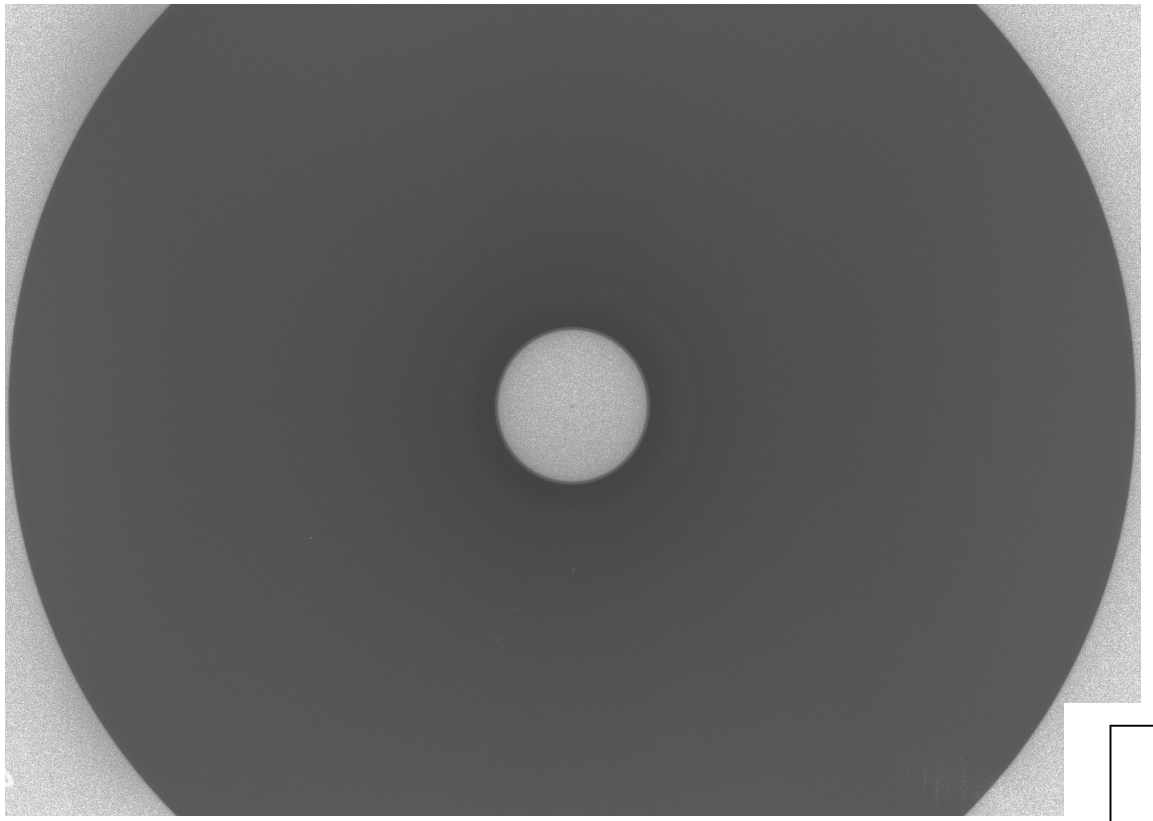


Conformational composition, %:

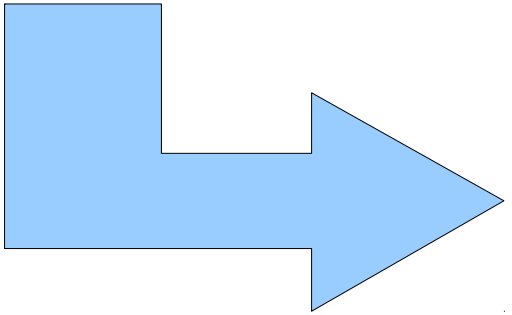
	Gauche	Syn
GED	68(6)	32(6)
QC	57-60	40-43

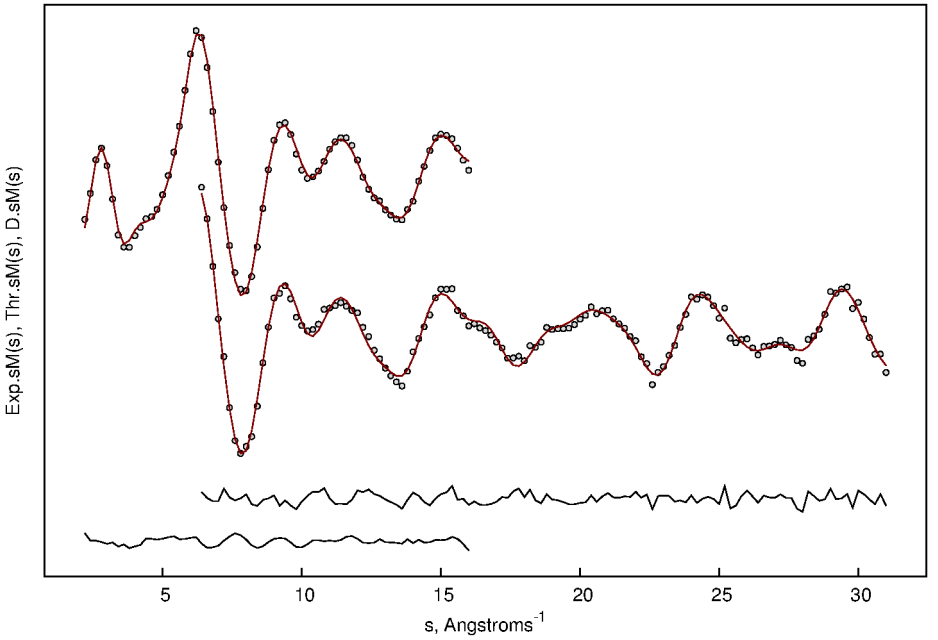


CF_3CF_2-C(O)-I



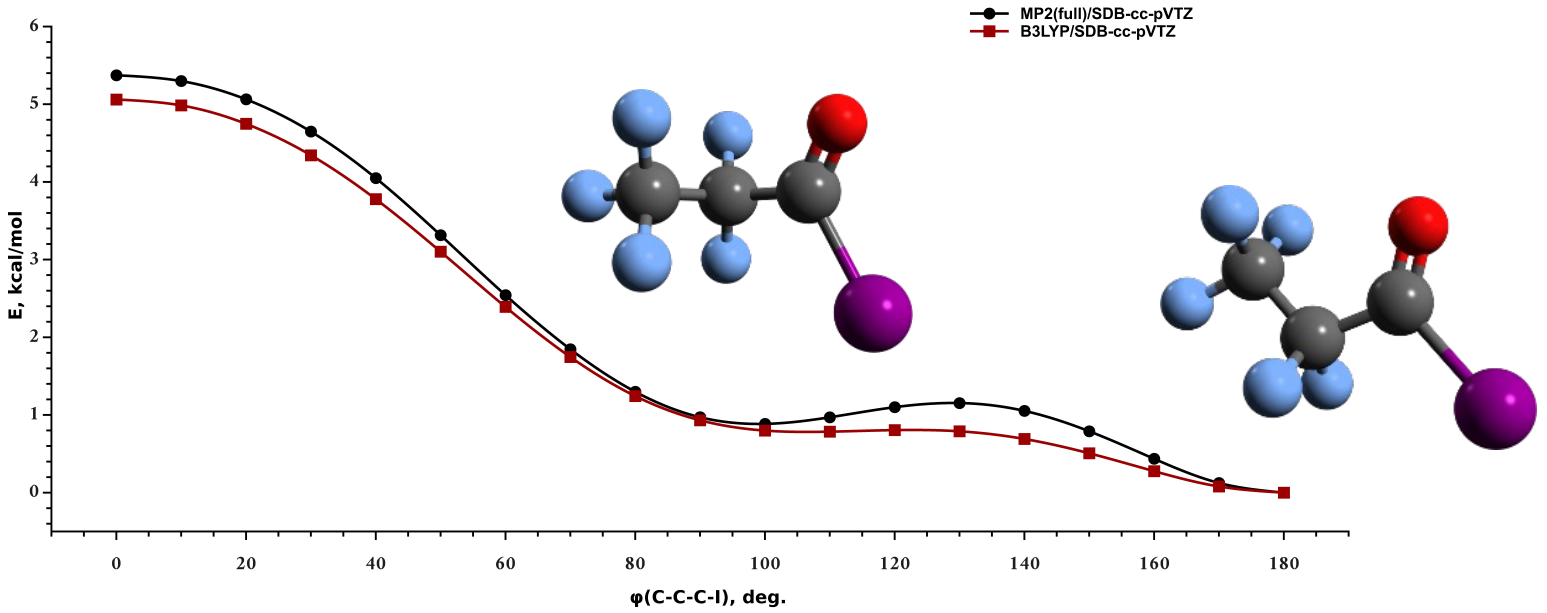
Very weak signal!





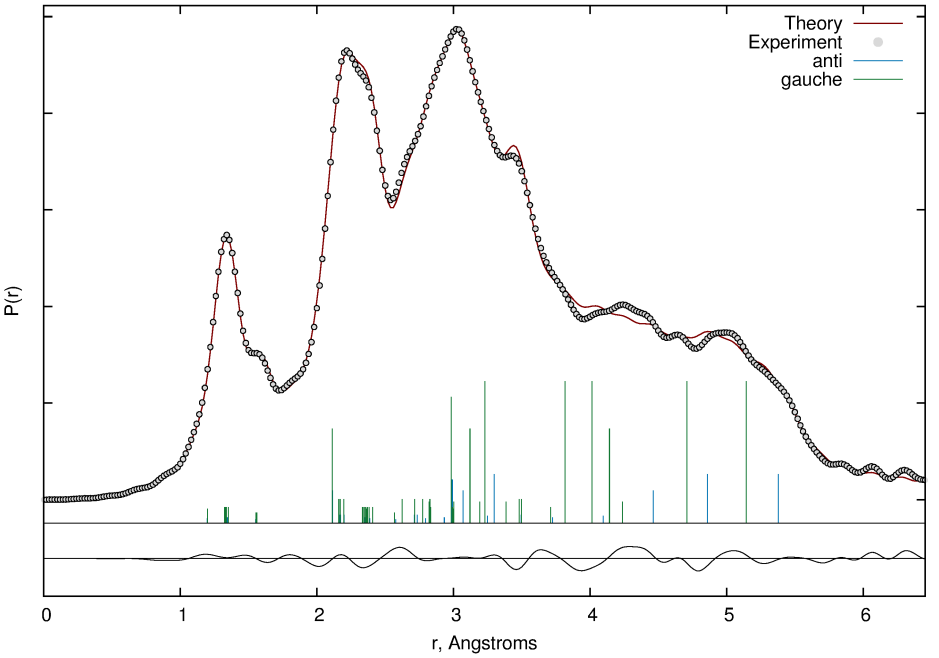
Universität Bielefeld

CF_3CF_2-C(O)-I



Conformational composition, %:

	Gauche	Syn
GED	74(16)	26(16)
QC	53-59	41-47



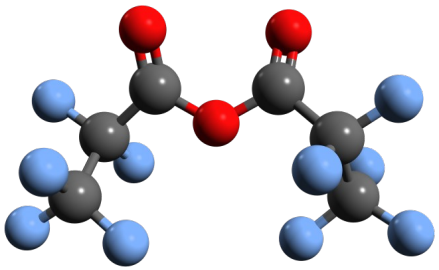
Universität Bielefeld

CF_3-CF_2-C(O)-O-C(O)-CF_2-CF_3

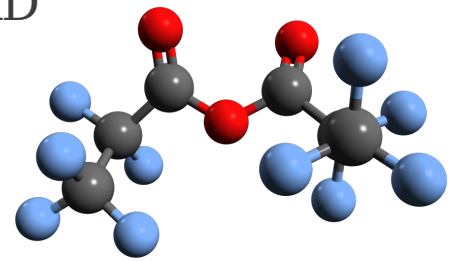
435 conformers generated;
22 unique found after RM1;
8 unique found after B3LYP/6-31+G(d).

Relative energies (kcal/mol), abundance (%), symmetry:

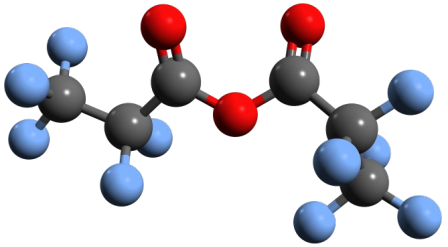
XRD



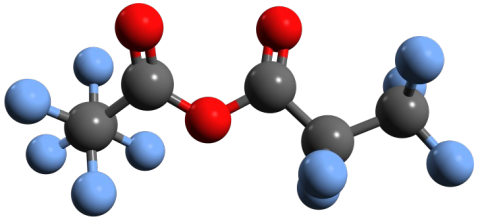
0.00 (18%), C_1



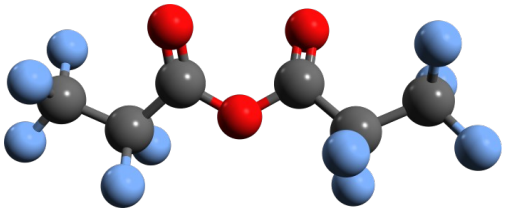
0.05 (16%), C_1



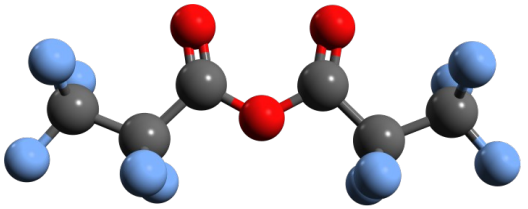
0.14 (27%), C_1



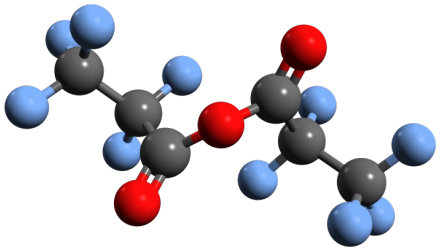
0.18 (26%), C_1



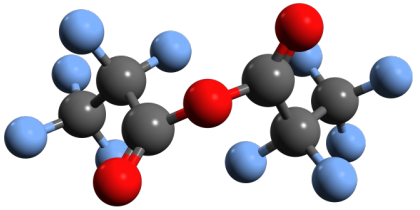
0.29 (10%), C_2



0.71 (2%), C_{2v}



6.28 (0%), C_2



7.27 (0%), C_2

Must be difficult case for GED!

Conclusions

- 18 molecules are involved in the project.
  - 3 published or in press.
  - 4 finished; manuscripts are in preparation.
  - 3 finished; GED part is to be written.
  - 7 in progress.
  - 1 failed.
- All molecules show interesting conformational problems.
- Some of them are difficult objects for GED.
- Close collaboration is important for successful results.

Thank you for attention!