UNIVERSITÄT BIELEFELD

Faculty of Chemistry

Mitzel Group
inorganic & structural chemistry

Investigations on tellurium-nitrogen interactions in the solid state and gas phase

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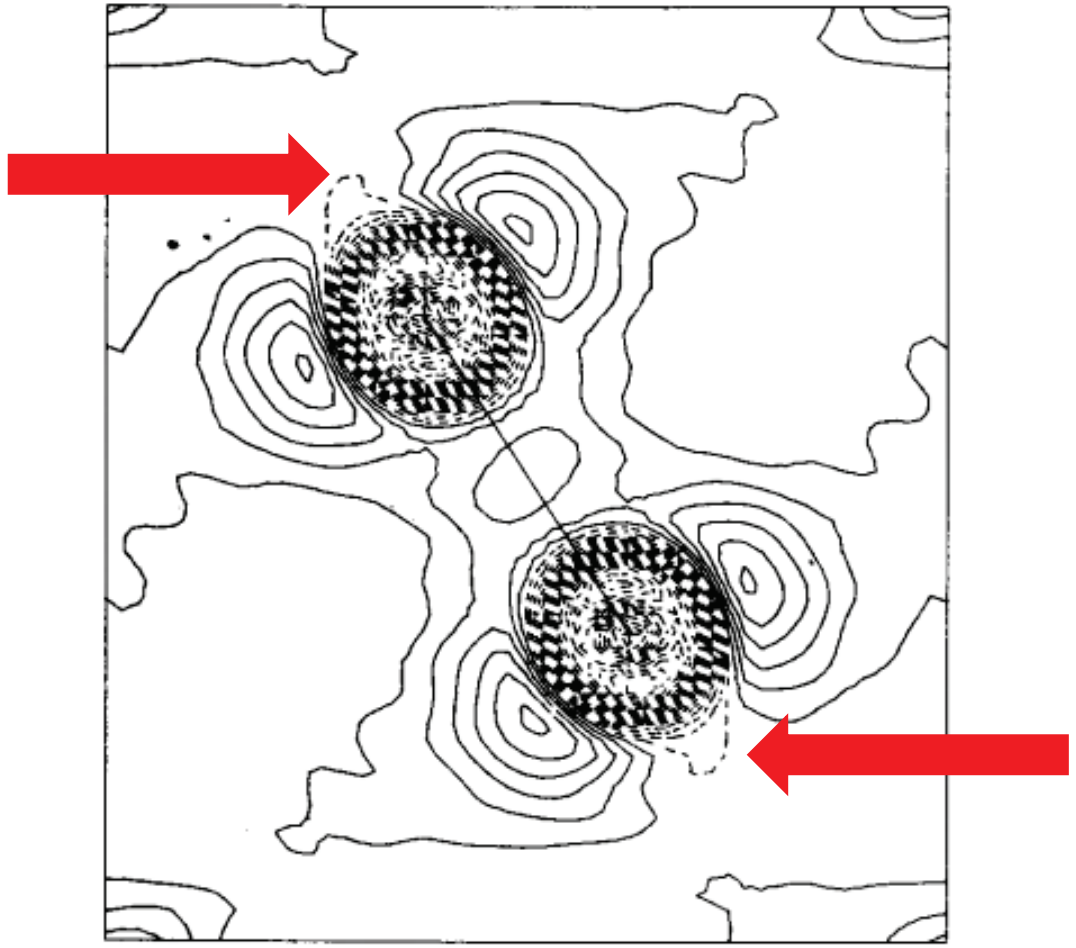
ESGED 18

3rd of July 2019

Kleinwalsertal / AT

Polar flattening

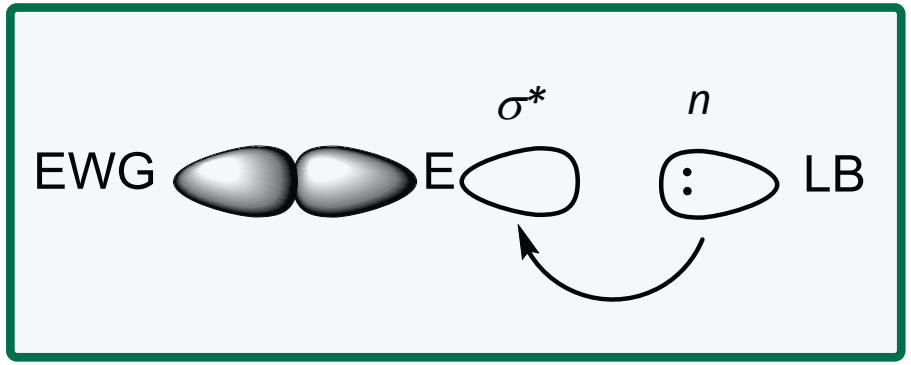
- Cl_2
- 0.03 $eÅ^{-3}$ / 90 K
- „flattening“ of the electron density
  - σ-hole concept

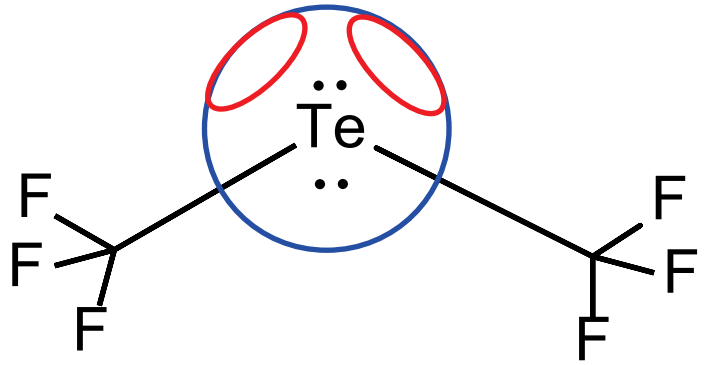


E. D. Stevens, *Molecular Physics* **1979**, *37*, 27-45

Introduction – σ-hole

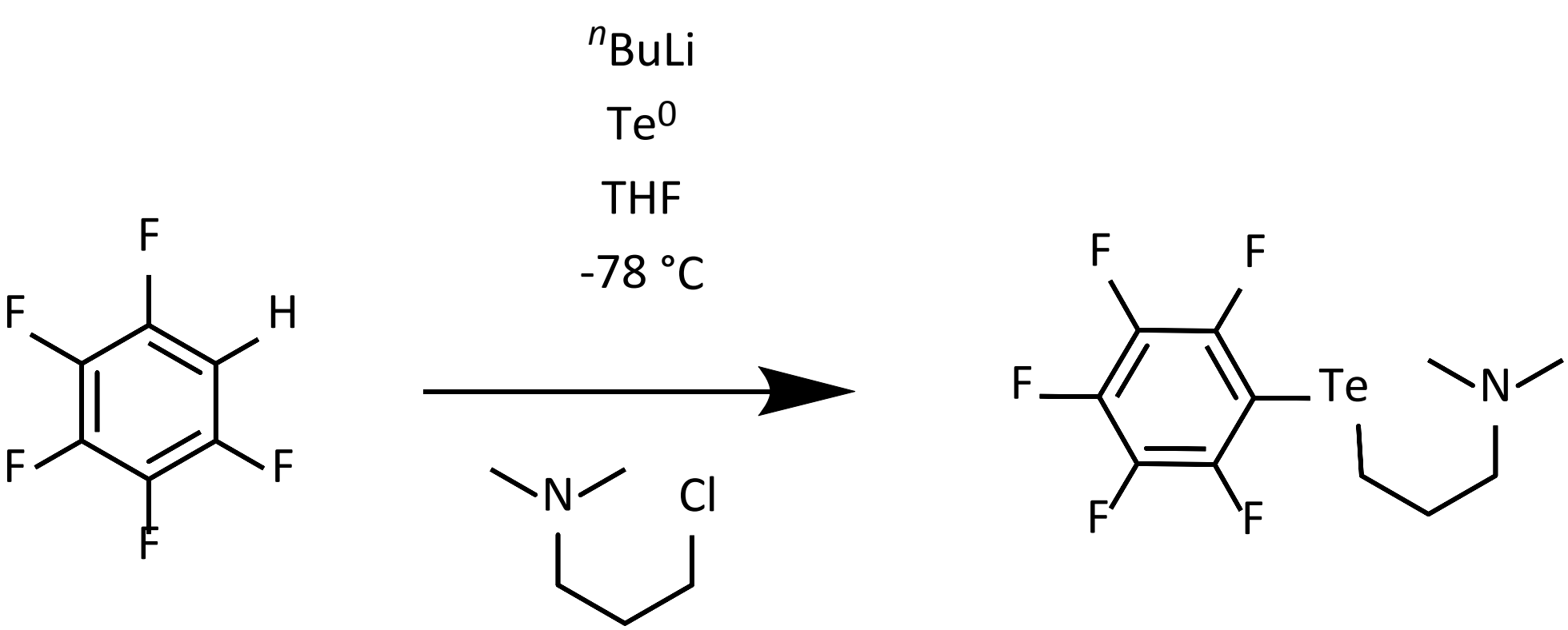
- $V_{s,max}$ = "σ-holes" / Lewis-acidic
- $V_{s,min}$ = "σ-lumps" / Lewis-basic





S. Benz *et al.*, *Angewandte Chemie*, **2018**, *57*, 5408

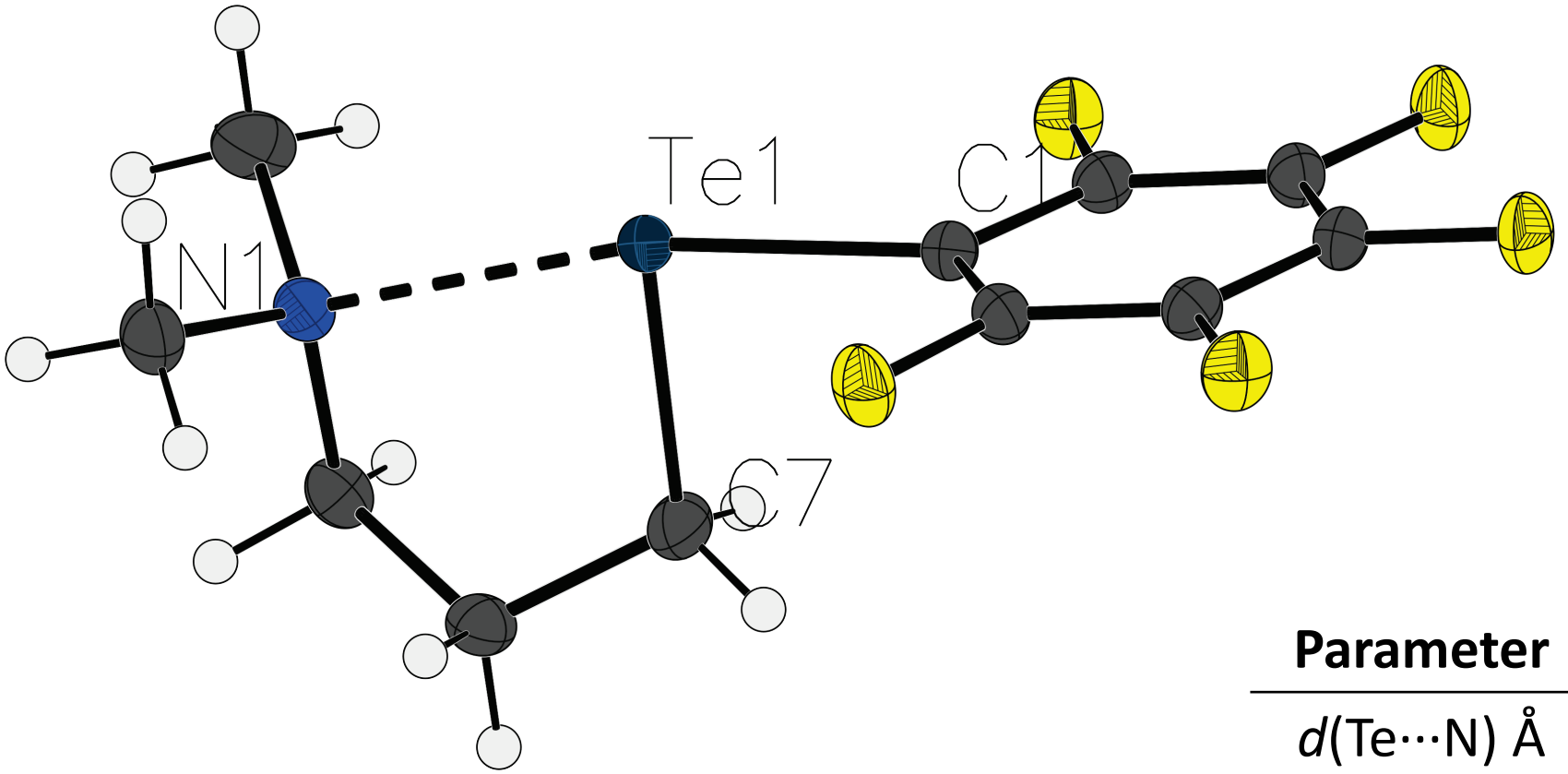
Flexible linker

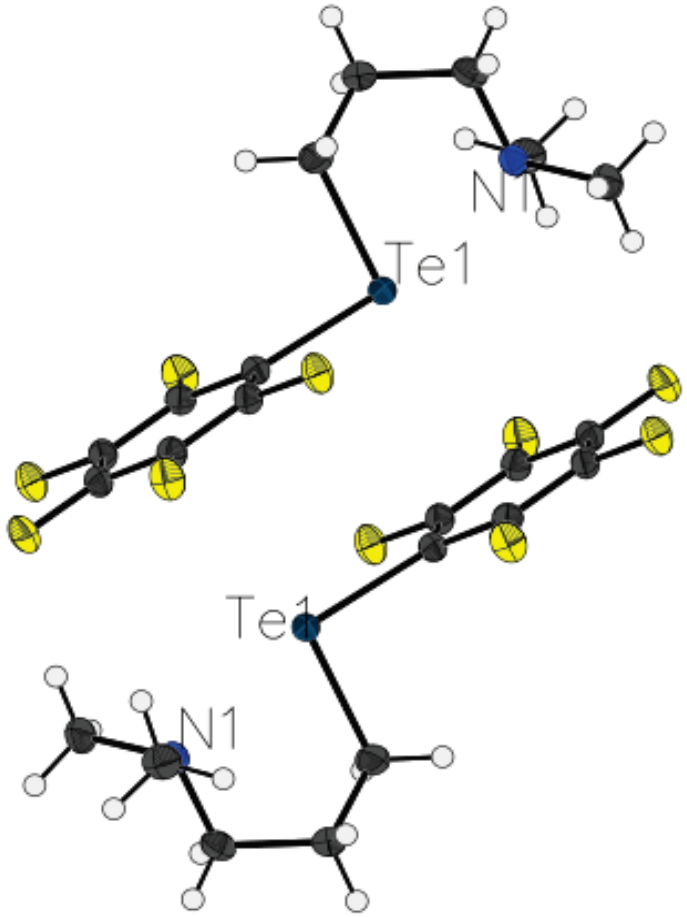


2.5 g / 47 %

^{125}Te-NMR δ / ppm = 353 (t) ($^{3}J_{Te,F}$ = 75 Hz)

Flexible linker

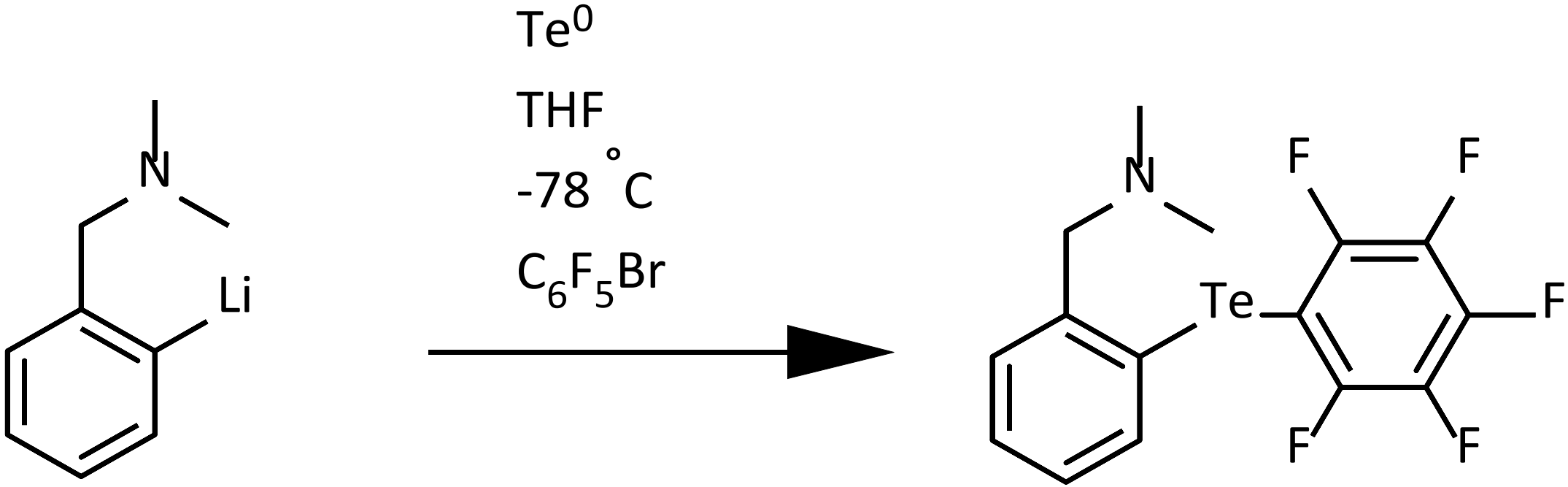




^{125}Te-NMR δ / ppm = 353 (t) ($^{3}J_{Te,F}$ = 75Hz)

Parameter	X-ray
d(Te···N) Å	2.639(1)
α(C-Te-C) °	91.3(1)
α(N···Te-C) °	166.4(1)

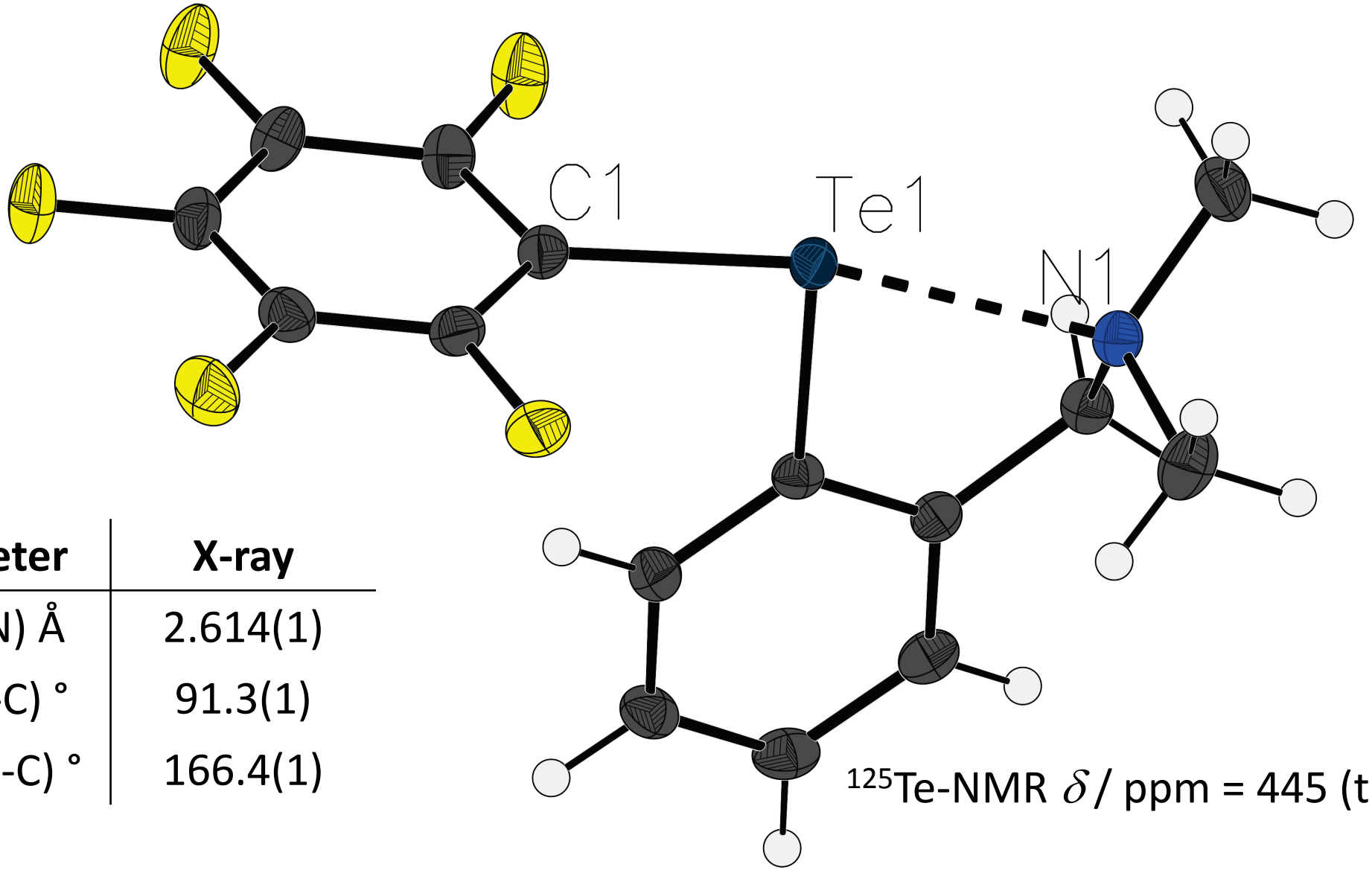
semiflexible linker



1.8 g / 22 %

^{125}Te-NMR δ / ppm = 445 (t) ($^{3}J_{Te,F}$ = 75Hz)

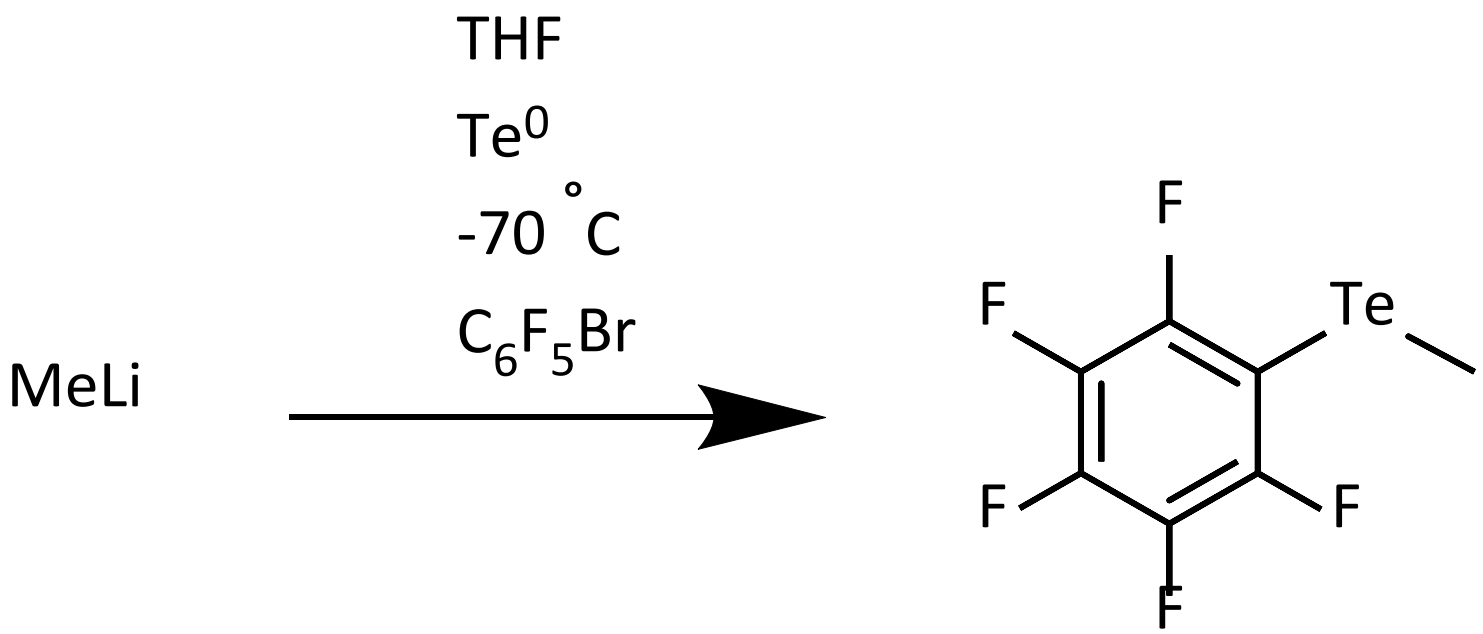
semiflexible linker



Parameter	X-ray
d(Te···N) Å	2.614(1)
α(C-Te-C) °	91.3(1)
α(N···Te-C) °	166.4(1)

^{125}Te-NMR δ / ppm = 445 (t) ($^{3}J_{Te,F}$ = 75Hz)

Perfluorophenylmethyltellane

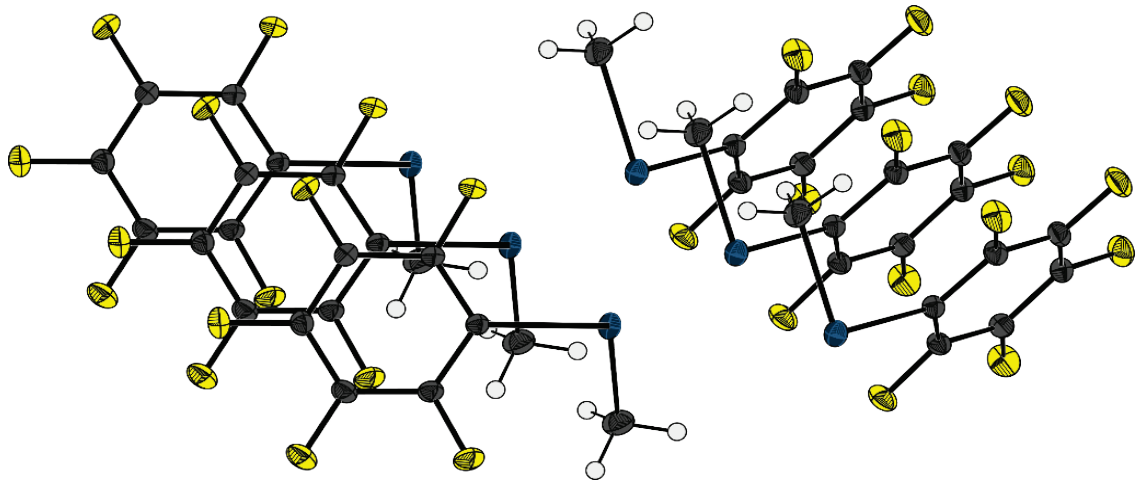


3.8 g / 53 %

^{125}Te-NMR δ / ppm = 210 (t) ($^{3}J_{Te,F}$ = 75Hz)

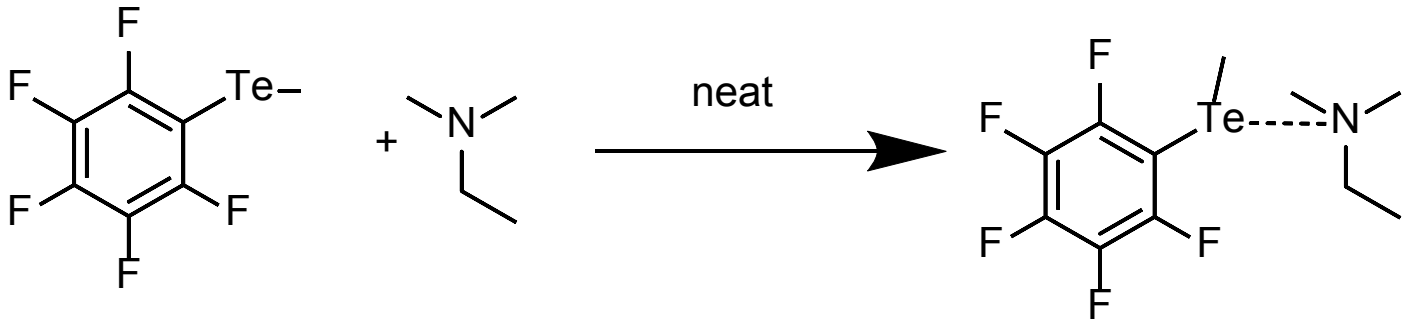
Perfluorophenylmethyltellane

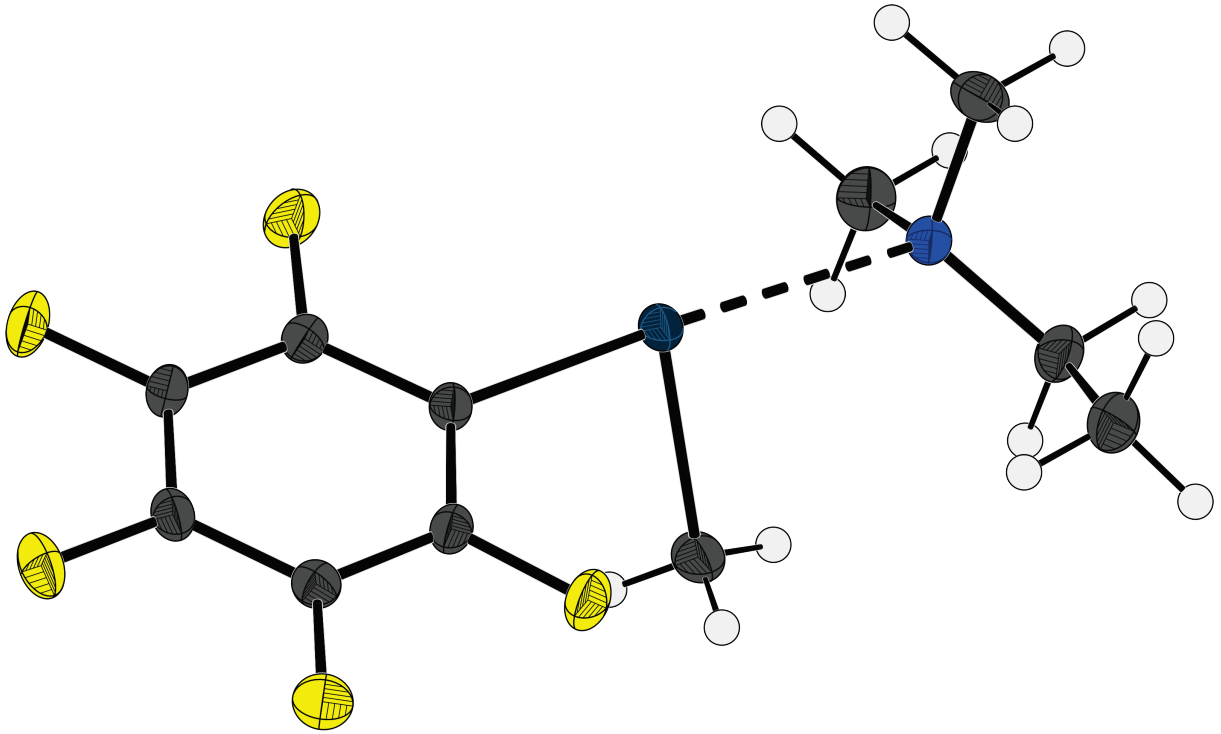
Parameter	X-ray
d(Te···Te) Å	3.761(1)
α(C-Te-C) °	94.3(1)
α(Te···Te-C) °	164.7(1)



^{125}Te-NMR δ / ppm = 210 (t) ($^{3}J_{Te,F}$ = 75Hz)

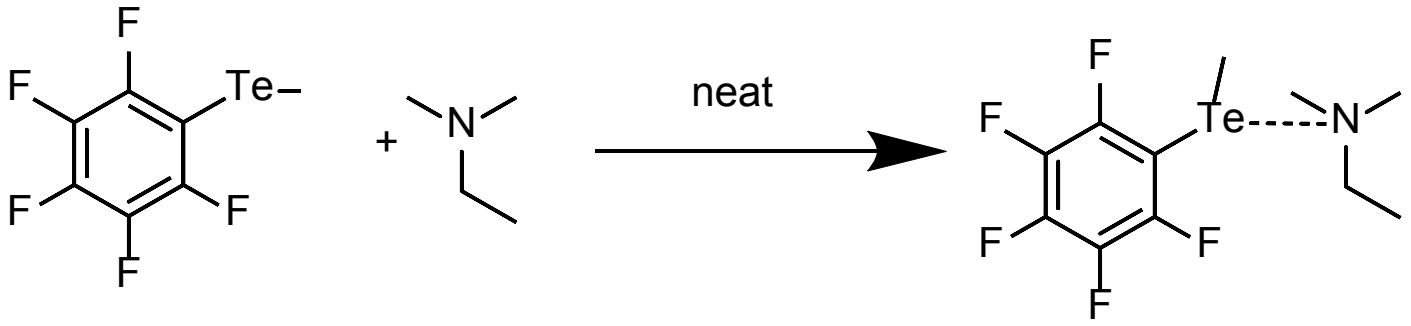
Perfluorophenylmethyltellane - complex

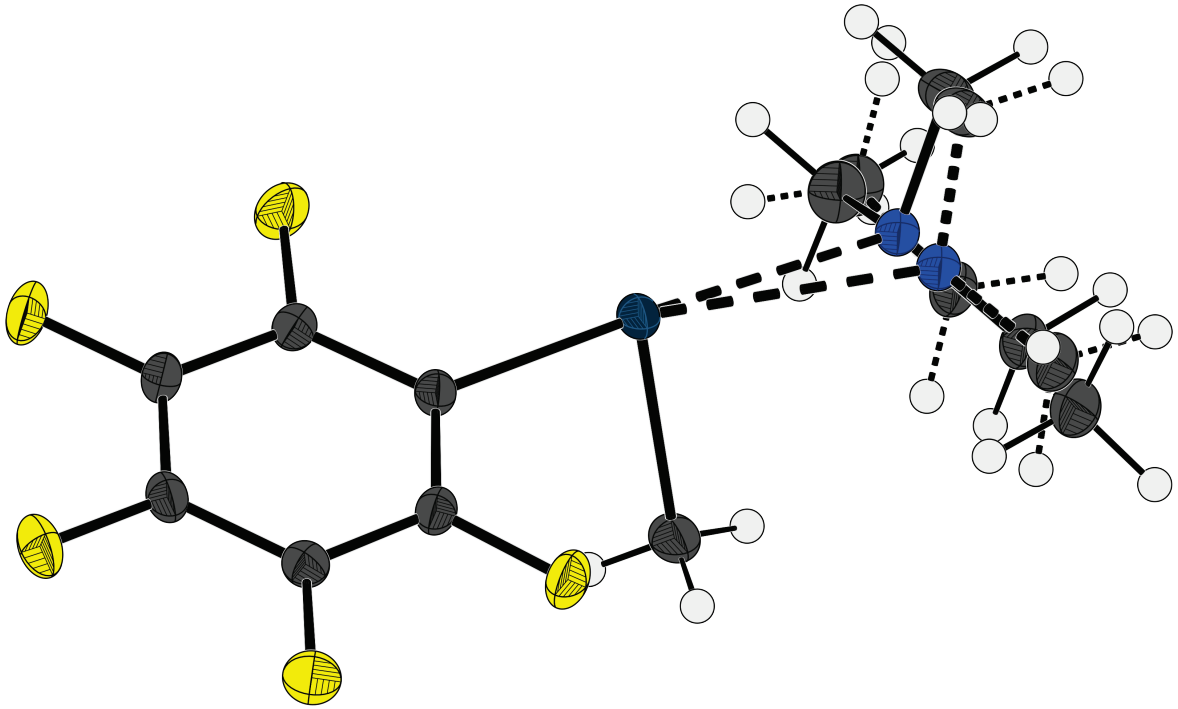




Parameter	X-ray
d(Te···N) Å	2.853(1)
α(C-Te-C) °	91.4(1)
α(N···Te-C) °	174.6(1)

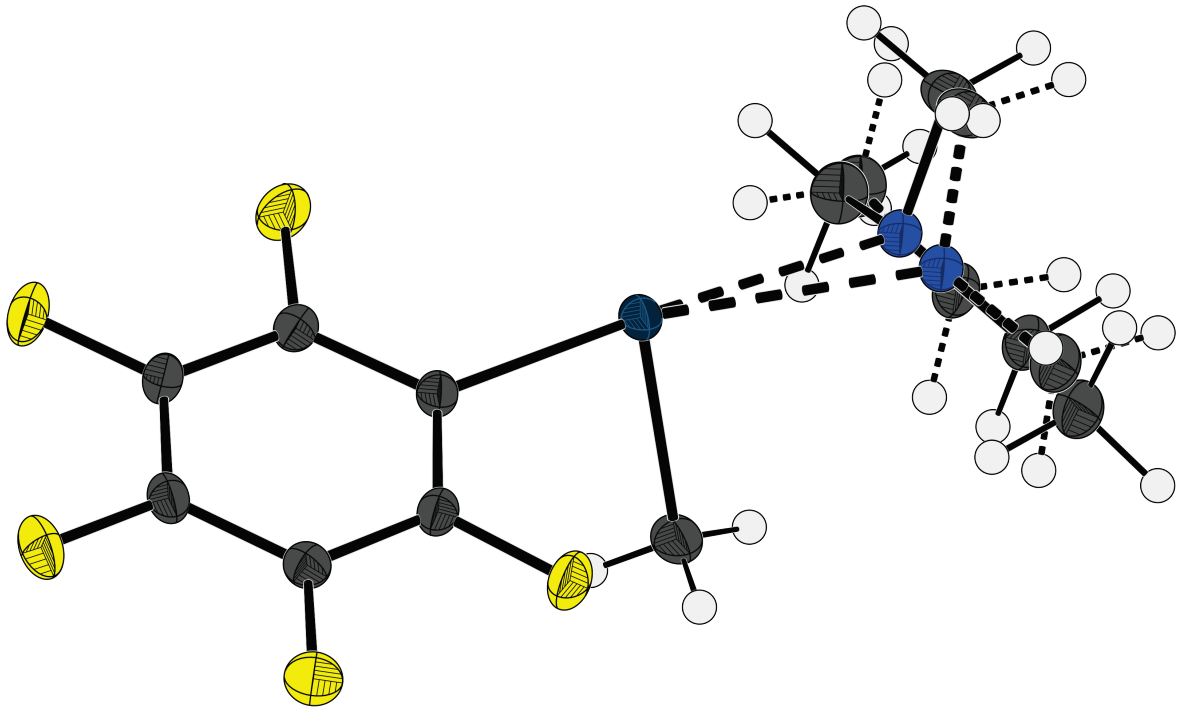
Perfluorophenylmethyltellane - complex





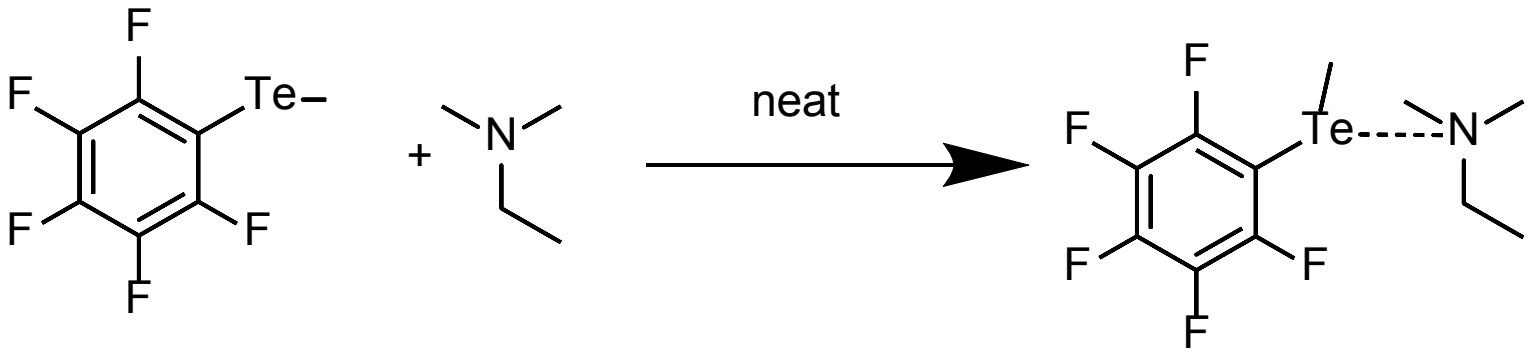
Parameter	X-ray
d(Te···N) / Å	2.853(1)
α(C-Te-C) / °	91.4(1)
α(N···Te-C) / °	174.6(1)

Reversable Twinning behavior



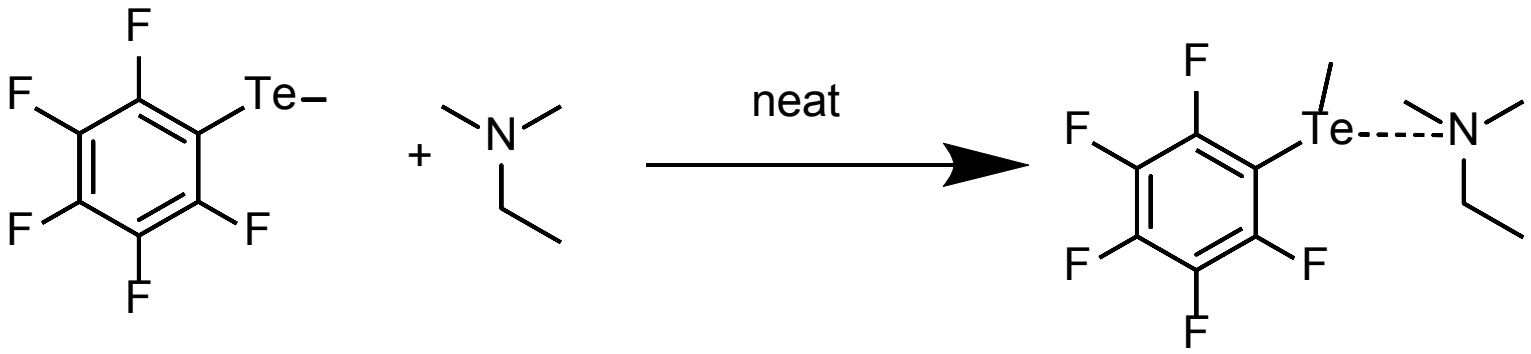
Temperature / K	Ratio of disorder
200	67:33
150	75:25
94	98:2

SAPT0 @ def2-TZVP



Basis Set	*ΔE*	*Electrostatics*	*Exchange*	*Induction*	*Dispersion*
def2-TZVP	-10.2	-16.1	22.5	-5.3	-11.3

LED study @ DLPNO-CCSD(T)



Basis Set	ΔE_{int}	E_{elint}	E_{exch}	E_{disp}	$E_{C\text{-}T}$	$\Delta E_{el\text{-}prep}$	$\Delta E_{geo\text{-}prep}$
def2-QZVPP	-21.4	-68.6	-13.9	-7.1	-2.2	70.4	12.7

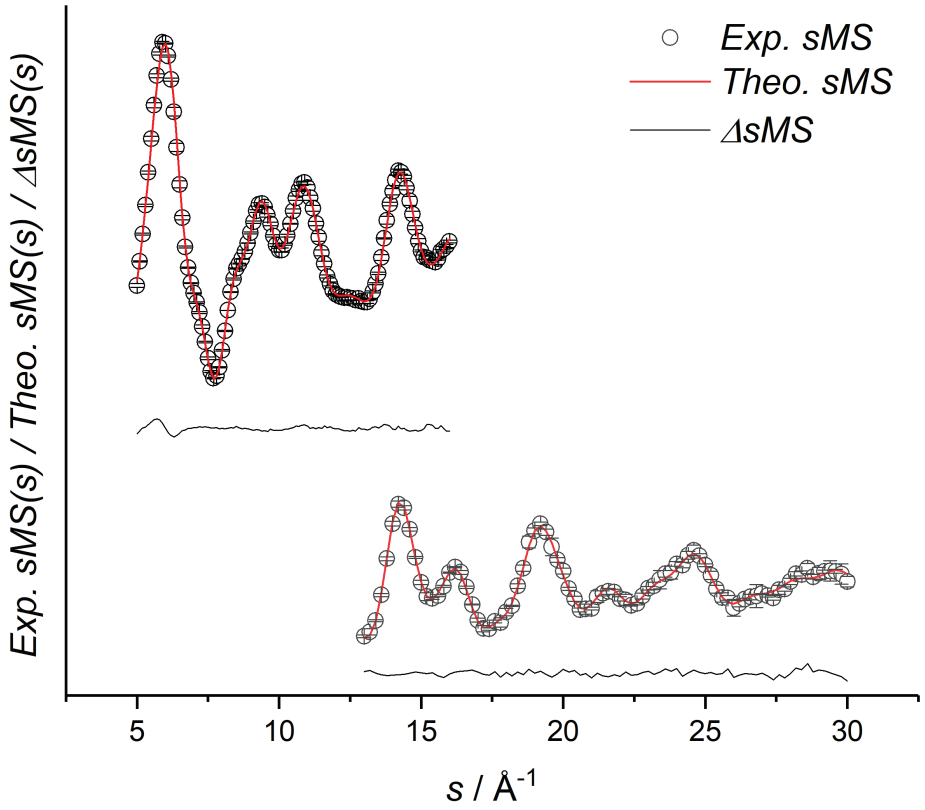
ΔE = - 8.7 kcal mol^{-1}

Summary – solid state

d(Te…N) / Å	linker
2.614(1)	benzyl
2.639(1)	propyl
2.853(1)	-

- Influence of the backbone
- Interaction exists even without backbone
- Strongly electrostatic interaction

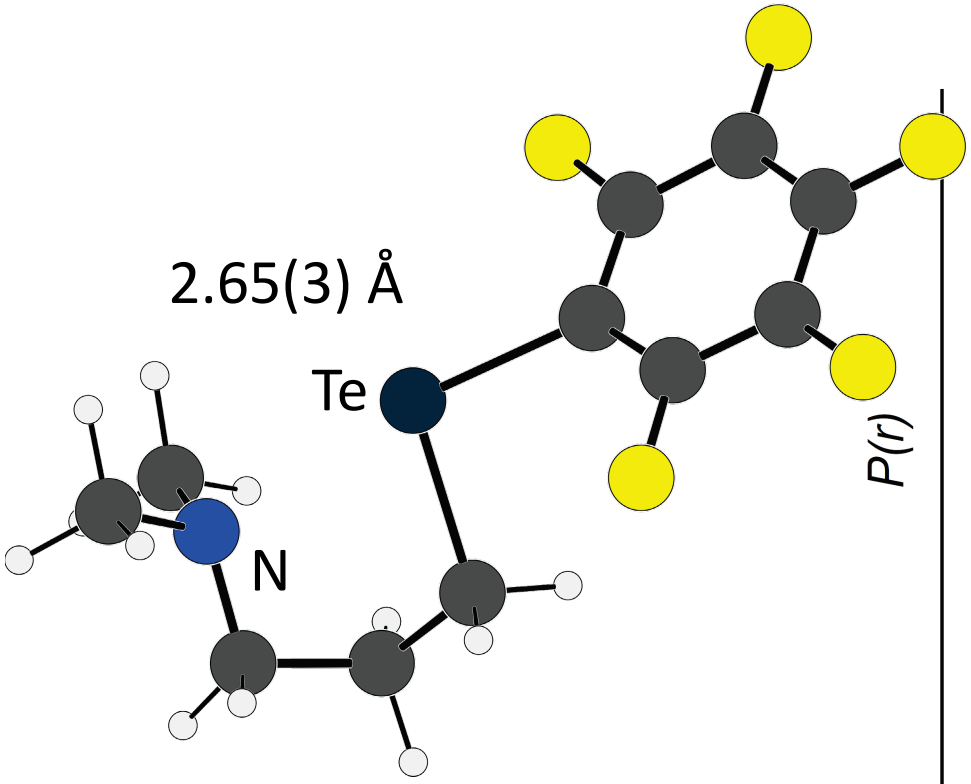
GED studies

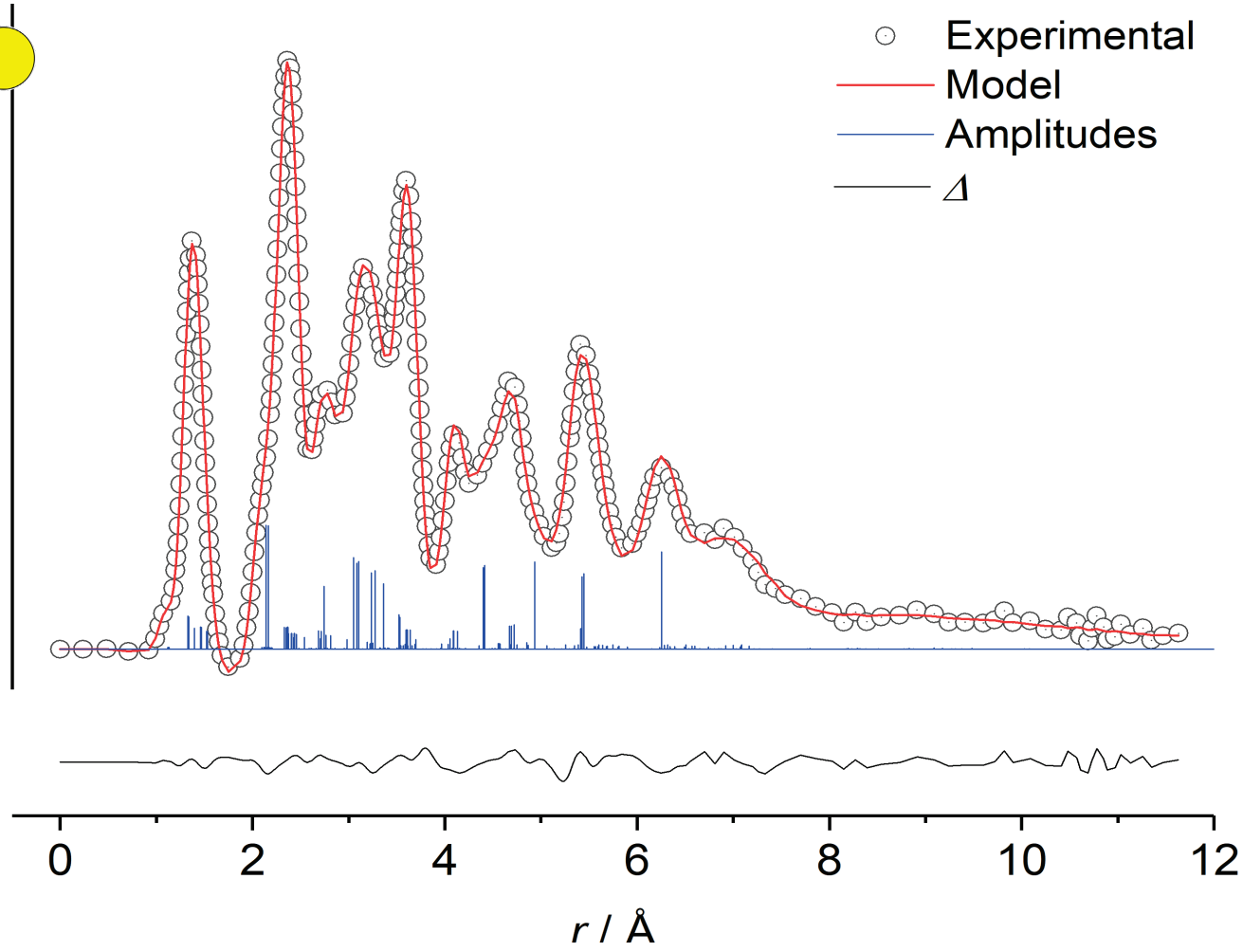


Nozzle-to-plate-distance / mm	250	500
nozzle temperature / K	443	443
accelerating voltage / kV	60	60
Rf / %	13.9	6.7
wRd / %	2.2	3.6

PBE-D3BJ / def2TZVPP / static model

GED studies

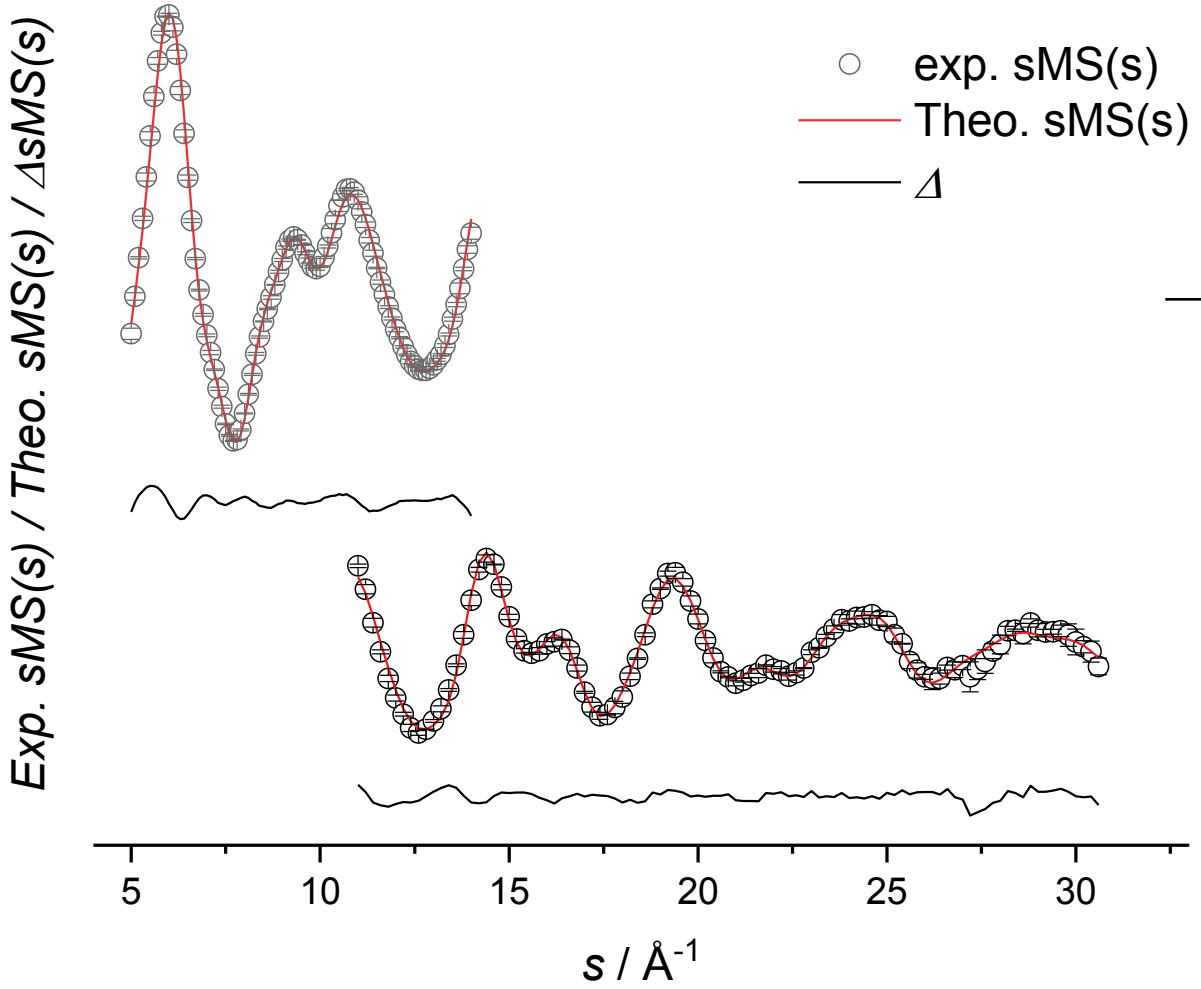




Rf = 5.6 %

wRd = 2.7 %

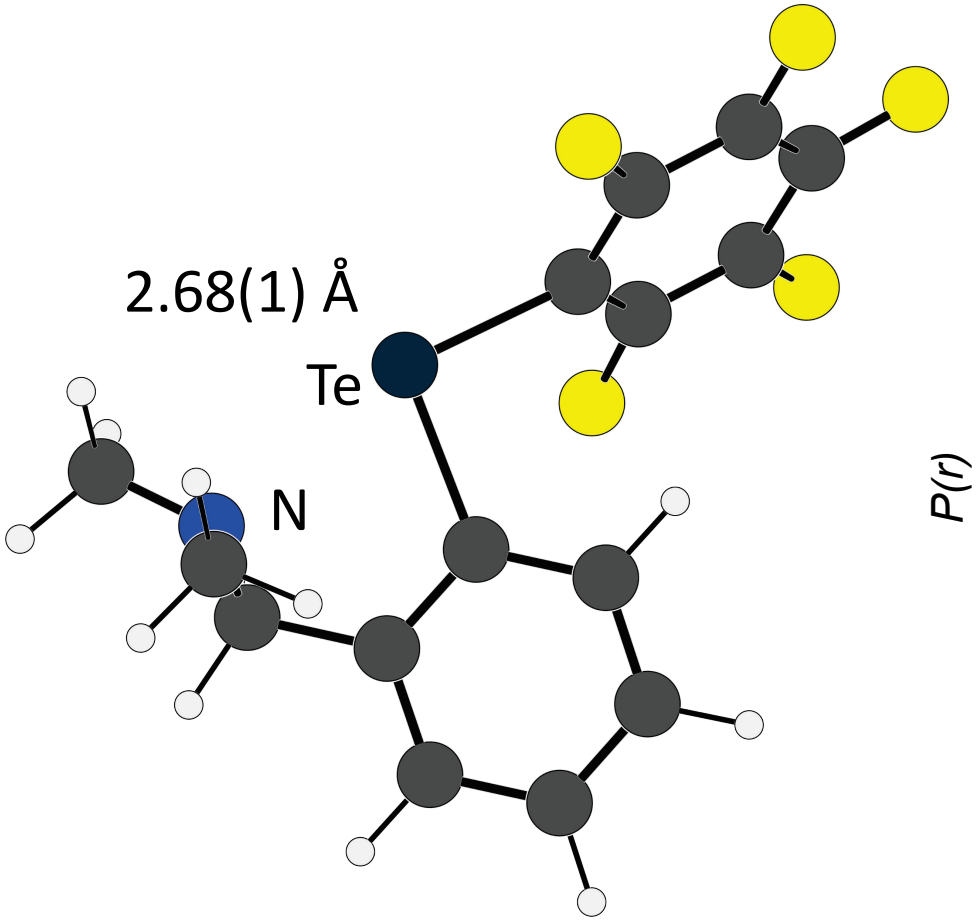
GED studies



Nozzle-to-plate-distance / mm	250	500
nozzle temperature / K	474	474
accelerating voltage / kV	60	60
Rf / %	18.1	7.8
wRd / %	2.8	4.6

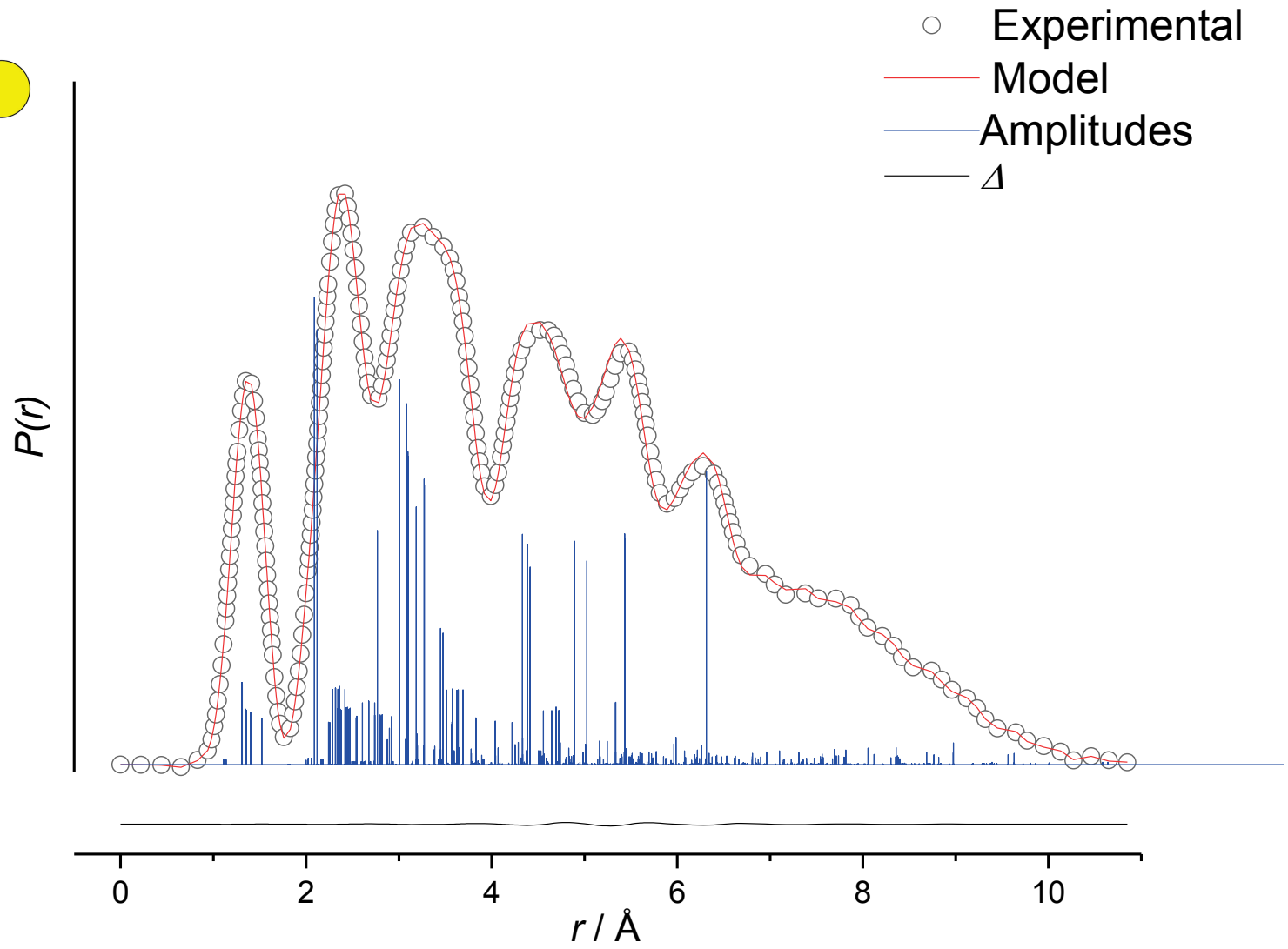
B3LYP-D3BJ / def2TZVPP / static model

GED studies



Rf = 9.9 %

wRd = 3.6 %



Summary – GED studies

Parameter	Benzylspacer	Propylspacer
d(Te-N) / Å	2.68(1)	2.65(3)
d(C-Te) / Å	2.077(2)	2.130(4)
α(C-Te-C) / °	93.8(1)	98(4)
α(C-Te…N) / °	164.4(1)	172(4)

- Te … N distance almost equal for the tested molecules
- Less dependence of the backbone
- Strong electrostatic effect

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fin

Financial support:

DFG Deutsche Forschungsgemeinschaft

… or other theories

(DSD-PBEP86-D3/def2TZVPP @ RIJK-SCS-MP2/def2TZVPP)

Compound	**Donor /Acceptor**	**Energy / kcal mol^{-1}**	***d*(Te,N)**
Complex	LP(N) / s*(Te-C)	8.1	2.91
Propyllinker	LP(N) / s*(Te-C)	12.9	2.75
Benzyllinker	LP(N) / s*(Te-C)	13.7	2.65

… or other theories

(DSD-PBEP86-D3/def2TZVPP @ RIJK-SCS-MP2/def2TZVPP)

Compound	**r / eÅ^{-3}**	**∇r / eÅ^{-5}**	**d(Te,N)**
Complex	0.024	0.054	2.91
Propylspacer	0.033	0.067	2.75
Benzylspacer	0.036	0.071	2.65