Strukturaufklärung in der molekularen anorganischen Chemie

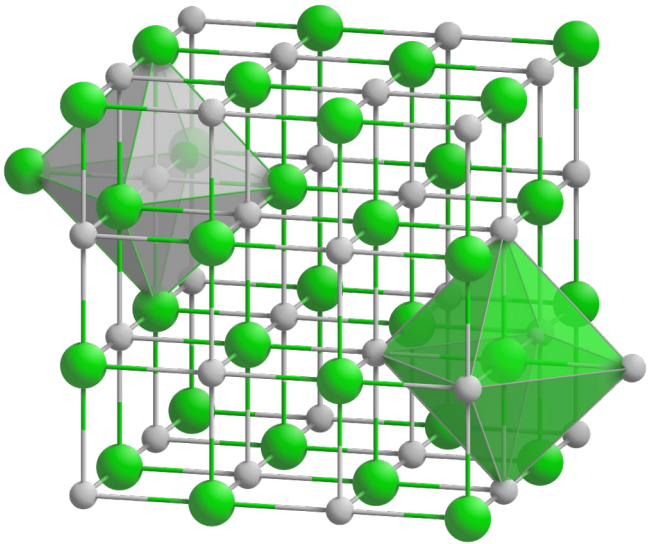
11. Strukturverfeinerung,

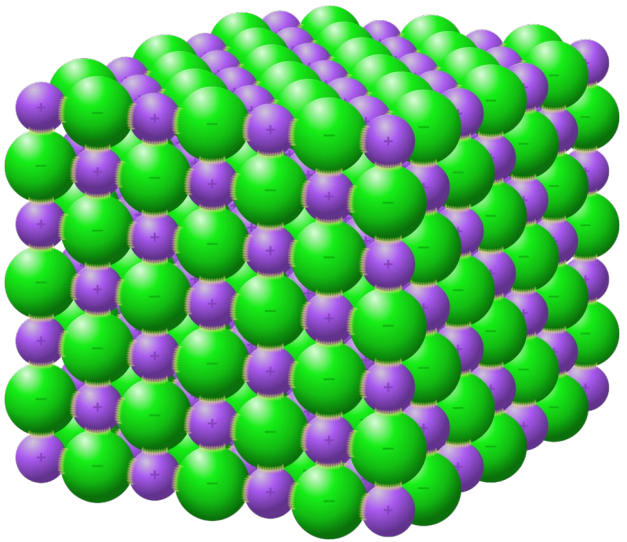
Phasenabhängige Strukturen

Strukturverfeinerung

Als Anekdote...

Natriumchlorid

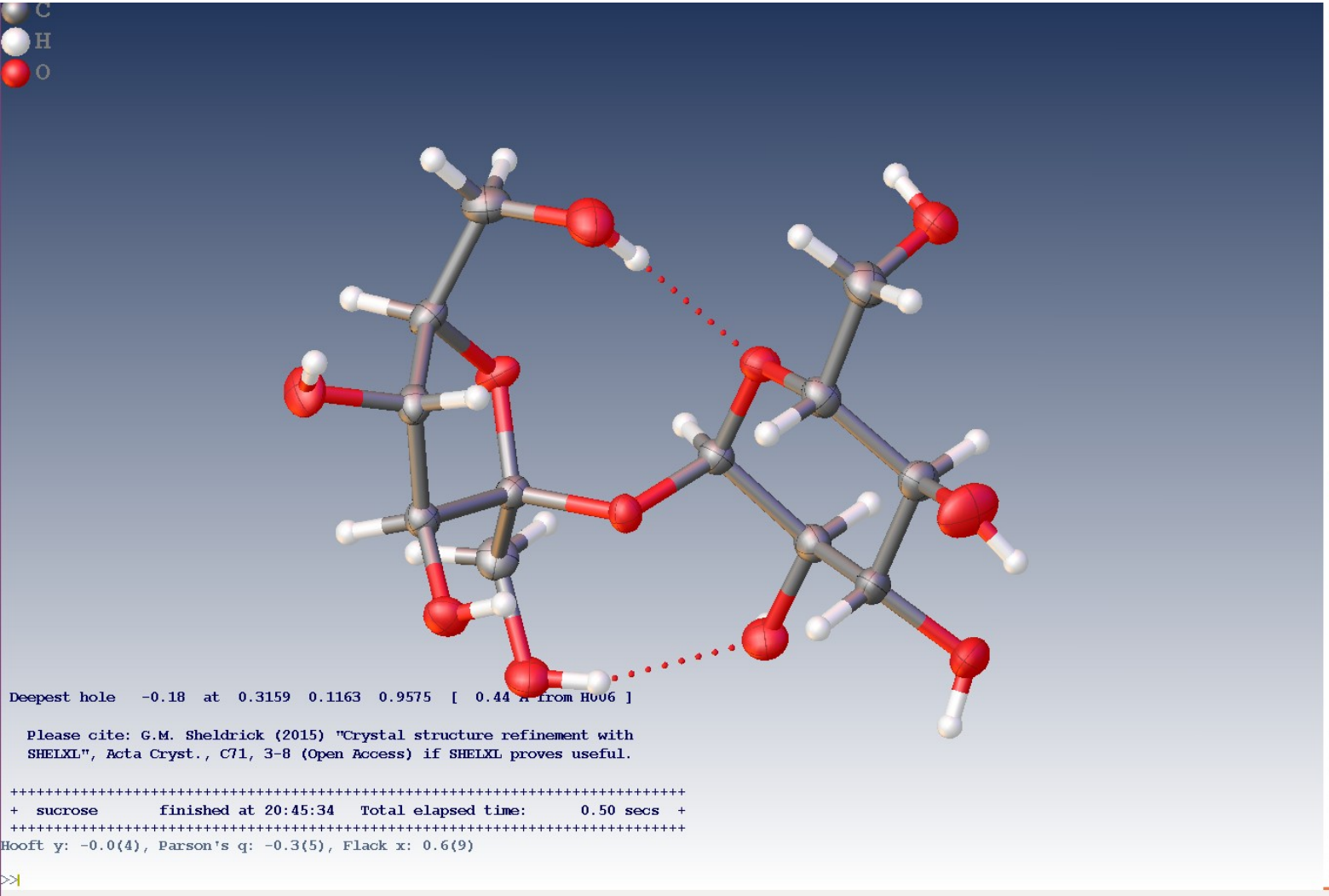


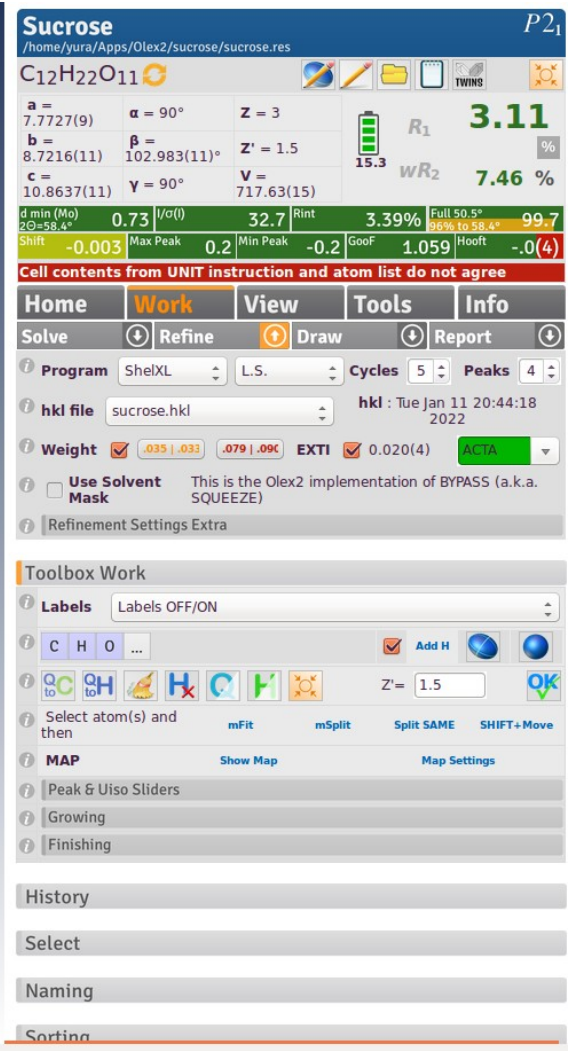


Kubisch *Fm3m*

Dichte ρ = 2.1615 g·cm^{-3} → r(Na–Cl) aus ρ [Versuche selber zu rechnen]

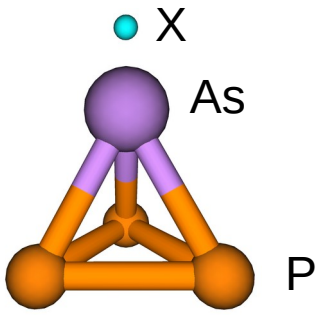
Olex2 für XRD

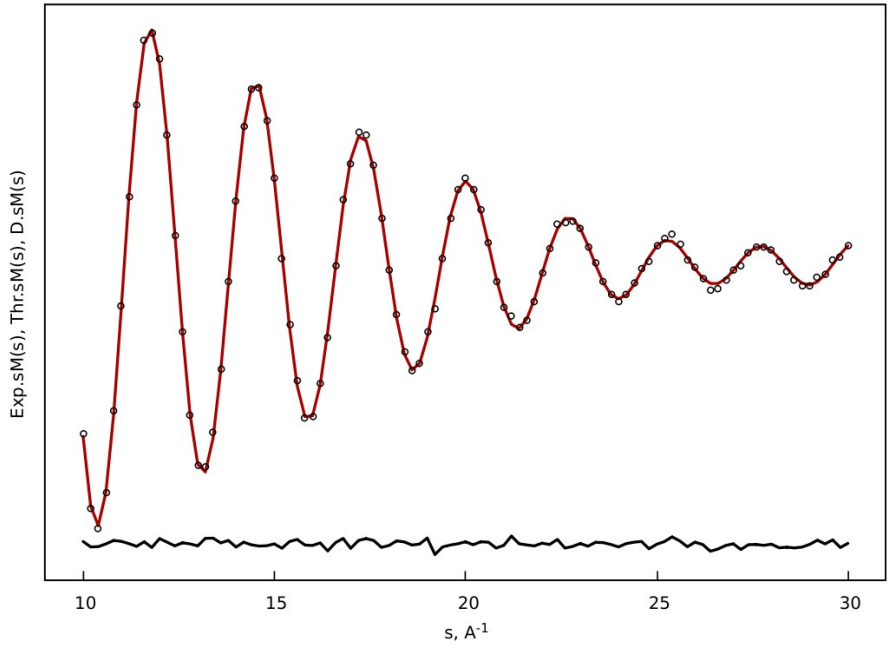


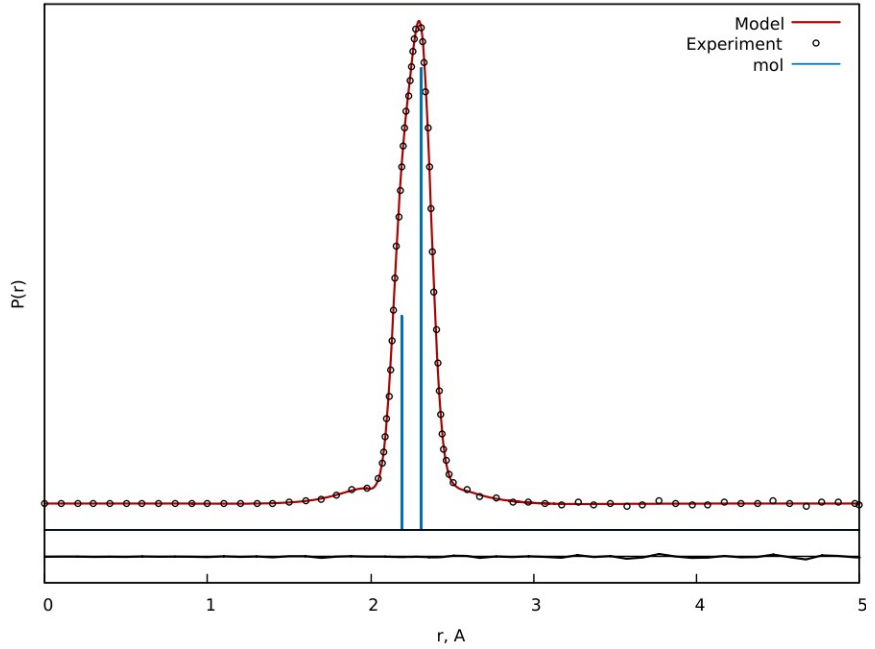


UNEX für GED u./o. Rot. Konstanten

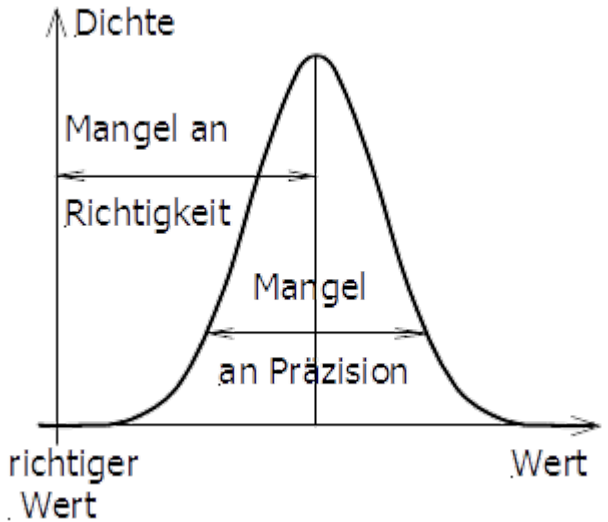
s. Beispiel für AsP_3







Statistik



Präzision ≠ Richtigkeit
Präzision + Richtigkeit = Genauigkeit

Phasenabhängige Strukturen

Feststoff ≠

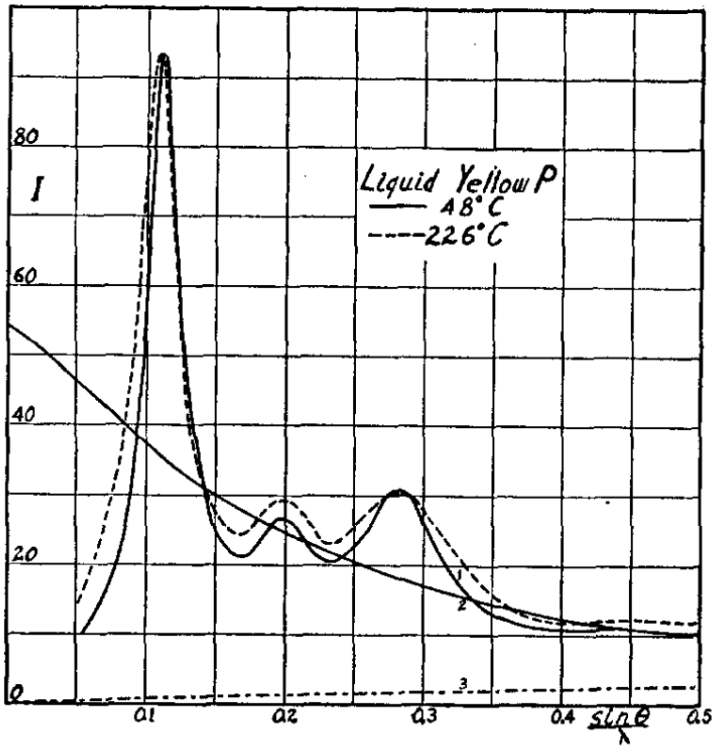
Flüssigkeit ≠

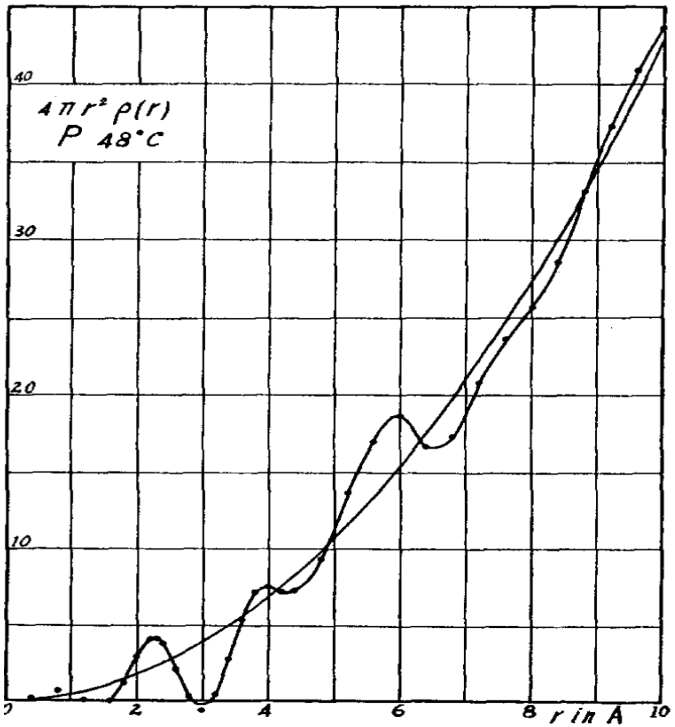
Gas

Themen

- Bindungslängenvariationen
- Schwache Bindungen / Sterische Effekte
- Packungseffekte generell
- Mesomerie / Polarität
- Dative Bindungen / Polarität
- Polymorphie
- Dispersive Wechselwirkungen

XRD an flüssigem P_4



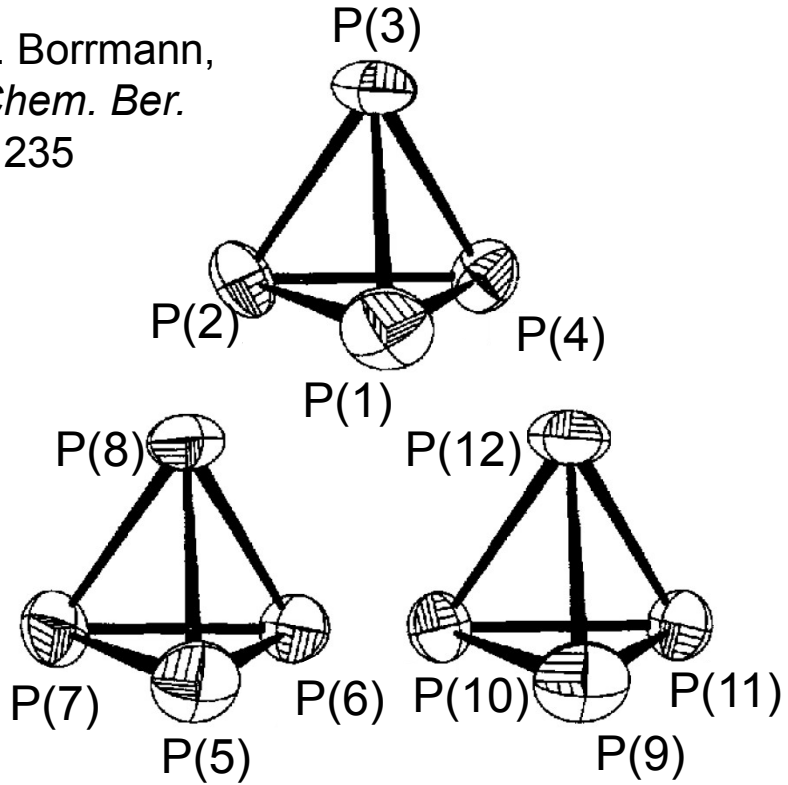


r = 2.25 Å bei 48°C

Thomas, Newell, Gingrich, *J. Chem. Phys.* **1938**, *6*, 659

P_4 Kristall

A. Simon, H. Borrmann, J. Horakh, *Chem. Ber.* **1997**, *130*, 1235



P(1)-P(2)	2.1819(5)	
P(1)-P(3)	2.1910(5)	
P(1)-P(4)	2.1801(5)	
P(2)-P(3)	2.1828(5)	
P(2)-P(4)	2.1849(5)	
P(3)-P(4)	2.1768(5)	
P(5)-P(6)	2.1771(5)	
P(5)-P(7)	2.1756(5)	← min
P(5)-P(8)	2.1866(5)	
P(6)-P(7)	2.1920(5)	← max
P(6)-P(8)	2.1777(5)	
P(7)-P(8)	2.1808(5)	
P(9)-P(10)	2.1851(5)	
P(9)-P(10)	2.1834(5)	
P(9)-P(12)	2.1834(5)	
P(10)-P(11)	2.1818(5)	
P(11)-P(12)	2.1841(5)	
P(10)-P(12)	2.1874(5)	

XRD Durchschnitt: 2.183(5) Å

Vgl.:

GED: r_g(P–P) = 2.1994(3) Å @ 373 K

XRD am flüssigk.: 2.25 @ 321 K

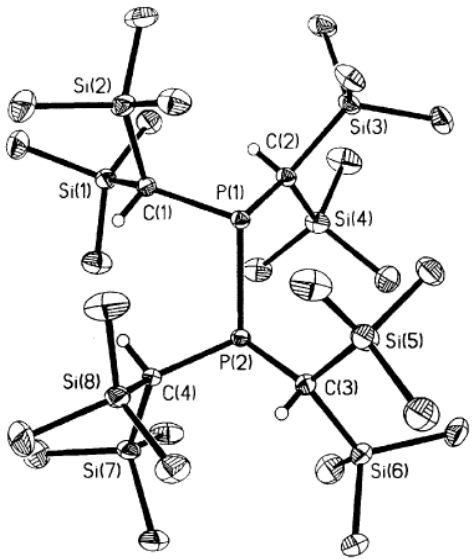
Rechnung: r_e = 2.1860 [CCSD(T)-F12/apwCV5Z]

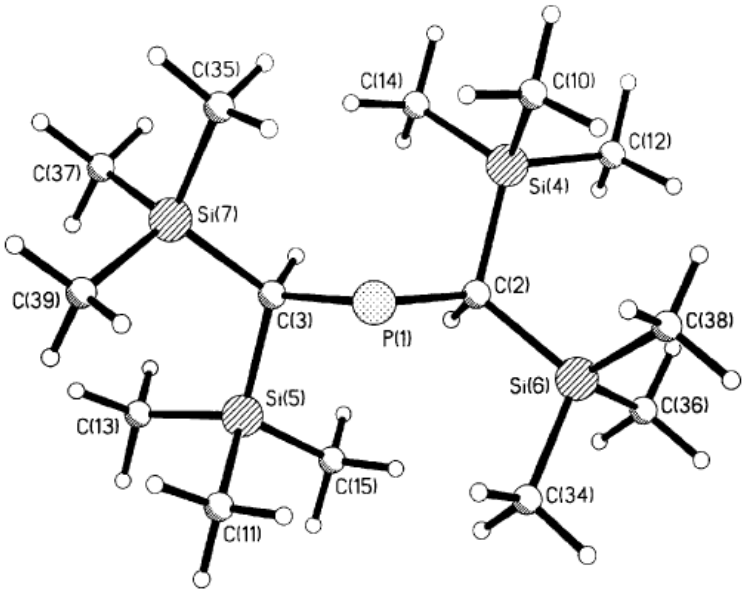
Schwache Bindungen + Sterische Effekte

“Persistente Phosphinyl-Radikale vs. Diphosphin: ein molekularer Kistenteufel“

$R_2P\text{-}PR_2 \rightleftharpoons 2 \cdot PR_2$ R = $CH(SiMe_3)_2$

P–P
2.310(1) Å



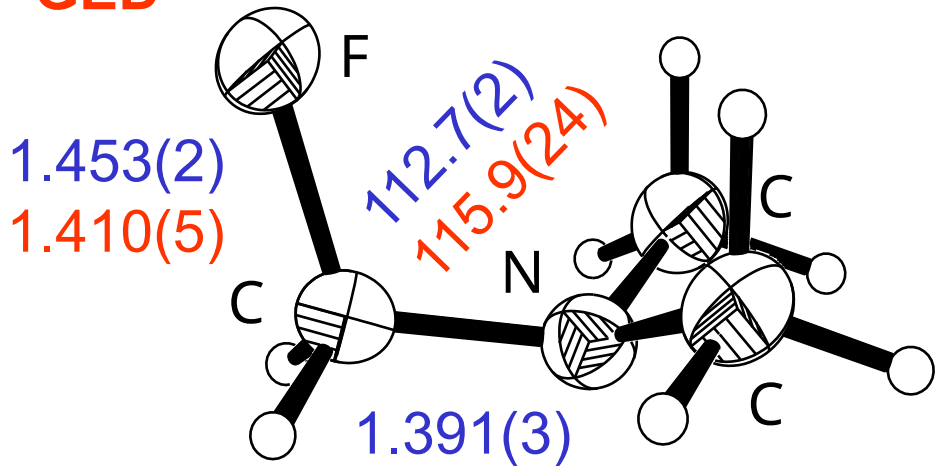


	Festkörper (dimer)	Gasphase (monomer)
P–C	1.893(2)-1.896(2)	1.856(9) Å
C–P–C	103.6(1)-107.9(1)	103.9(10)°

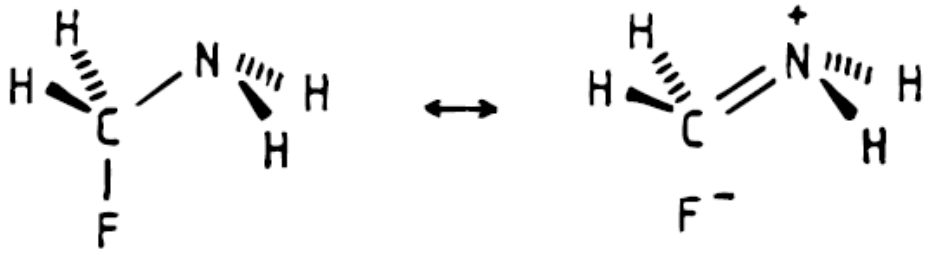
S. L. Hinchley, D. W. H. Rankin, A. H. Cowley, et al. *Chem. Commun*. **2000**, 2045

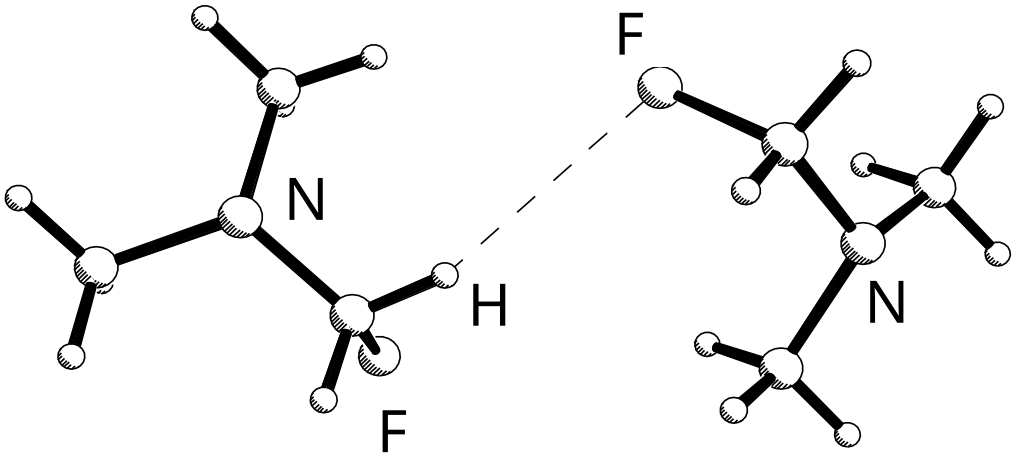
Polarität + Mesomere Effekte

XRD
GED



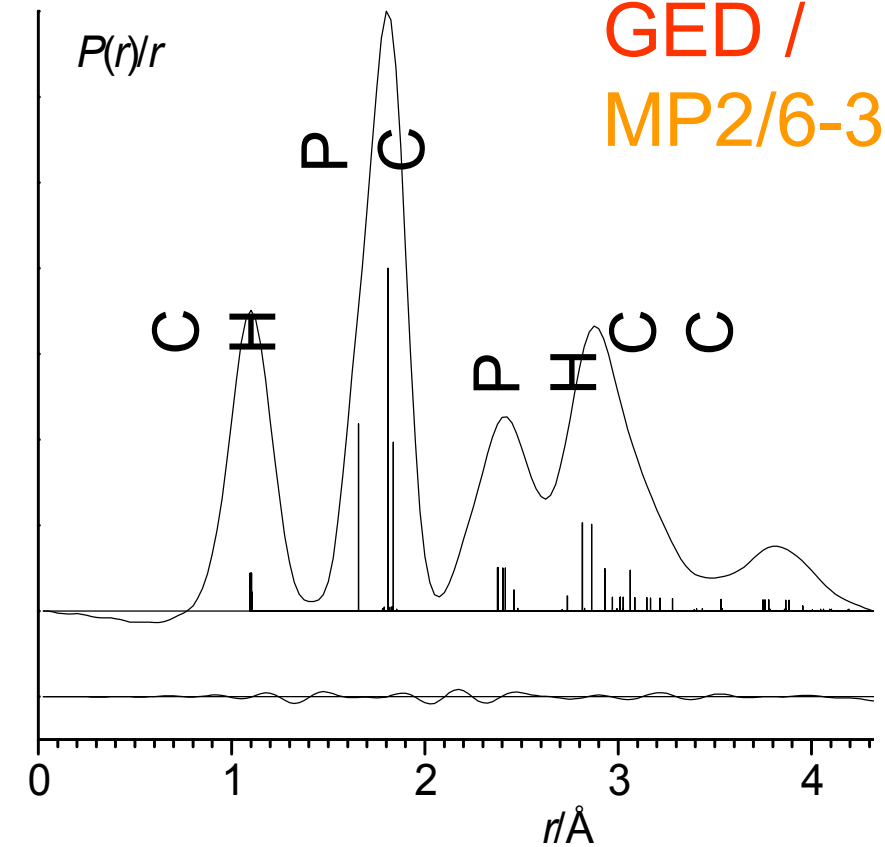
$\Sigma\alpha$(N):
343.4
333.3



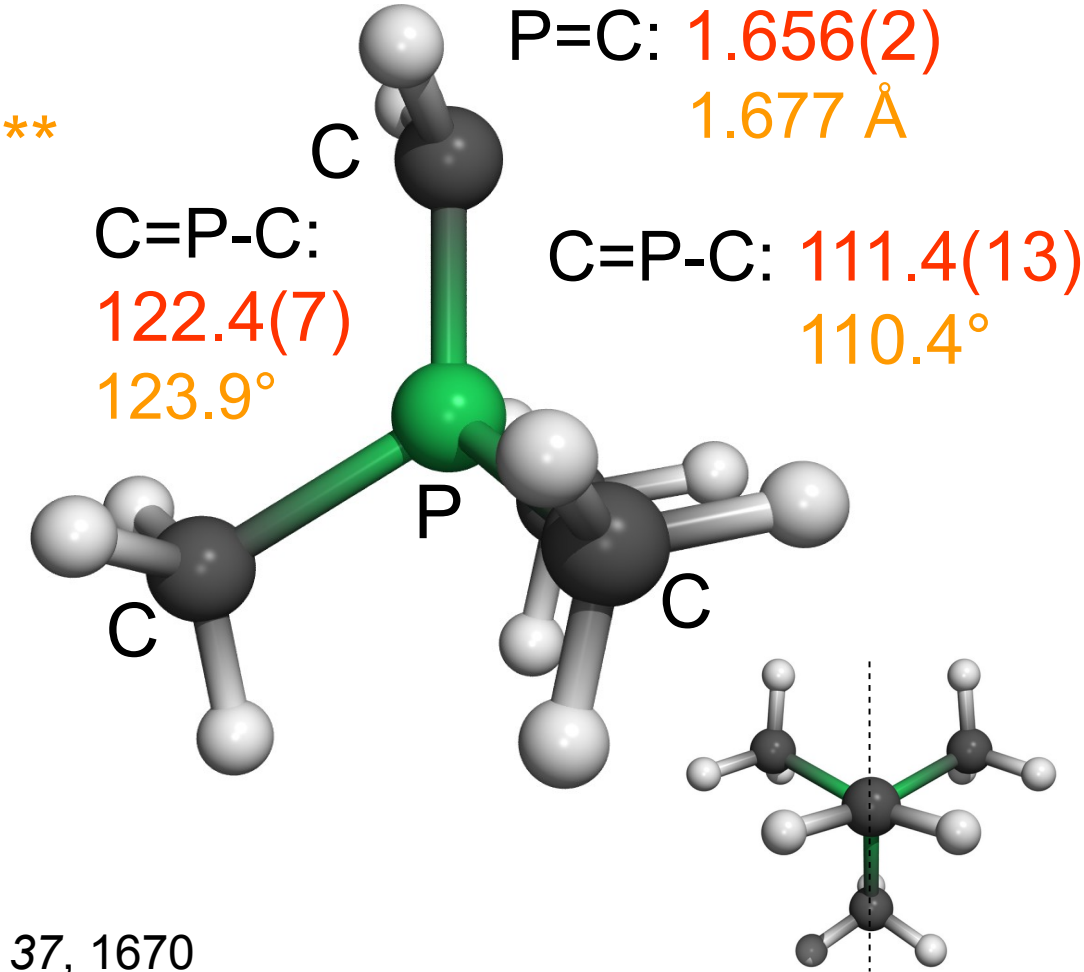


XRD: K. Vojinovic, N. W. Mitzel
GED: H. Oberhammer et al. *J. Am. Chem. Soc.* **1996**, *118,* 3720

Packungseffekte: $Me_3P{=}CH_2$

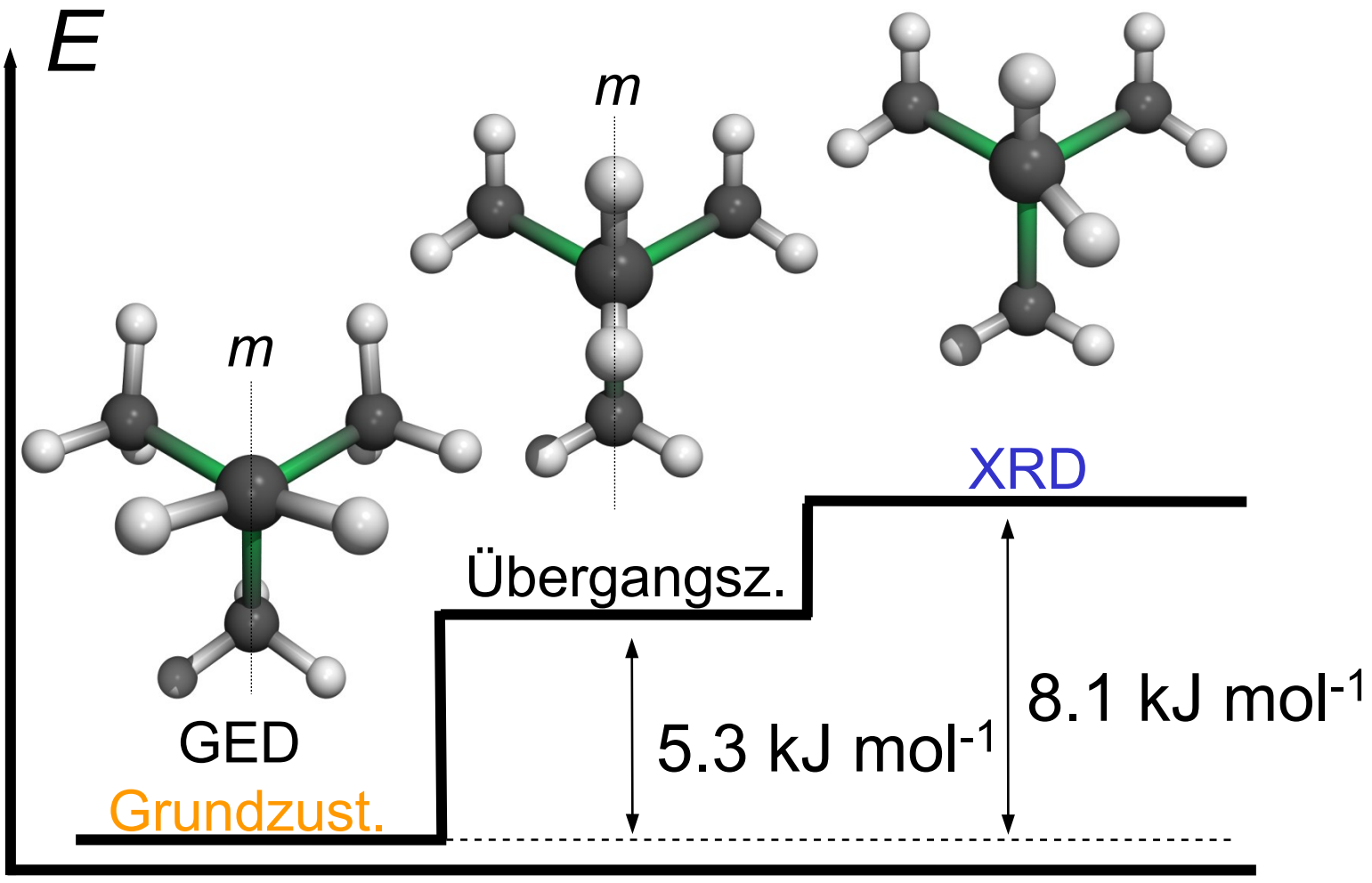


GED /
MP2/6-311G**

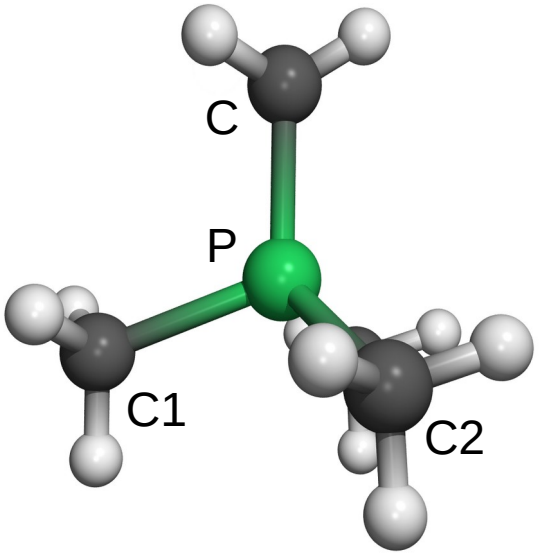


N. W. Mitzel et al. *Angew. Chem. Int. Ed.* **1998**, *37*, 1670

$Me_3P{=}CH_2$ (Rechnungen)



Packungseffekte: $Me_3P{=}CH_2$ (XRD)

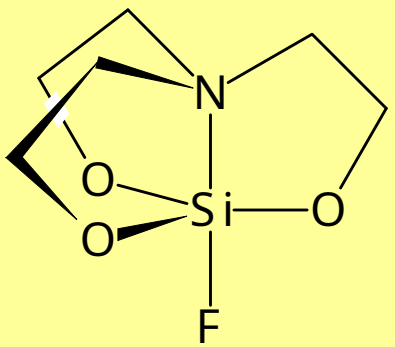


Die molekulare Geometrie im Festkörper ist ähnlich Derjenigen eines berechneten Übergangszustandes der Rotation der CH_2-Gruppe um die P=C-Bdg.

	XRD	TS MP2/6-311G**
C=P-C1	110.6(2)°	110.3°
C=P-C2	115.6(1)°	117.5°
C1-P-C2	105.6(1)°	104.8°
C2-P-C2‘	102.9(2)°	100.5°

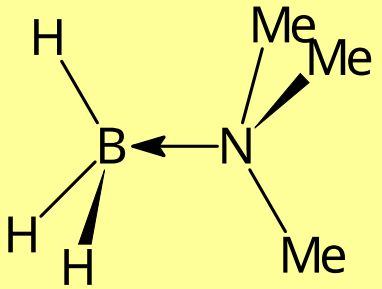
Vgl. Gas:
C=P-C: 122.4(7)°

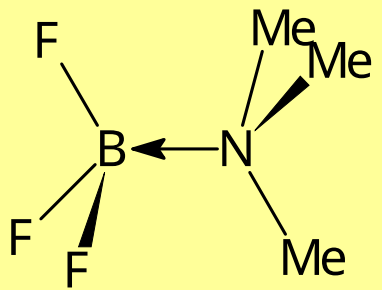
Dative Bindungen / Polarität



r(Si-N) / Å

fest	2.042(1)
gasf.	2.324(14)

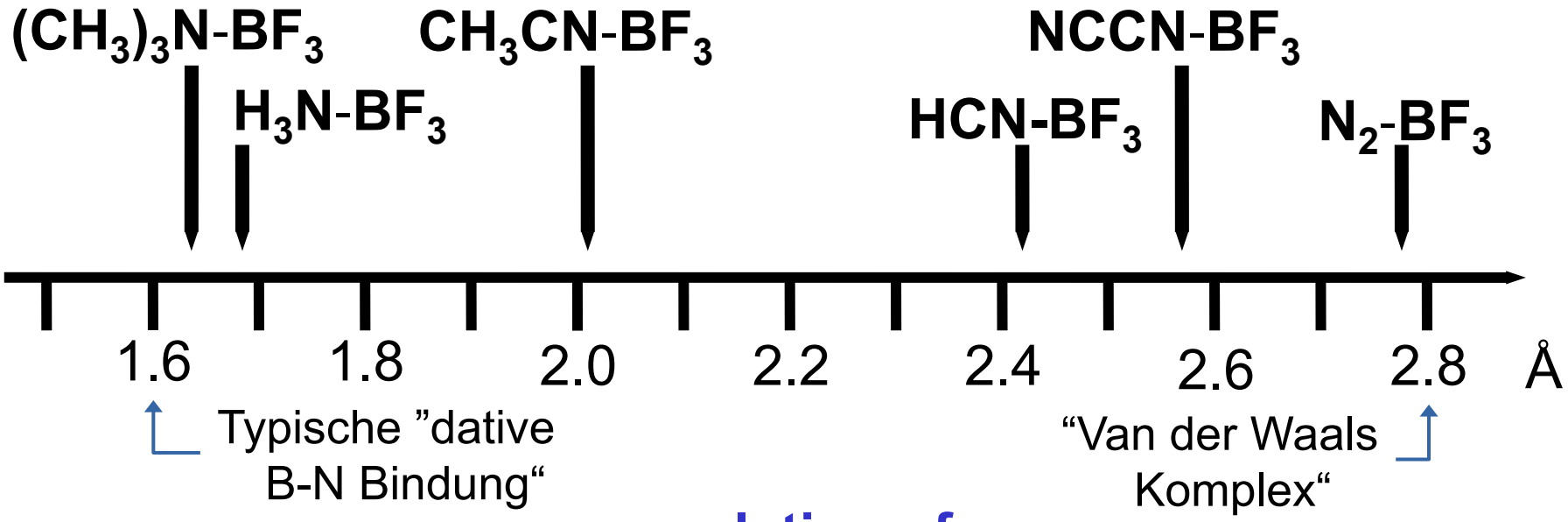




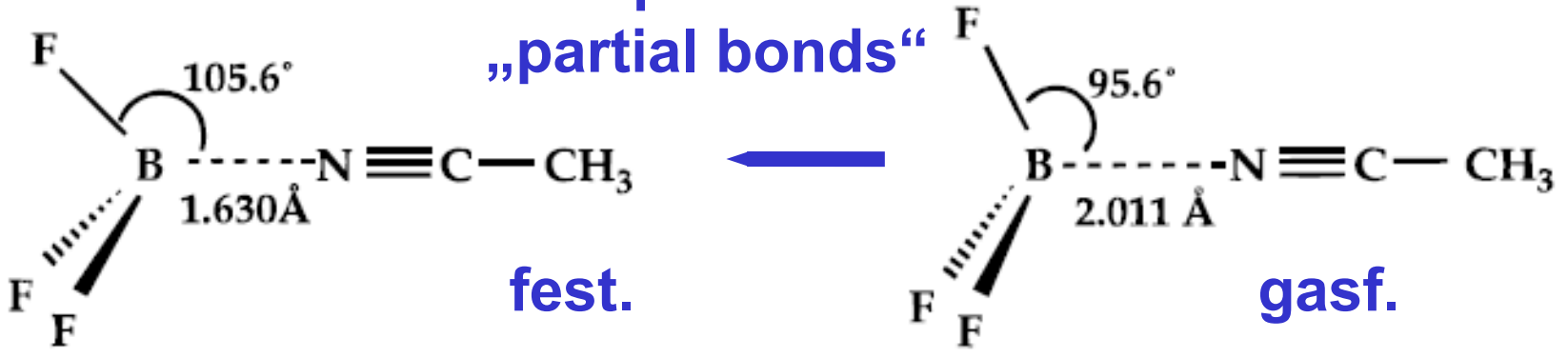
r(B-N) / Å	
fest	gasf.
1.564	1.672
1.58	1.669

Review:
K. R. Leopold, M. Canagaratna, J. A. Phillips, *Acc. Chem. Res.* **1997**, *30*, 57.

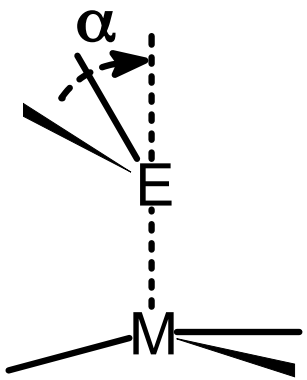
Gasphasen-Werte für B-N

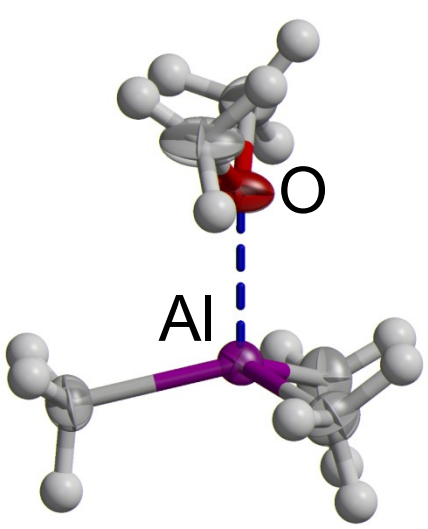


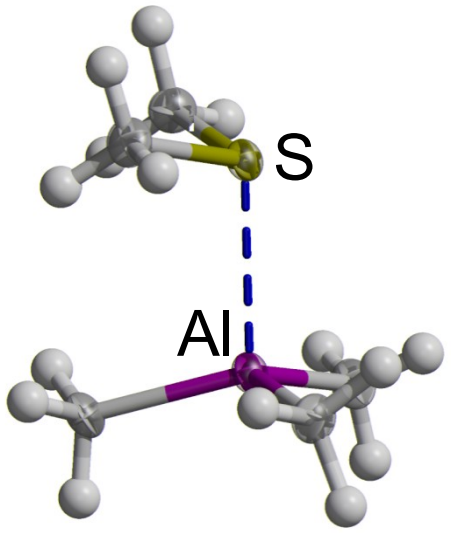
completion of „partial bonds“

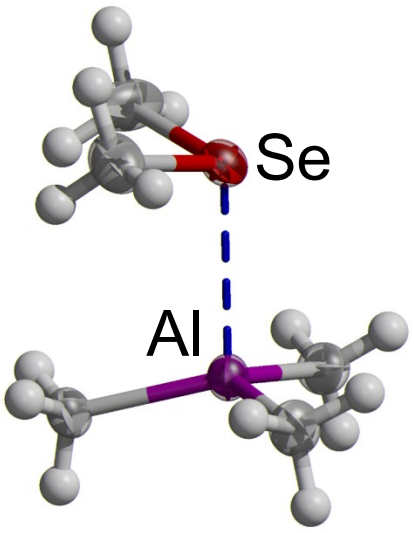


Me_2E-$AlMe_3$-Addukte





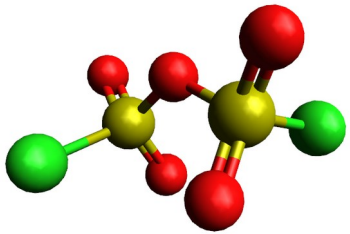




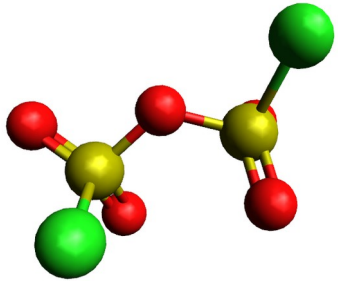
Al-E [Å]	**1.940(2)**	**2.461(av)**	**2.605(av)**
XRD	2.014(14)	2.55(2)	[?]
GED			
α [°]	**12.5(1)°**	**69.2(av)°**	**73.6(av)°**
	5(4)°	31(5)°	[?]

Polymorphie: $Cl(O)_2SOS(O)_2Cl$

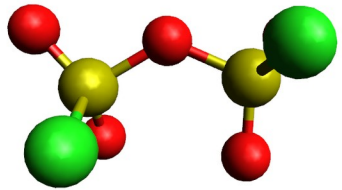
Gas:



anti

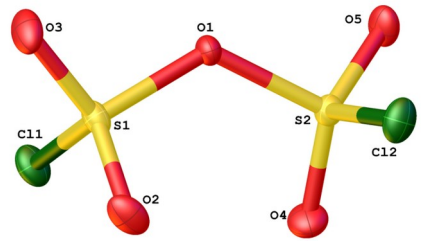


gauche



syn

Kristall:



anti

	Anteil	S-Cl	S-O	Cl-S-S-Cl
Gas *anti*	50	1.993(11)	1.642(10)	80.5(7)
Gas *gauche*	25	2.006(11), 2.004(11)	1.641(12) – 1.660(12)	163.0(15)
Gas *syn*	25	1.989(11)	1.639(13) – 1.640(13)	-110.9(15)

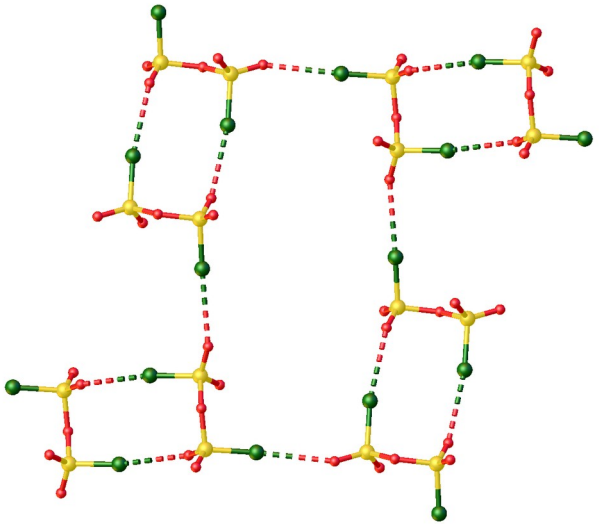
A. M. Betancourt, J. Schwabedissen et al., *Chem. Eur. J.* 2018, 24, 10409.

Polymorphie: $Cl(O)_2SOS(O)_2Cl$ (XRD)

Phase 1

$P2_1/c$, $Z = 4$

$\rho = 2.211$ g/cm^3

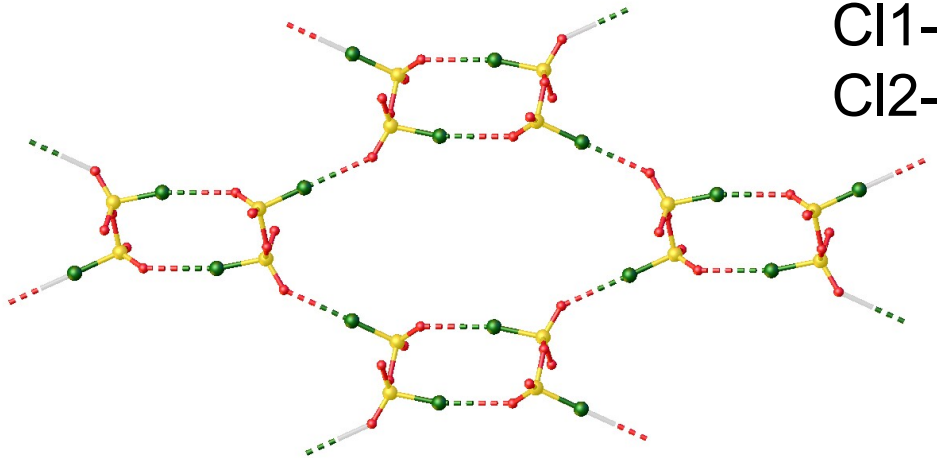


Cl1-S1 1.9729(2)
Cl2-S2 1.9661(2)

Phase 2

$P2_1/c$, $Z = 4$

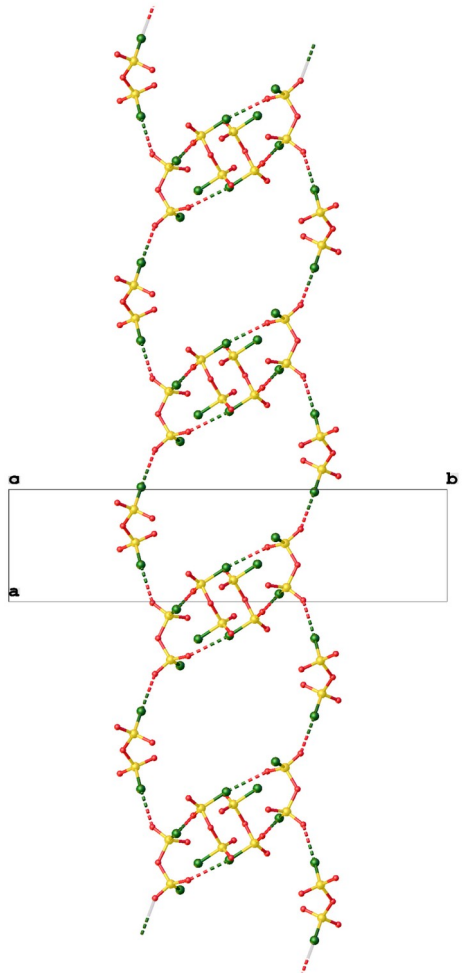
$\rho = 2.234$ g/cm^3



Cl1-S1 1.9724(1)
Cl2-S2 1.9714(1)

Polymorphie: $Cl(O)_2SOS(O)_2Cl$ (XRD)

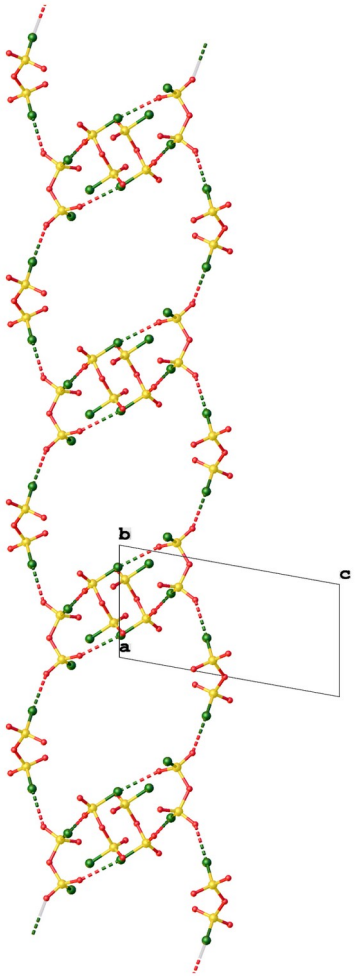
Cl1-S1 1.9729(1)
Cl2-S2 1.9661(1)



Phase 3

$P2_1/c$, $Z = 4$

$\rho = 2.212$ g/cm^3



S1-Cl1 1.9708(2)
S2-Cl2 1.9763(3)
S3-Cl3 1.9786(3)
S4-Cl4 1.9674(2)
S5-Cl5 1.9715(2)
S6-Cl6 1.9754(2)

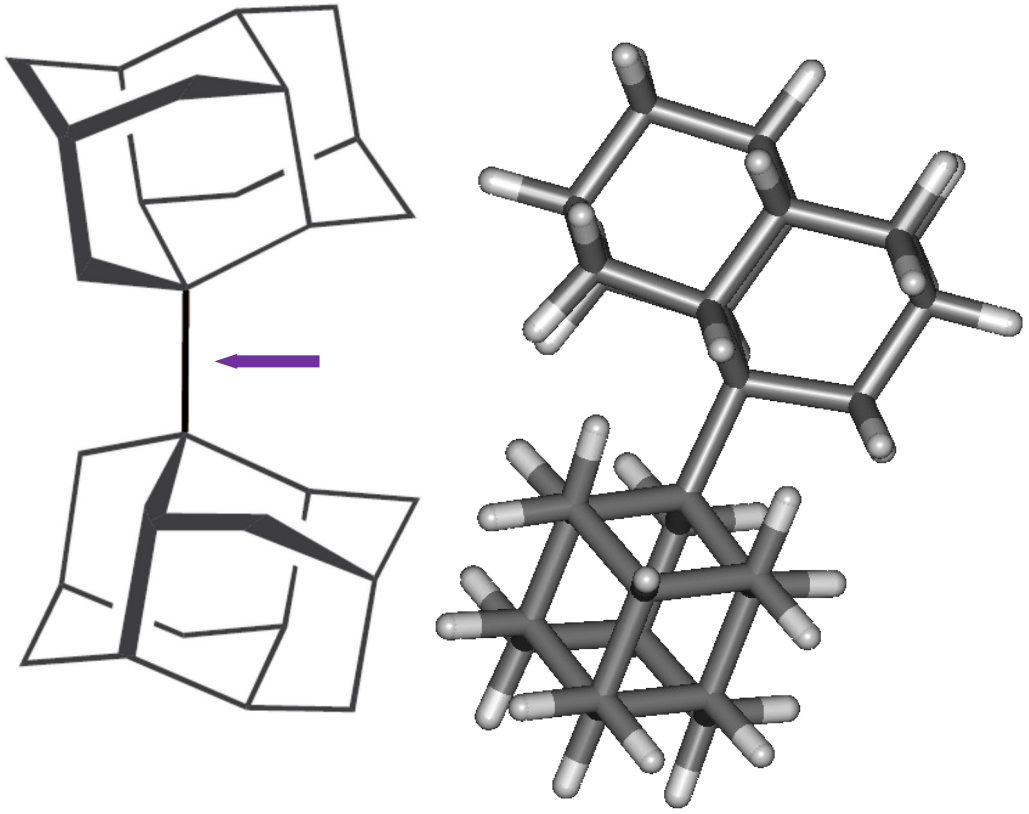
Phase 4

$P\bar{1}$, $Z = 12$

$\rho = 2.211$ g/cm^3

Dispersive Wechselwirkungen

Bis(diamantan) $C_{28}H_{38}$



Zentral-*r*(C-C), Å

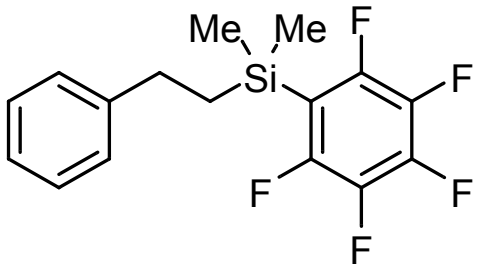
B3LYP/6-31G(d,p)	1.674*
B3LYP-D3/6-31G(d,p)	1.653*
B97D/6-31G(d,p)	1.668*
M06-2X/6-31G(d,p)	1.648*
XRD, Einkristall	**1.647(4)***
GED, Gasphase	**1.630(5)**

A. A. Fokin et al., *J. Am. Chem. Soc.,* 2017, 139, 16696.

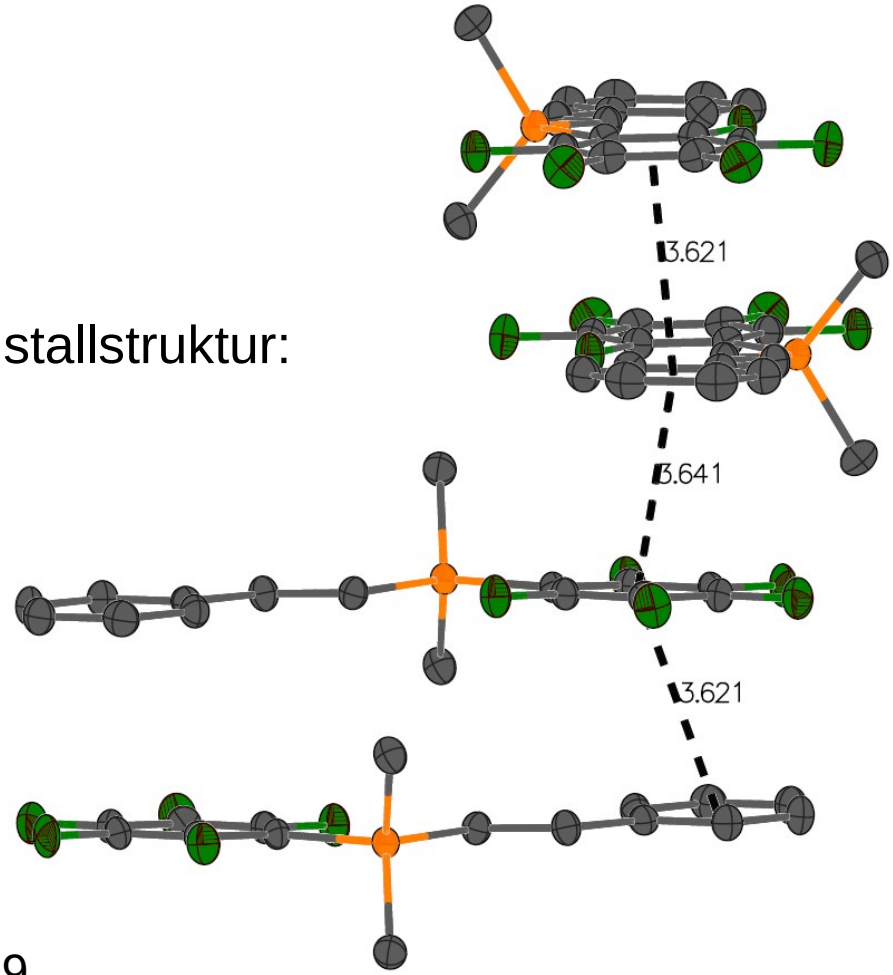
Übersichtsartikel:
N. W. Mitzel, J.-H. Lamm,
Acc. Chem. Res., 2023, 56, 3379.

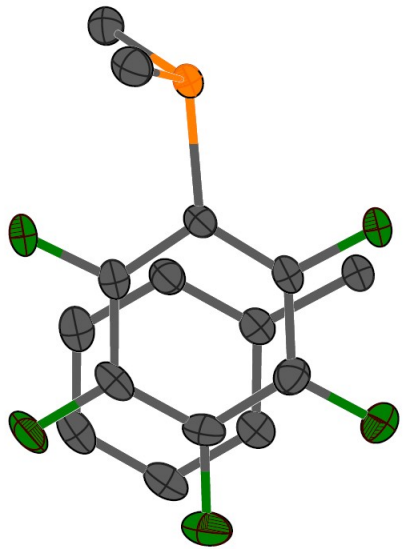
Dispersion + Polarität

$H_5C_6(CH_2)_2Si(Me)_2C_6F_5$



Kristallstruktur:





S. Blomeyer et al., *Angew. Chem. Int. Ed.* 2017, 56, 13259.

Vgl: $C_6H_6 \cdot C_6F_6$ – Kristallstruktur

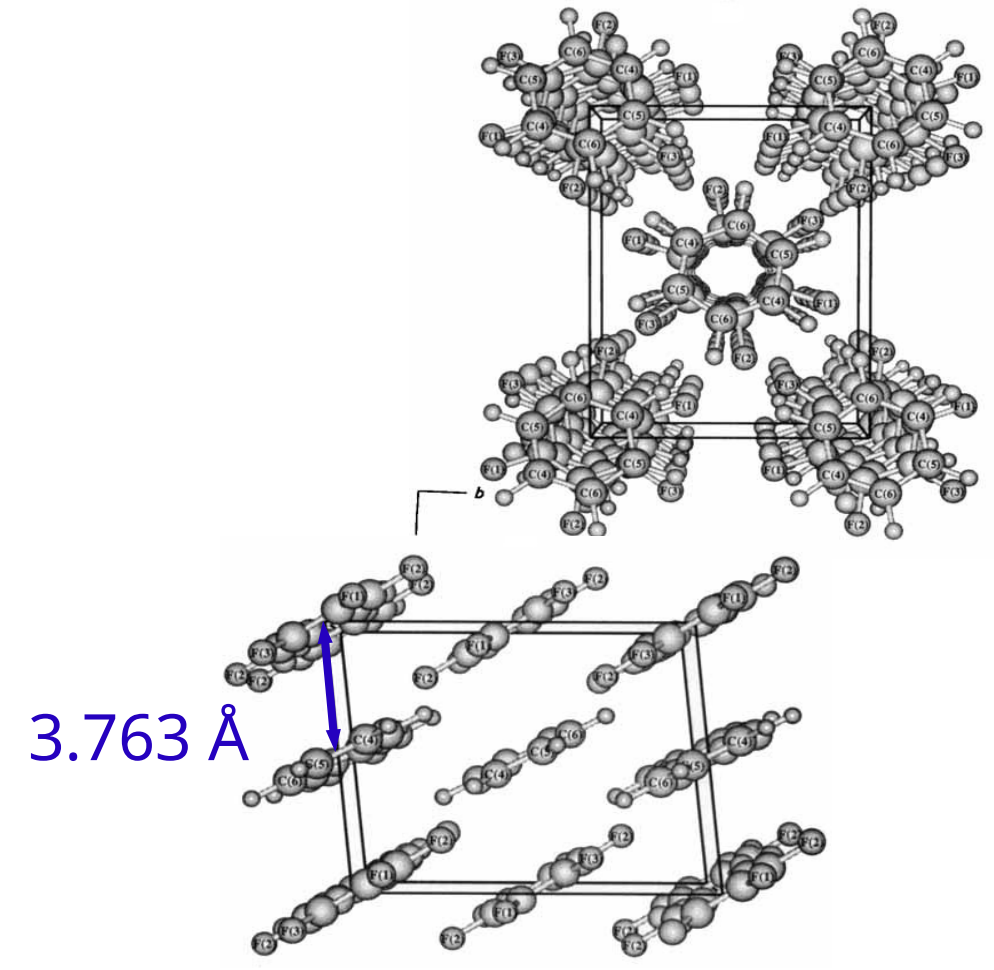
$C_6H_6 + C_6F_6$

Smp. 6°C | Smp. 4°C

↓

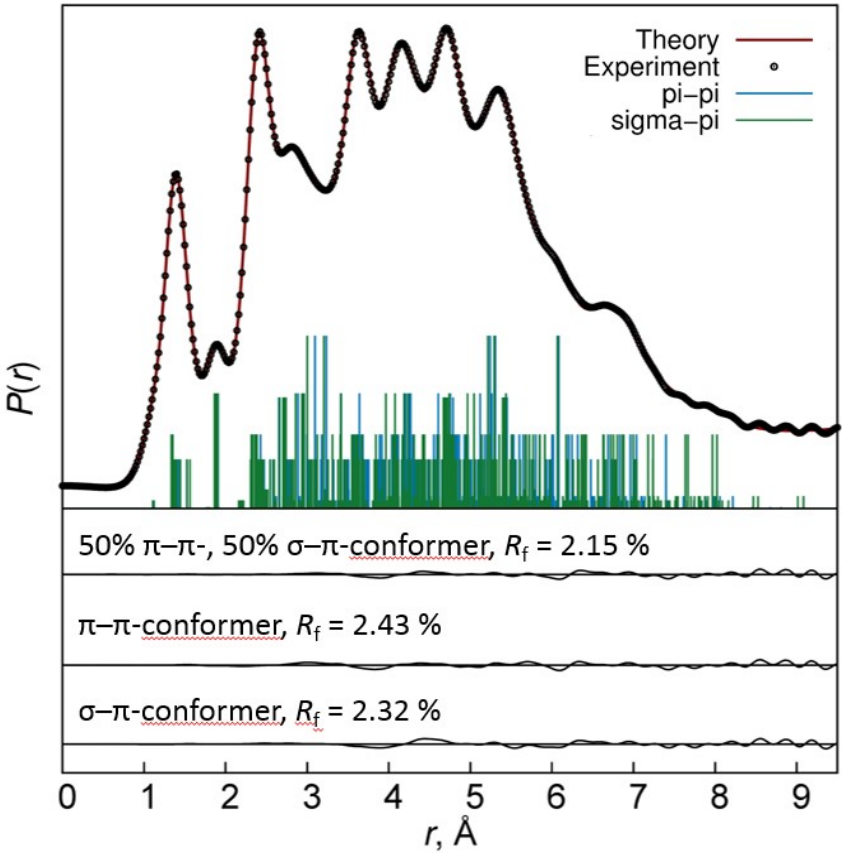
$C_6H_6 \cdot C_6F_6$

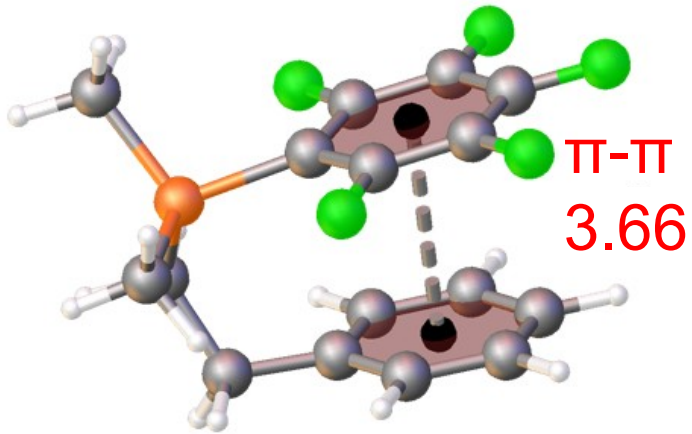
Smp. 24°C

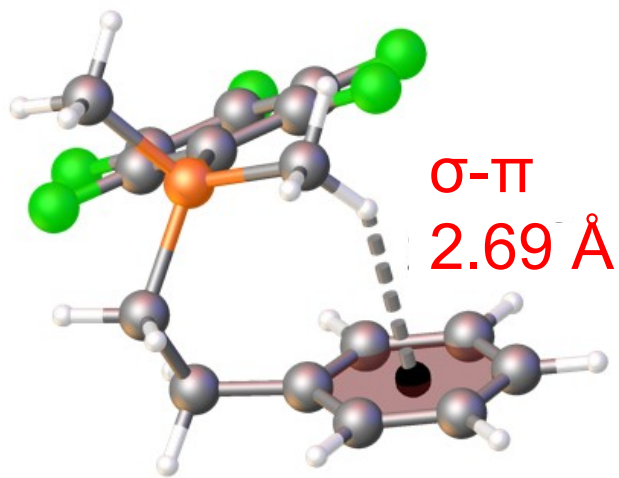


J. H. Williams,
J. K. Cockcroft, N. Fitch,
Angew. Chem. Int. Ed. **1992**, *31*, 1655

$H_5C_6(CH_2)_2Si(Me)_2C_6F_5$ – GED

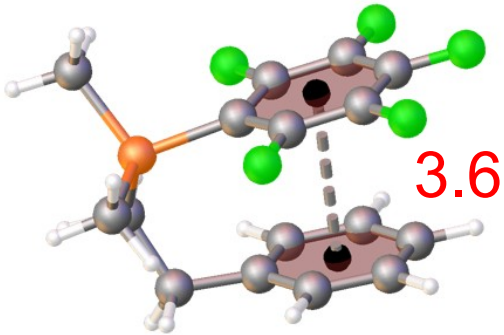




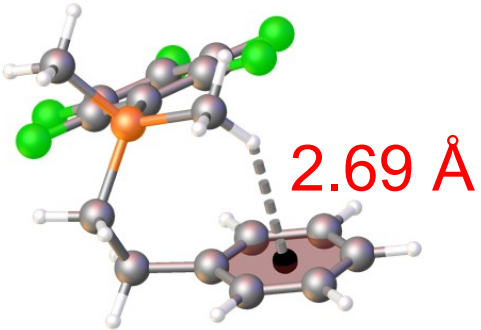


S. Blomeyer et al., *Angew. Chem. Int. Ed.* 2017, 56, 13259.

Gasphase/Festkörper



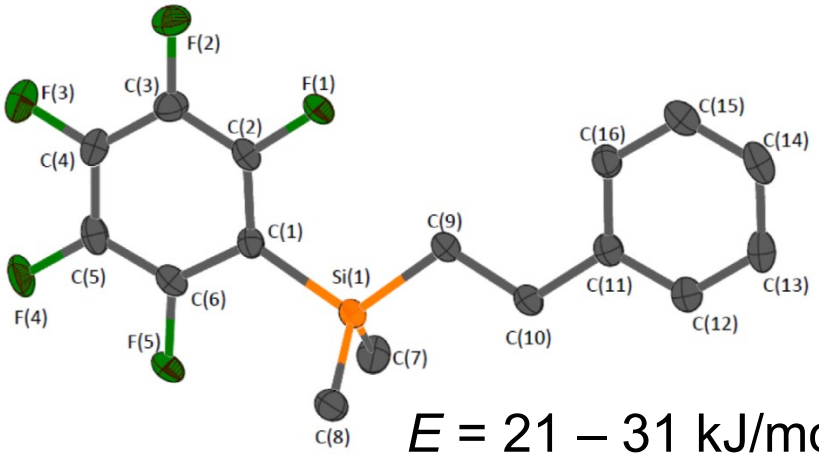
E = 0 kJ/mol*



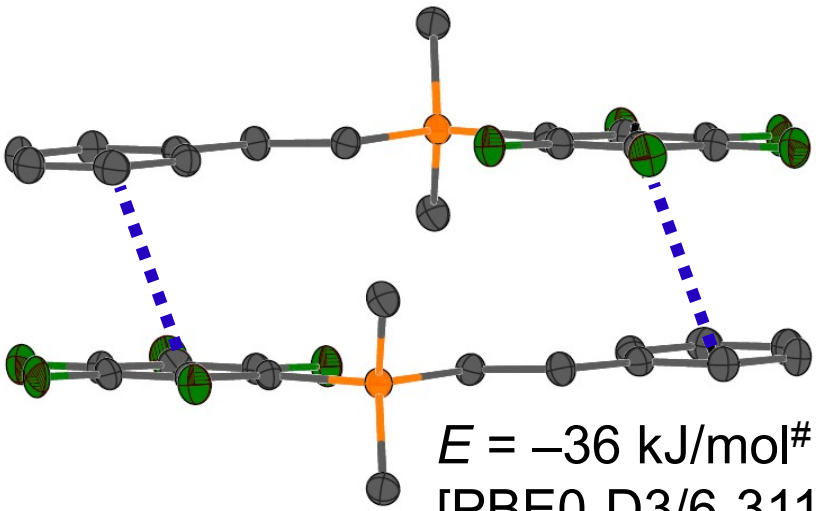
E = 6 – 9 kJ/mol*

* Einzelmolekül mit
B97D/
TPSS-D3/
PBE0-D3/
B3LYP-D3/
B2PLYP-D3

Vgl. Kristall:



E = 21 – 31 kJ/mol*



E = –36 kJ/mol#
[PBE0-D3/6-311G(d,p)]

Molekül(e) des Tages

Decamethylsilicocene – The First Stable Silicon(II) Compound: Synthesis, Structure, and Bonding

Peter Jutzi*[a], Udo Holtmann[a], Dieter Kanne[a], Carl Krüger[b], Richard Blom[c], Rolf Gleiter[d], and Isabella Hyla-Kryspin[d]

Fakultät für Chemie der Universität Bielefeld[a],
Universitätsstraße, D-4800 Bielefeld, F.R.G.

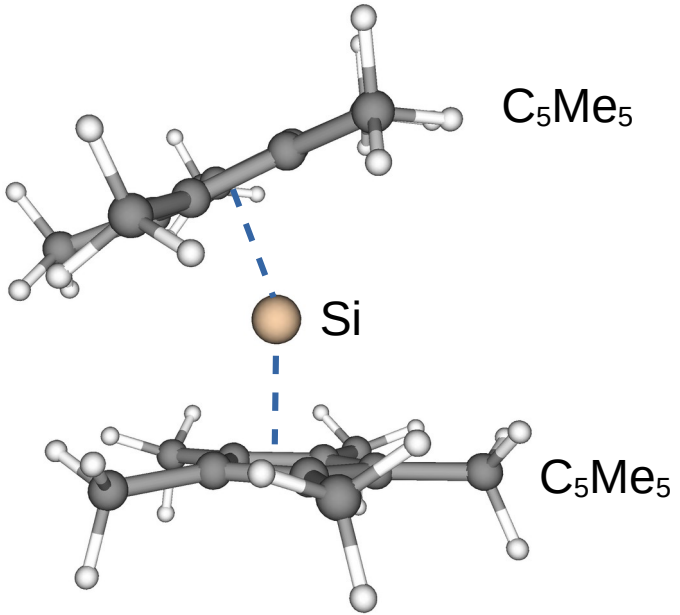
Max-Planck-Institut für Kohlenforschung[b],
Kaiser-Wilhelm-Platz 1, D-4330 Mülheim-Ruhr, F.R.G.

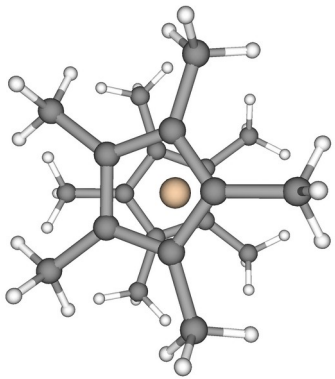
Department of Chemistry, University of Oslo[c],
Blindern, N-0315 Oslo 3, Norway

Organisch-Chemisches Institut der Universität Heidelberg[d],
Im Neuenheimer Feld 270, D-6900 Heidelberg, F.R.G.

Chemische Berichte, 122 (1989) 1629 - 1639

Rechnungen





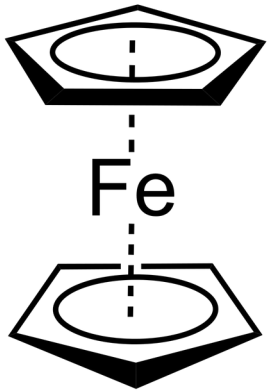
Gestaffelt?

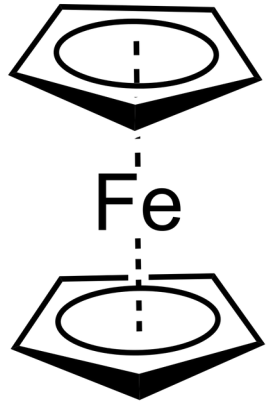
Ekliptisch?

Gewinkelt?

Vgl. Ferrocen:

gestreckt





~Gestaffelt

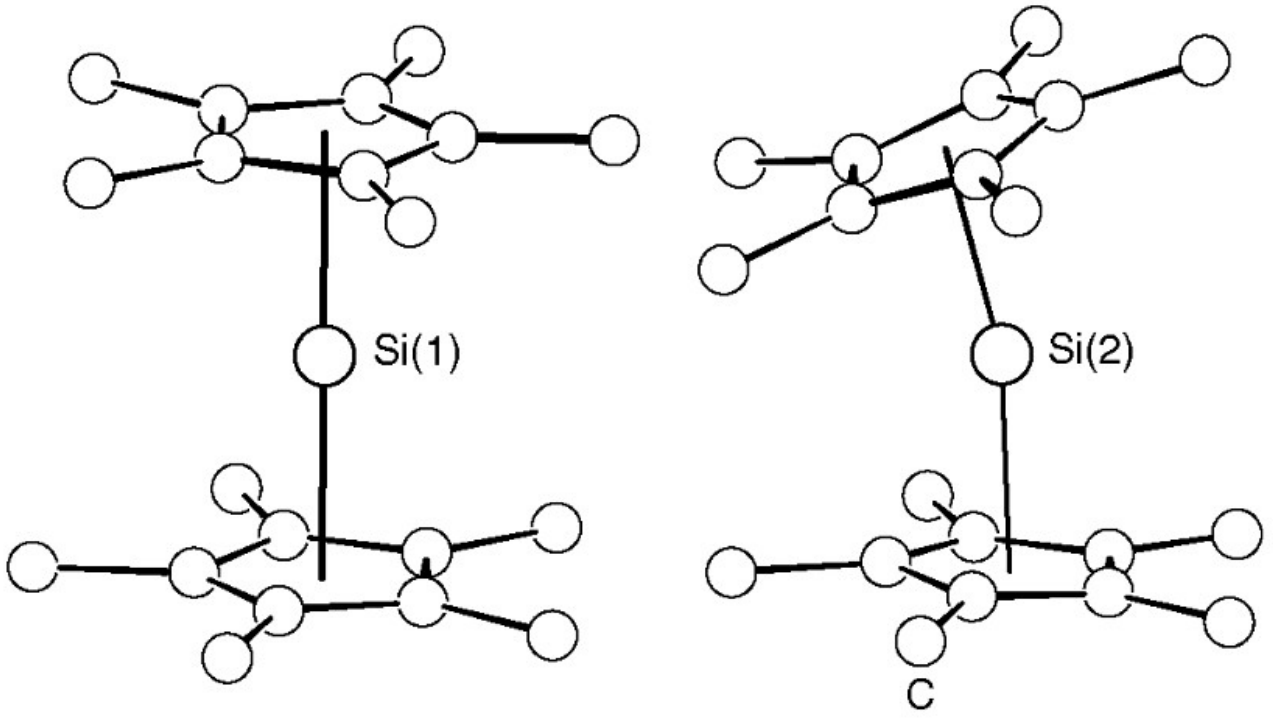
im Kristall

(**ND**, Brock, 1997

T-abh! Fehlordnung!)

Ekliptisch
in der Gasphase
(**GED**, Haaland, 1968)

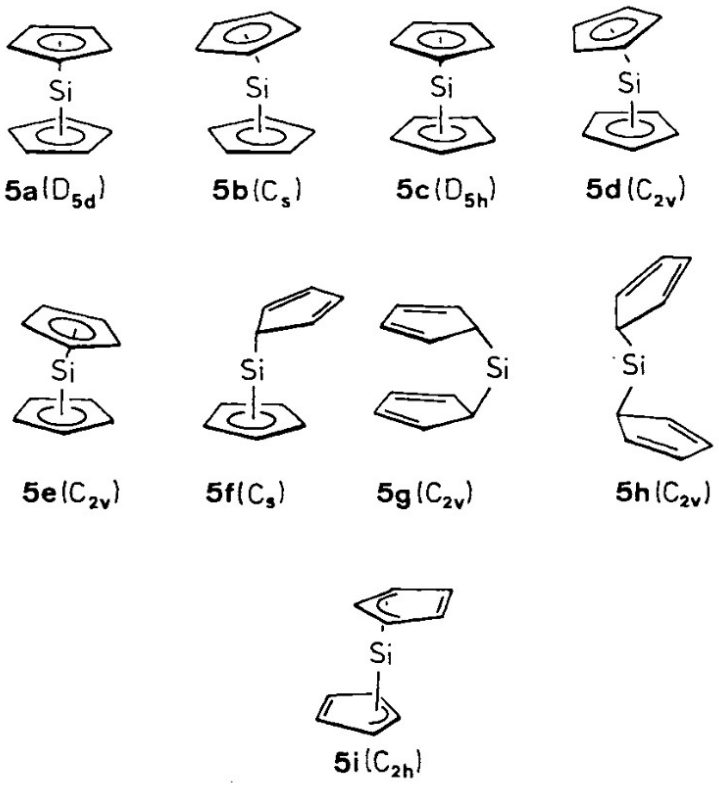
Kristallstruktur



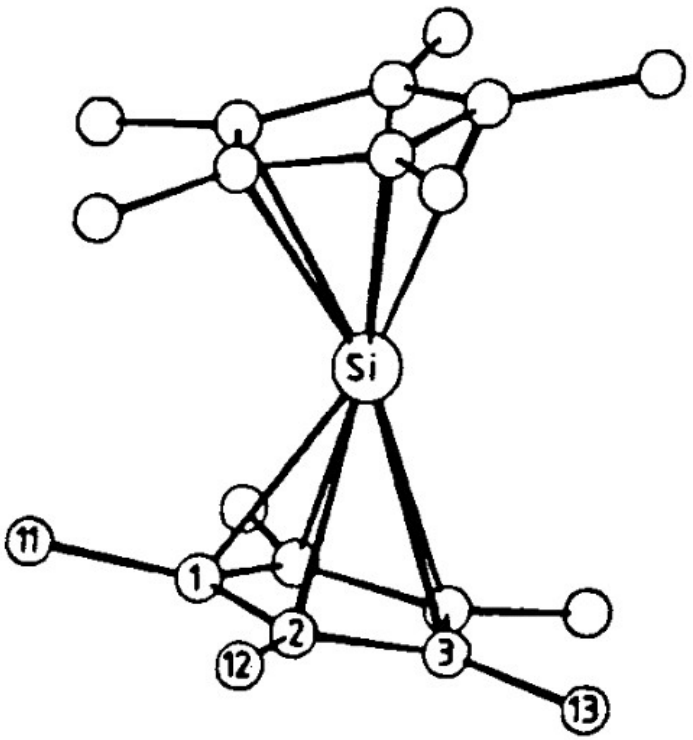
Gestaffelt, gestreckt **und** gewinkelt!

Gasphase: GED

Getestete Modelle



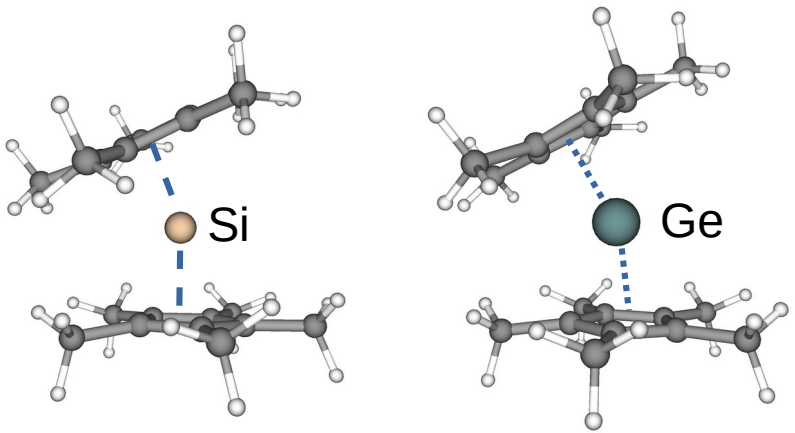
Das beste Modell (**5b**) ist gestaffelt und gewinkelt



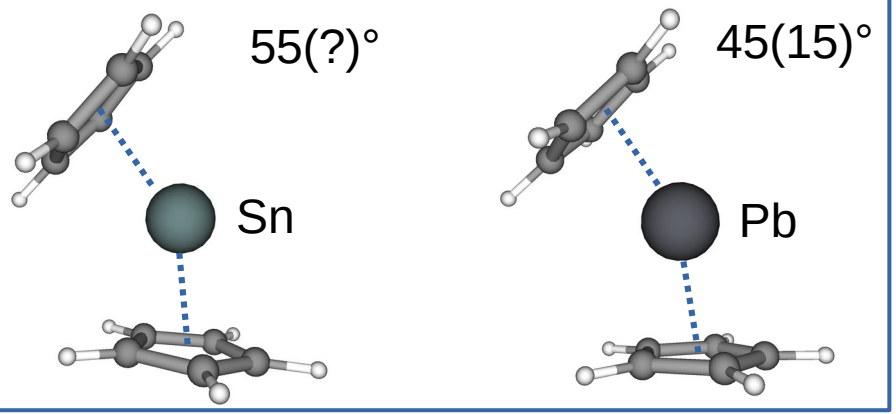
Gasphase / Festkörper

	Method[a]	d [b] [Å]	r(M–C)[c] [Å]	δ[d] [Å]	∢ C_5C_5 [°]	Ref.
$(Me_5C_5)_2Si$ **4a**	X	2.11	2.42(1)	0	0	this work
$(Me_5C_5)_2Si$ **4b**	X	2.12	2.42(6)	0.023	25.3	this work
$(Me_5C_5)_2Si$ **4**	GED	2.129(12)	2.45(2)	0.021	22.4(12)	this work
$(Me_5C_5)_2Ge$ **6**	GED	2.21(3)	2.52(3)	0.015	23(3)	[14]
$(Me_5C_5)_2Sn$ **7**	X	2.39	2.68	0.023	36	[26]
$(Me_5C_5)_2Pb$ **8**	X	2.48	2.79	0.029	43	[27]

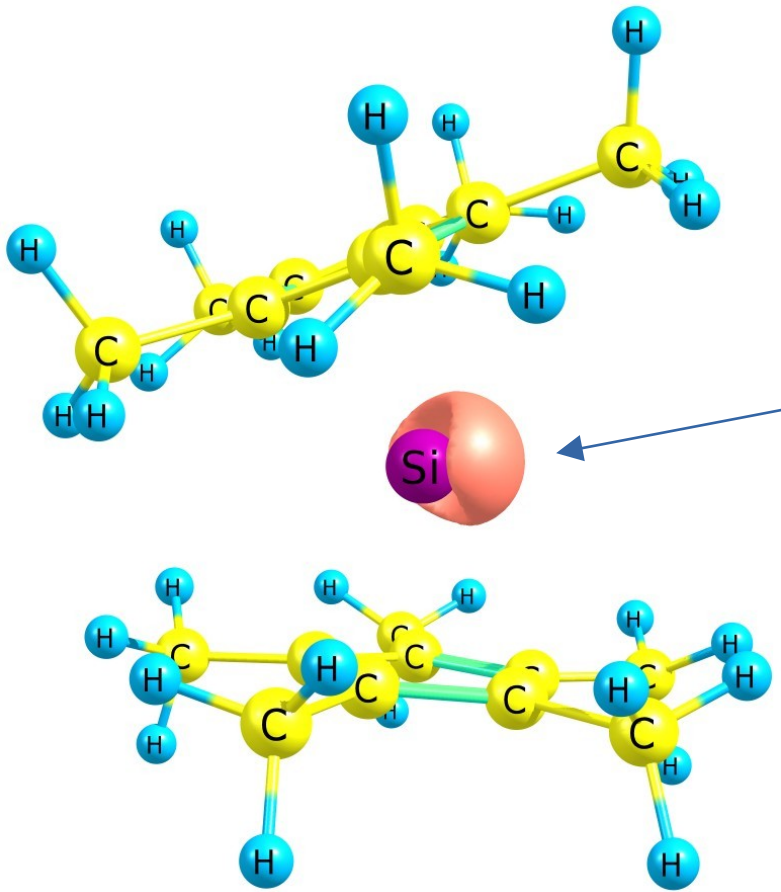
[a] X = X-ray crystallography, GED = gas-phase electron diffraction. – [b] The distance from the central atom to the ring centroid. – [c] Mean distances. – [d] Mean values of the distances from the center of mass of each C_5 ring to the projection of the group 14 element into the ring plane.



Vgl. GED f. $Sn(Cp)_2$ und $Pb(Cp)_2$:



$Si(C_5Me_5)_2$: NBO



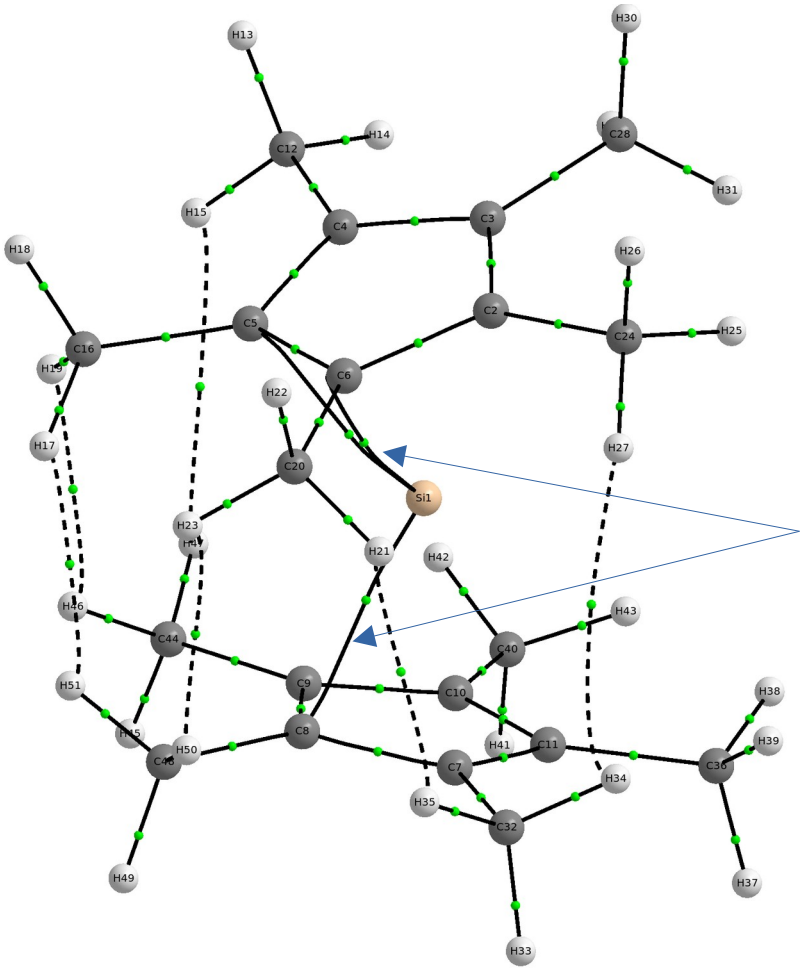
NBO: **N**atural **B**ond **O**rbitals
(F. Weinhold)

[PBE0-D3BJ/def2-TZVPP]

NBO #26: freies Elektronenpaar an Si,
n = 1.98 e,
keine WWs mit anderen NBOs!

Stereochemisch aktiv!

$Si(C_5Me_5)_2$: QTAIM



QTAIM:
Quantum **T**heory of **A**toms **I**n **M**olecules
(R. Bader)

Bindungspfaden für Si–C

Quellen / Literatur

- D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, Structural Methods in Molecular Inorganic Chemistry, John Wiley & Sons, Chichester, 2013.
- K. R. Leopold, M. Canagaratna, J. A. Phillips, *Acc. Chem. Res.,* 1997, *30*, 57
- N. W. Mitzel, J.-H. Lamm, *Acc. Chem. Res.* 2023, 56, 3379–3391.
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