Mitzel Group
inorganic & structural chemistry

Intramolecular dispersion interactions

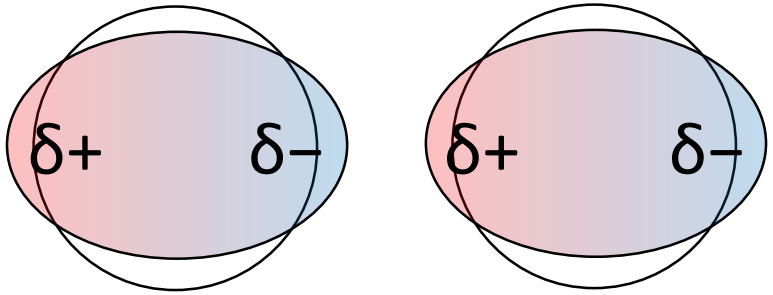
Sebastian Blomeyer

17th European Symposium on Gas-Phase Electron Diffraction

Hirschegg, Kleinwalsertal, Austria

04/07/2017

London dispersion forces

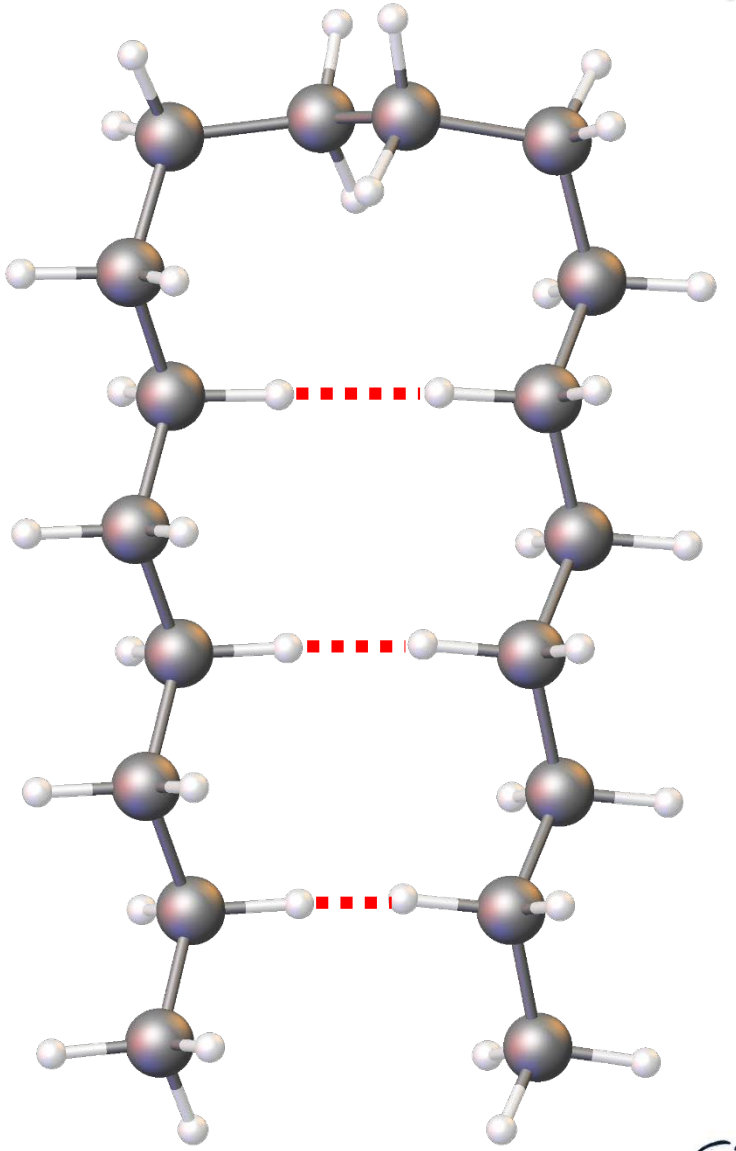


$E < 10$ kJ mol^{-1}

hydrogen bonds

$E \approx 40$ kJ mol^{-1}

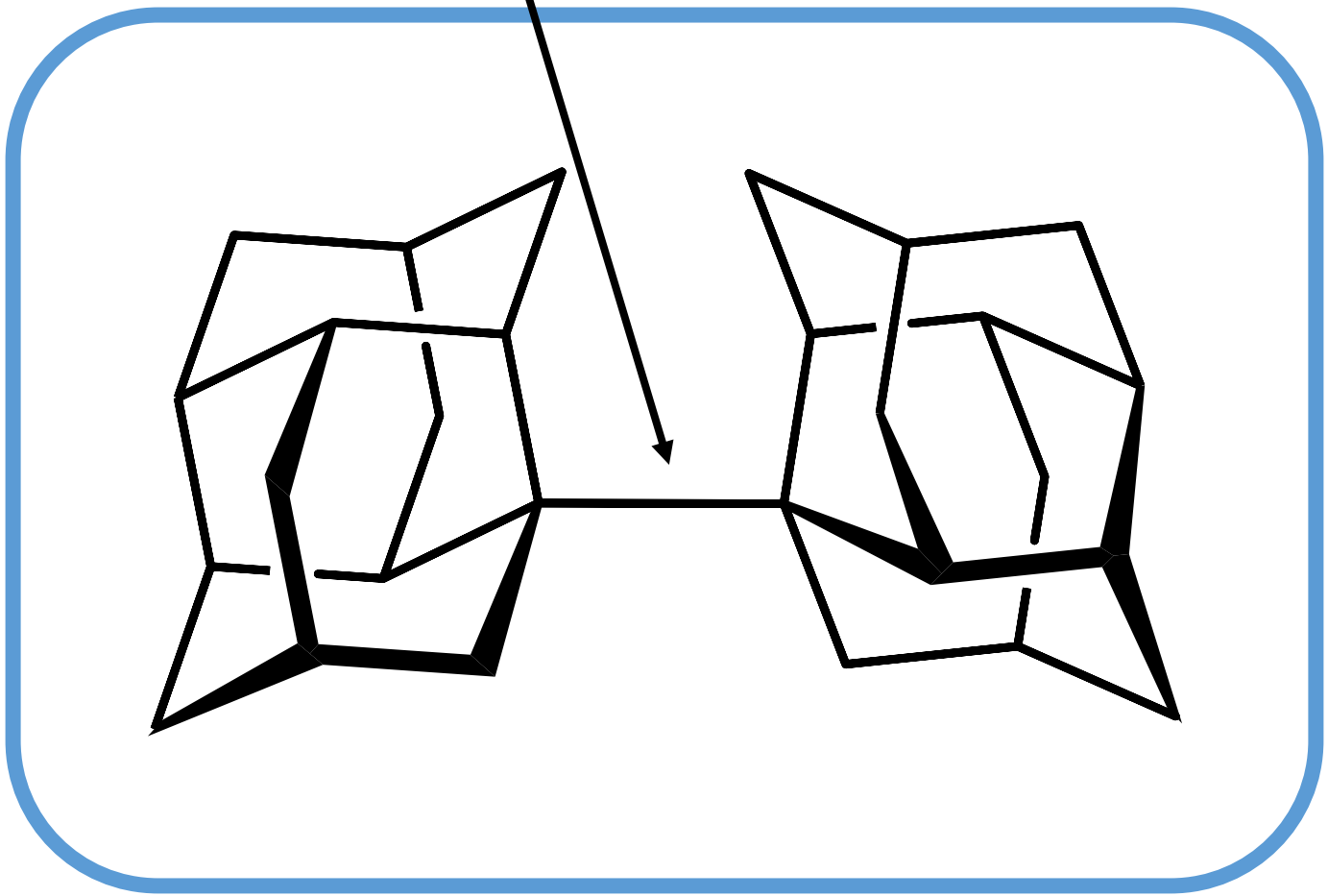
	boiling point / K[1]
He	4
Ne	27
Ar	87
Kr	120
Xe	165



[1] GESTIS Stoffdatenbank, http://gestis.itrust.de.
[2] N. O. B. Lüttschwager, T. N. Wassermann, R. A. Mata, M. A. Suhm, *Angew. Chem. Int. Ed*. **2013**, *52*, 463 – 466.

XRD: 1.647(2) Å[3] ↔ propane: 1.521(1) Å[4]

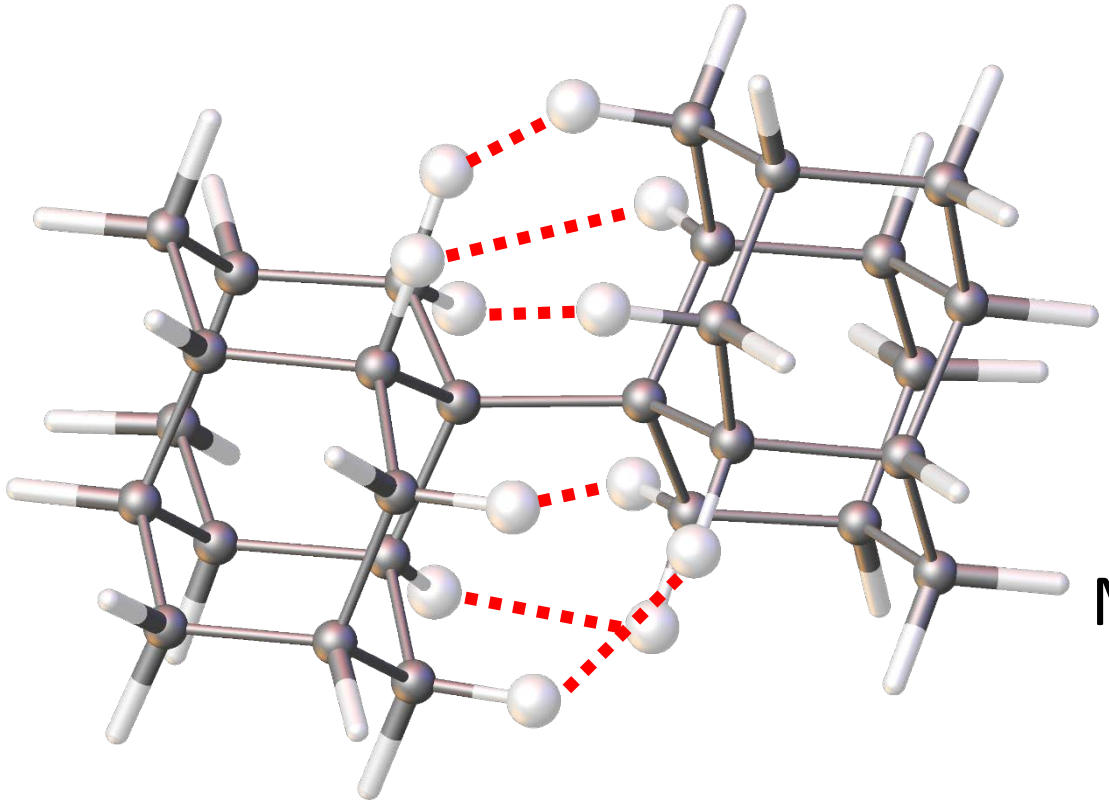
stable up to 350 °C



[3] 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 – 311.

[4] R. Boese, H.-C. Weiss, D. Bläser, *Angew. Chem.* **1999**, *38*, 988 – 992.

QC



* DFT/cc-pVDZ[5]

\# MP2/cc-pVTZ

MP2# B3LYP-D* M06-2X* B3LYP-D3* B3LYP*

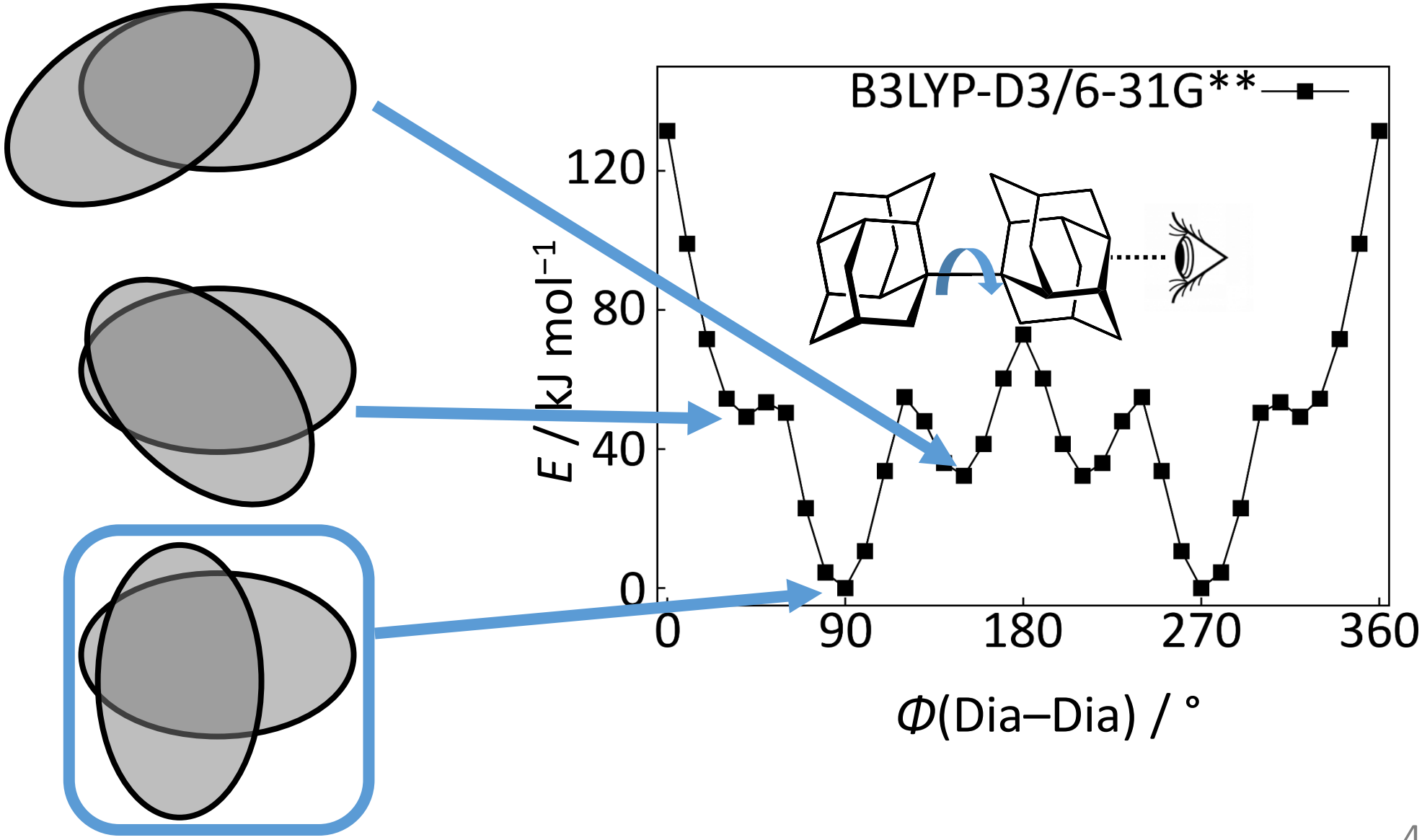
1.62 1.63 1.64 1.65 1.66 1.67

$d(C–C)_{central}$ / Å

GED → benchmark

[5] 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 – 13650.

QC



T = 583 K

χ = 99 %

GED

$d(\text{C–C})_{\text{central}}$

1.630(5) Å

$d(\text{C–C})_{\text{intra-fragment}}$

1.530(1) – 1.573(1) Å

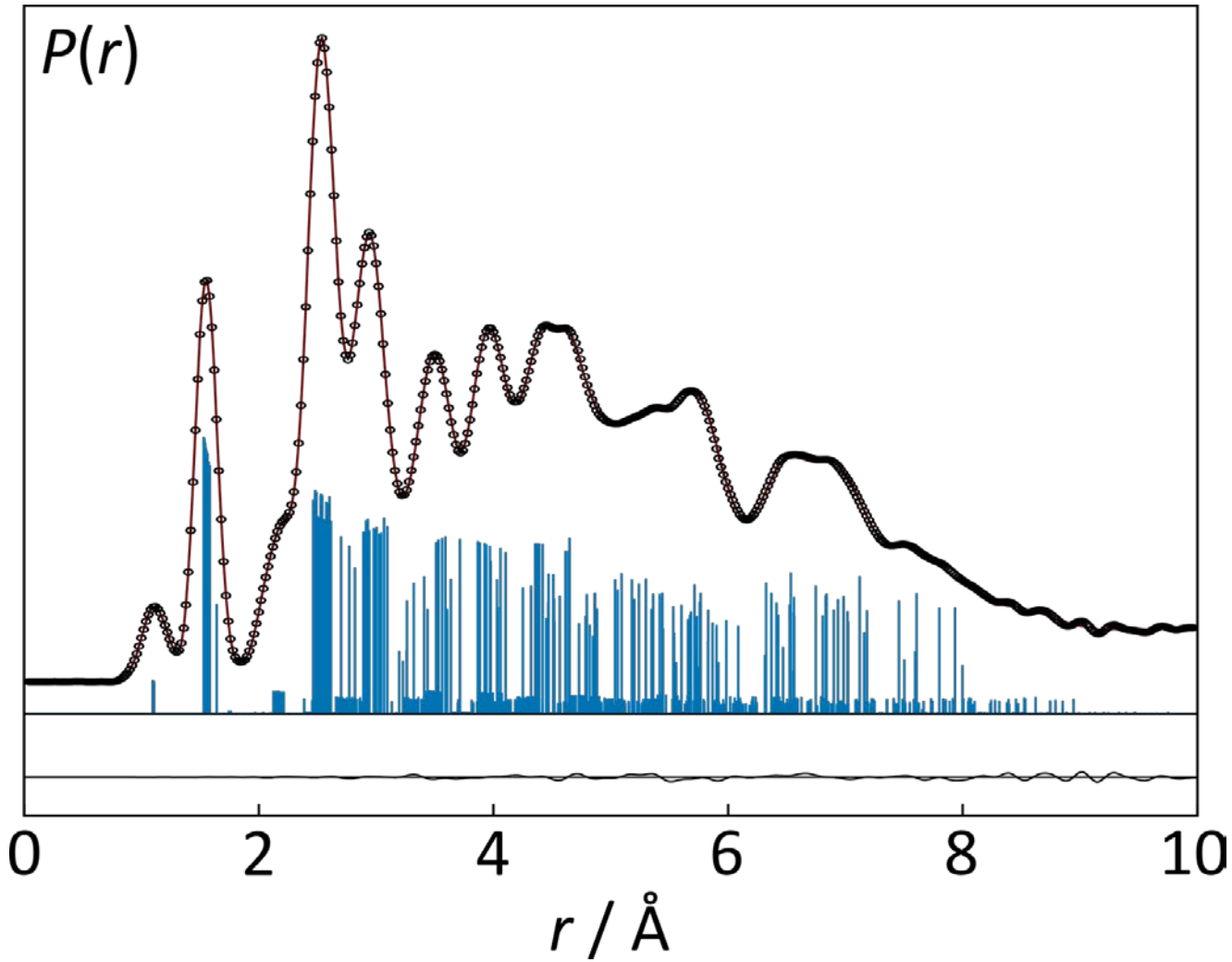
$d(\text{C–H})$

1.095(2) – 1.106(2) Å

$\Phi(\text{Dia–Dia})$

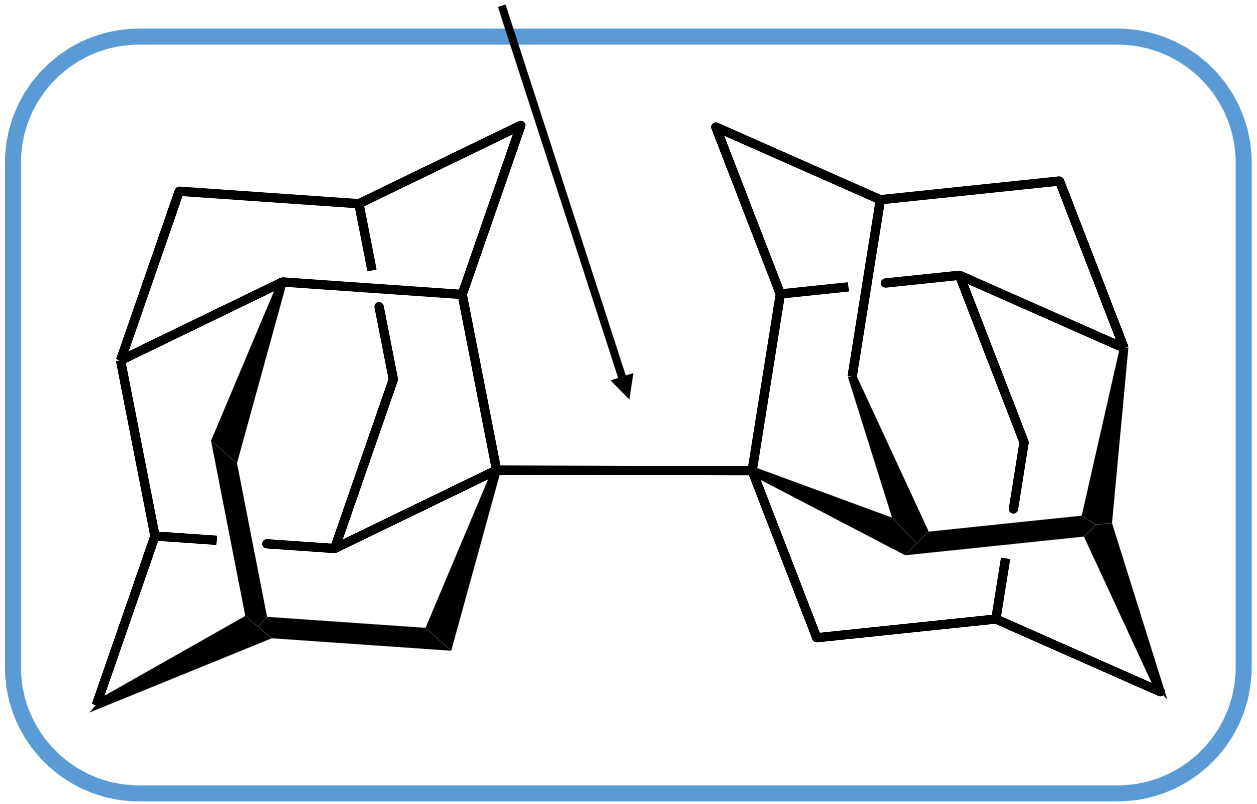
87(2)°

R_f = 1.9 %

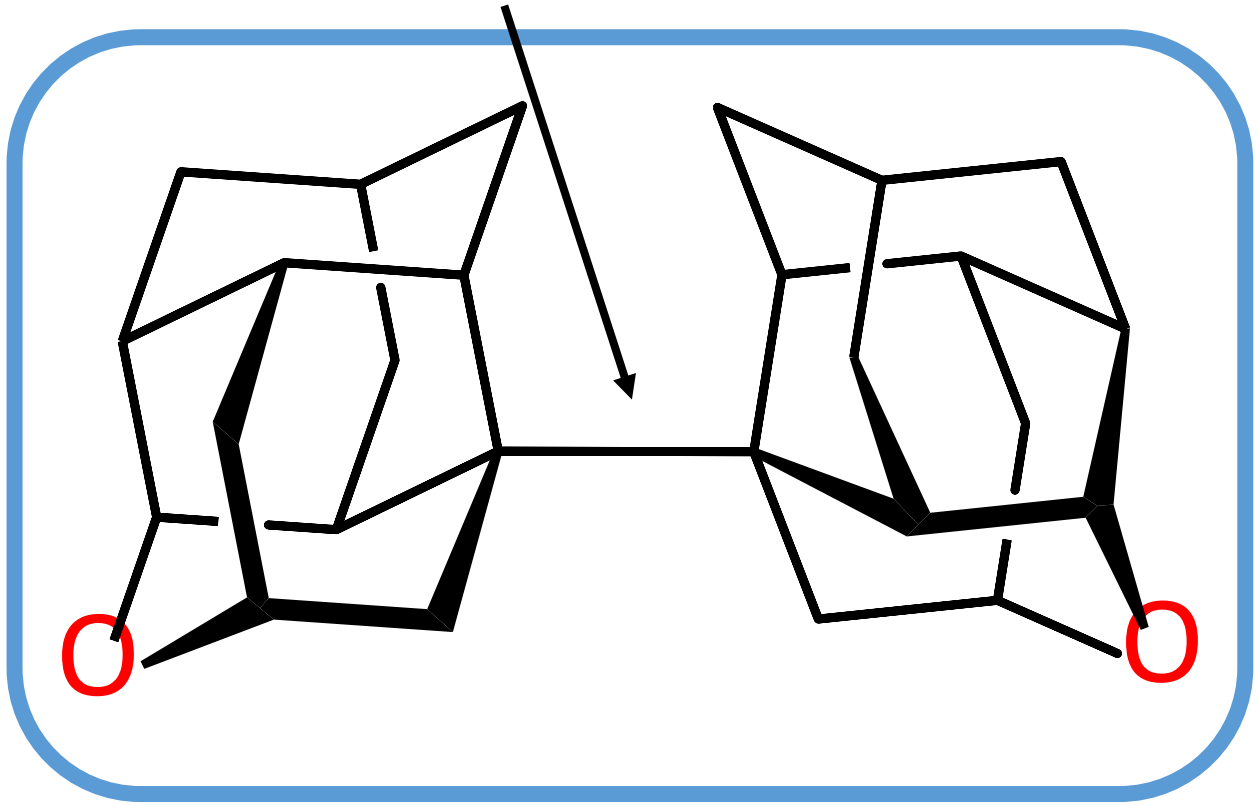


XRD: 1.647(2) Å[3]

GED: 1.630(5) Å



XRD: 1.643(4) Å



[3] 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 – 311.

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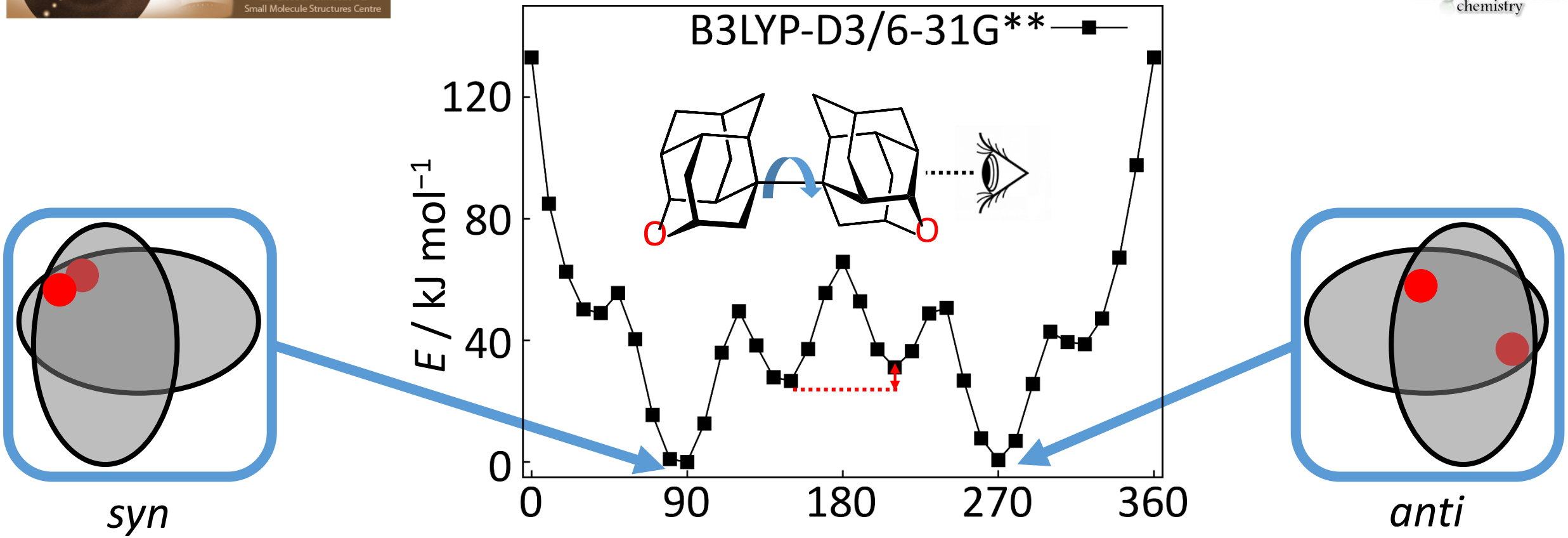
QC



$\Delta E_{syn-anti}$ = 1.2 kJ mol^{-1}
→ 2 conformer model

additional parameters:

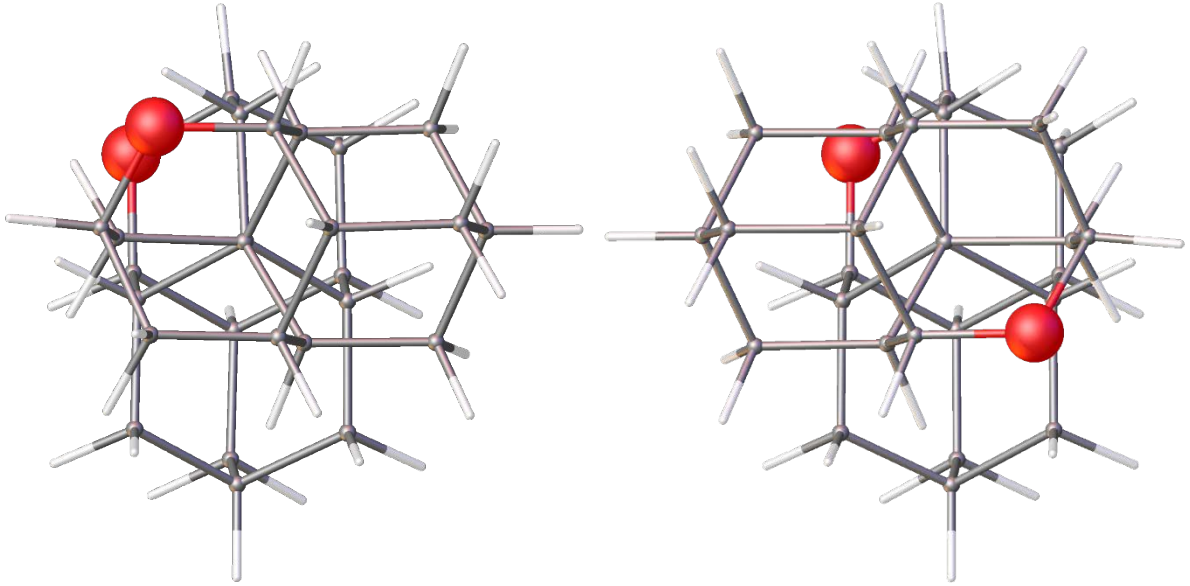
- d(C–O)
- Φ_2(Dia–Dia)
- $\chi_{syn:anti}$

FTMW

syn

$\mu_A = \mu_B = 0$ D

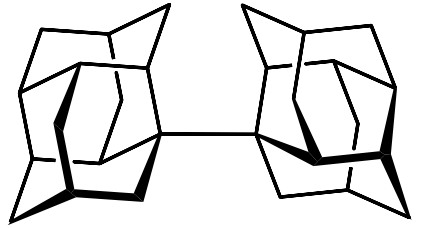
$\mu_C = 2.5$ D*



anti

$\mu_A = \mu_B = 0$ D

$\mu_C = 0.4$ D*



$\mu_A = \mu_B = 0$ D

$\mu_C = 0.05$ D*

*PBEh-3c

rotational constants

A = 396.3518(1) MHz

B = 158.91216(8) MHz

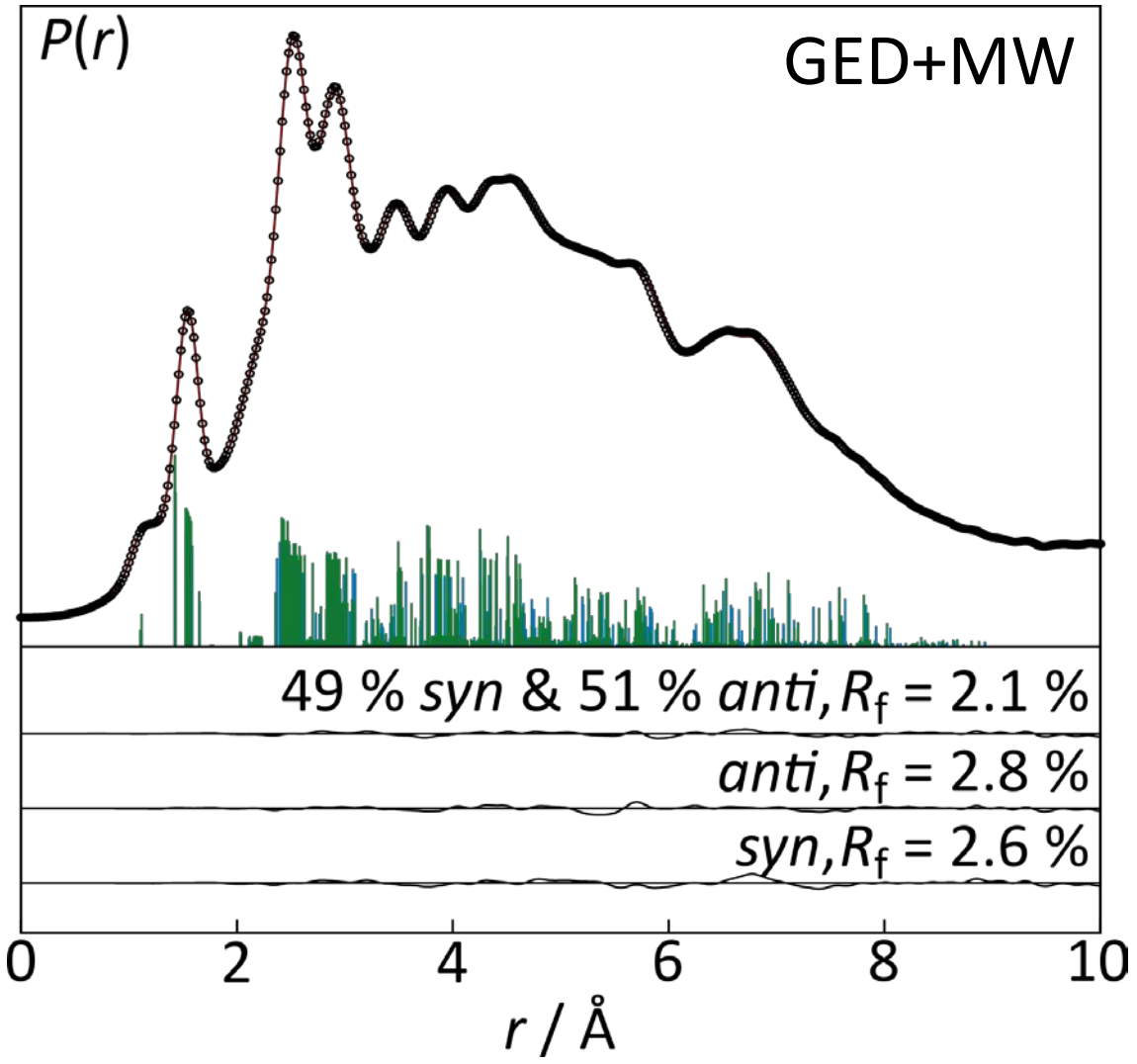
C = 158.83150(8) MHz

MW → B_0 → B_e ↘

GED → r_a → r_e ↗

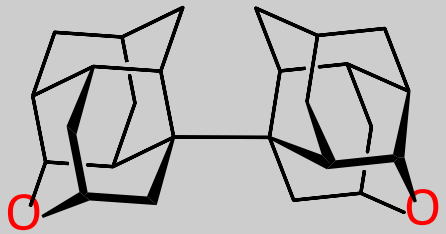
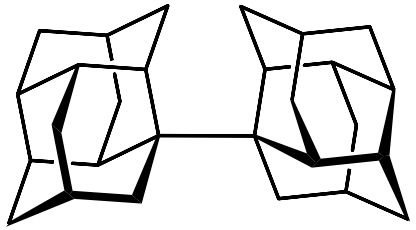
GED+MW structure refinement

GED & FTMW



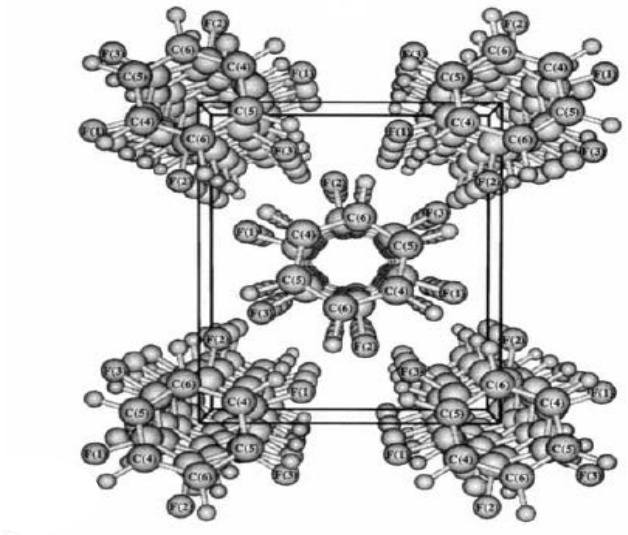
	GED	GED+MW
R_f / %	2.1	2.1
syn:*anti*	50:50(11)	49:51(14)
Φ_{syn} / °	87(2)	87(1)
Φ_{anti} / °	–92(2)	–93(2)
d(C–C)$_{central}$ / Å	1.632(9)	1.632(5)

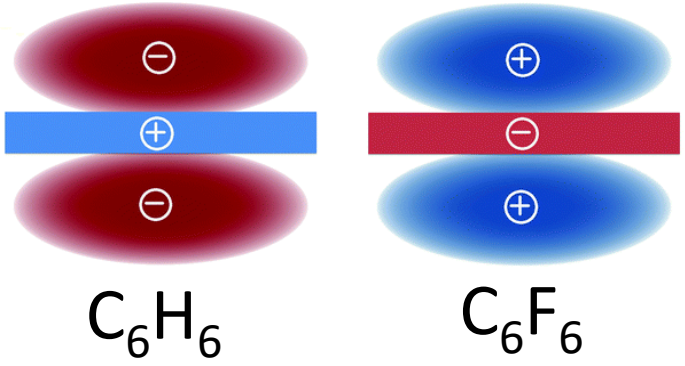
experiment/theory

	$d(C–C)_{central}$ / Å				
	GED	GED+MW	M06-2X/ cc-pVDZ	MP2/ cc-pVTZ	XRD
 *syn*	1.632(9)	1.632(5)	1.636	1.622	1.643(4)
	1.630(5)	–	1.646	1.633	1.647(2)

London dispersion forces: π–π

	m.p. / °C[6]
C_6H_6	6
C_6F_6	4
C_6H_6:C_6F_6 (1:1)	24





π-stacking in general[9]

magnitude: dispersion

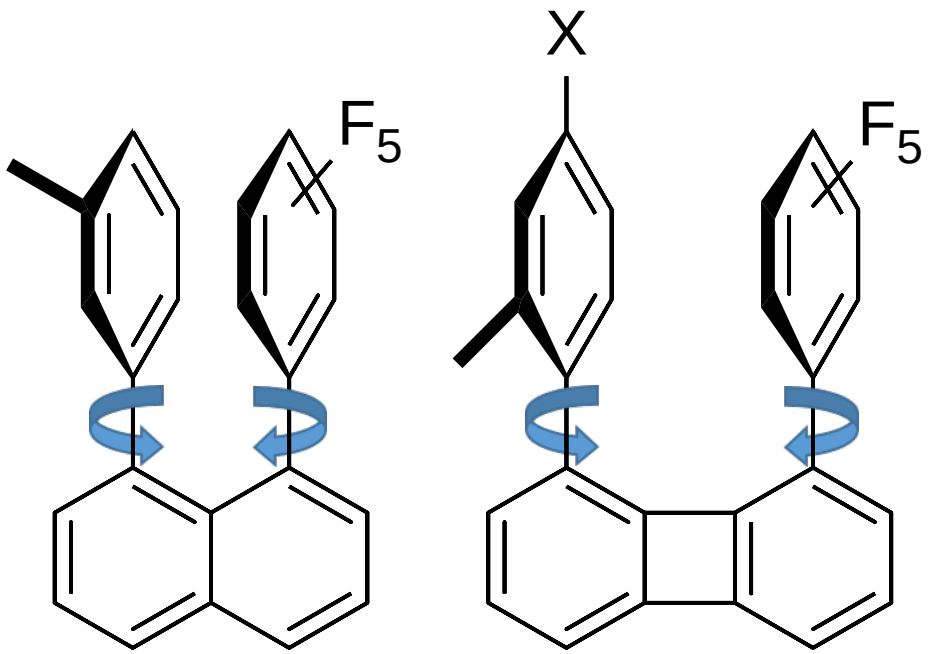
substituent effects: electrostatic

C_6H_6–C_6F_6 dimer[10]

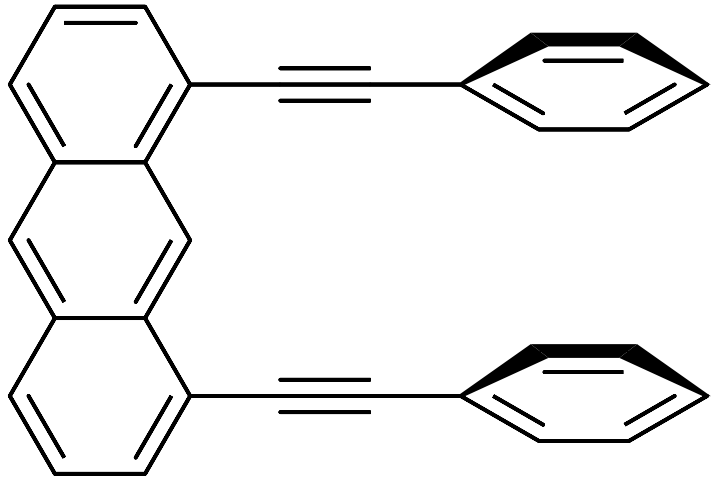
major source of attraction: dispersion

[6] C. R. Patrick, G. S. Prosser, *Nature* **1960**, *187*, 1021.
[7] J. H. Williams, J. K. Cockcroft, A. N. Fitch, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1655 – 1657.
[8] C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa, P. M. Deya, *Chem. Phys. Chem.* **2003**, *4*, 1344 – 1348.
[9] M. O. Sinnokrot, C. D. Sherrill, *J. Am. Chem. Soc.* **2004**, *126*, 7690 – 7697.
[10] S. Tsuzuki, T. Uchimaru, M. Mikami, *J. Phys. Chem. A* **2006**, *110*, 2027 – 2033.

London dispersion forces: π–π



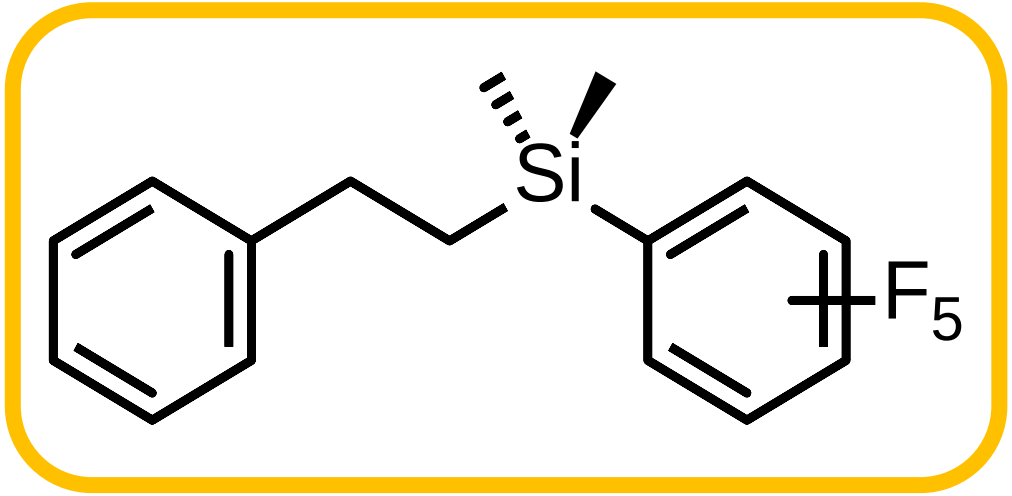
rotational dynamics (NMR)[11,12]

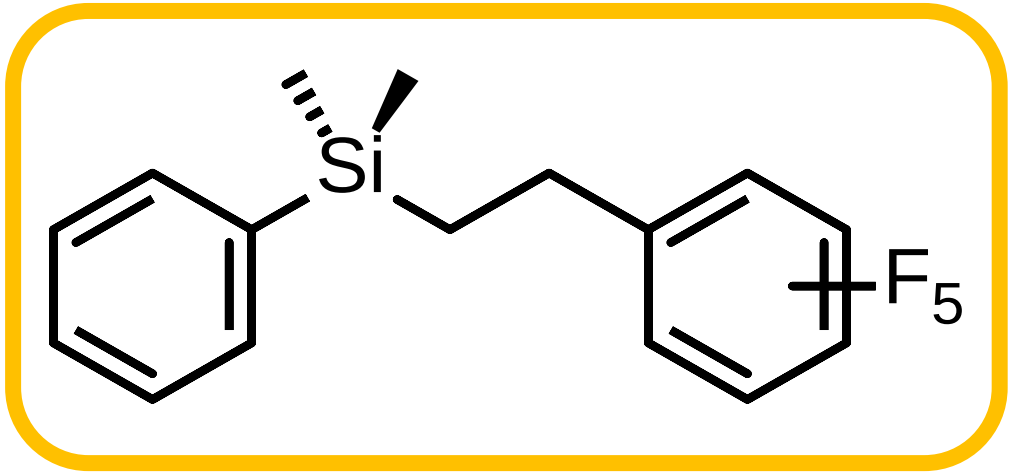


XRD: Anth–Ph interactions

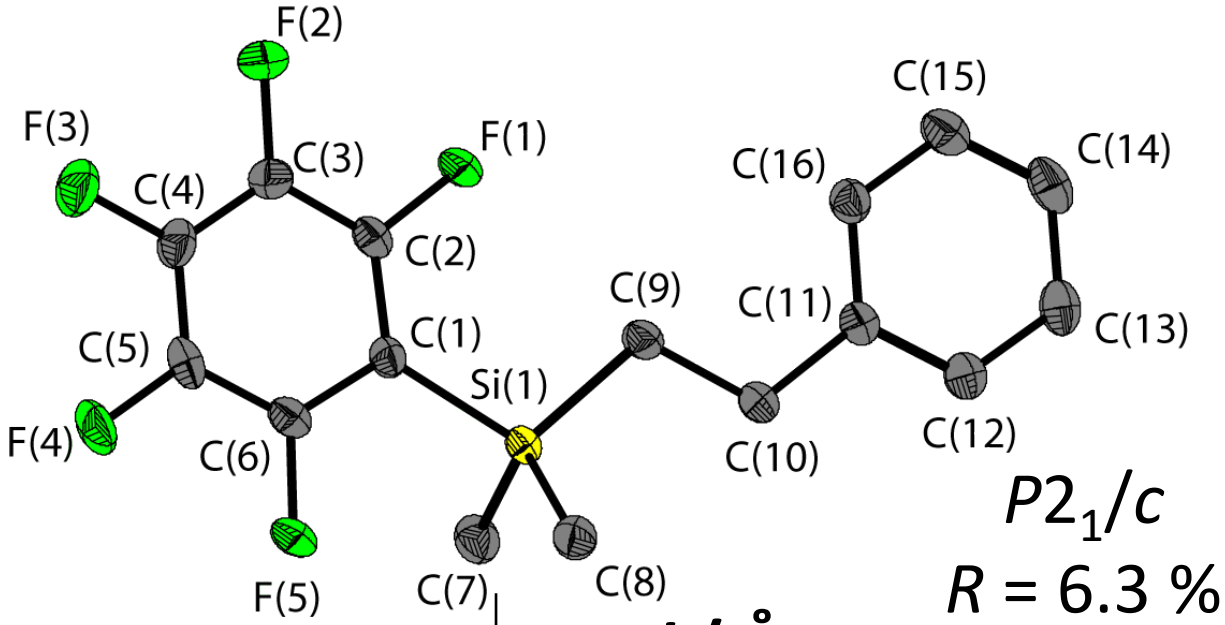
GED: Ph–Ph (parallel displaced)

[11] F. Cozzi, J. S. Siegel, *Pure Appl. Chem.* **1995**, *67*, 683.
[12] F. Cozzi, R. Annunziata, M. Benaglia, K. K. Baldridge, G. Aguirre, J. Estrada, Y. Sritana-Anant, J. S. Siegel, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2686.
[13] J.-H. Lamm, J. Horstmann, H.-G. Stammler, N. W. Mitzel, Yu. A. Zhabanov, N. V. Tverdova, A. A. Otlyotov, N. I. Giricheva, G. V. Girichev, *Org. Biomol. Chem.* **2015**, *13*, 8893.


Si
F5

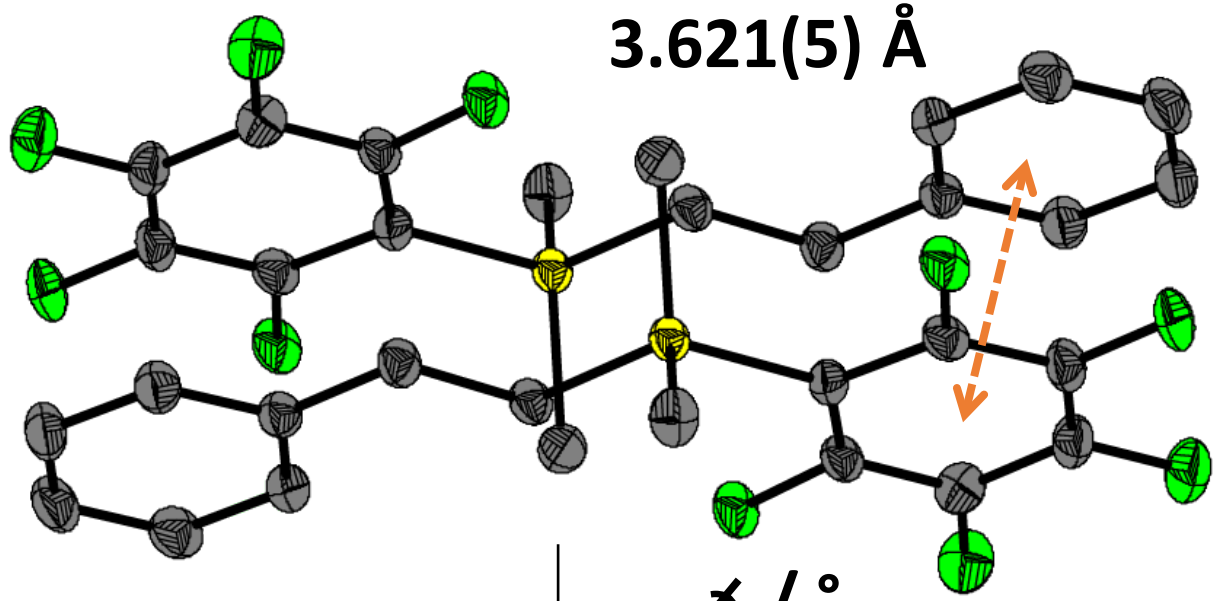

Si
F5

XRD



$P2_1/c$

R = 6.3 %

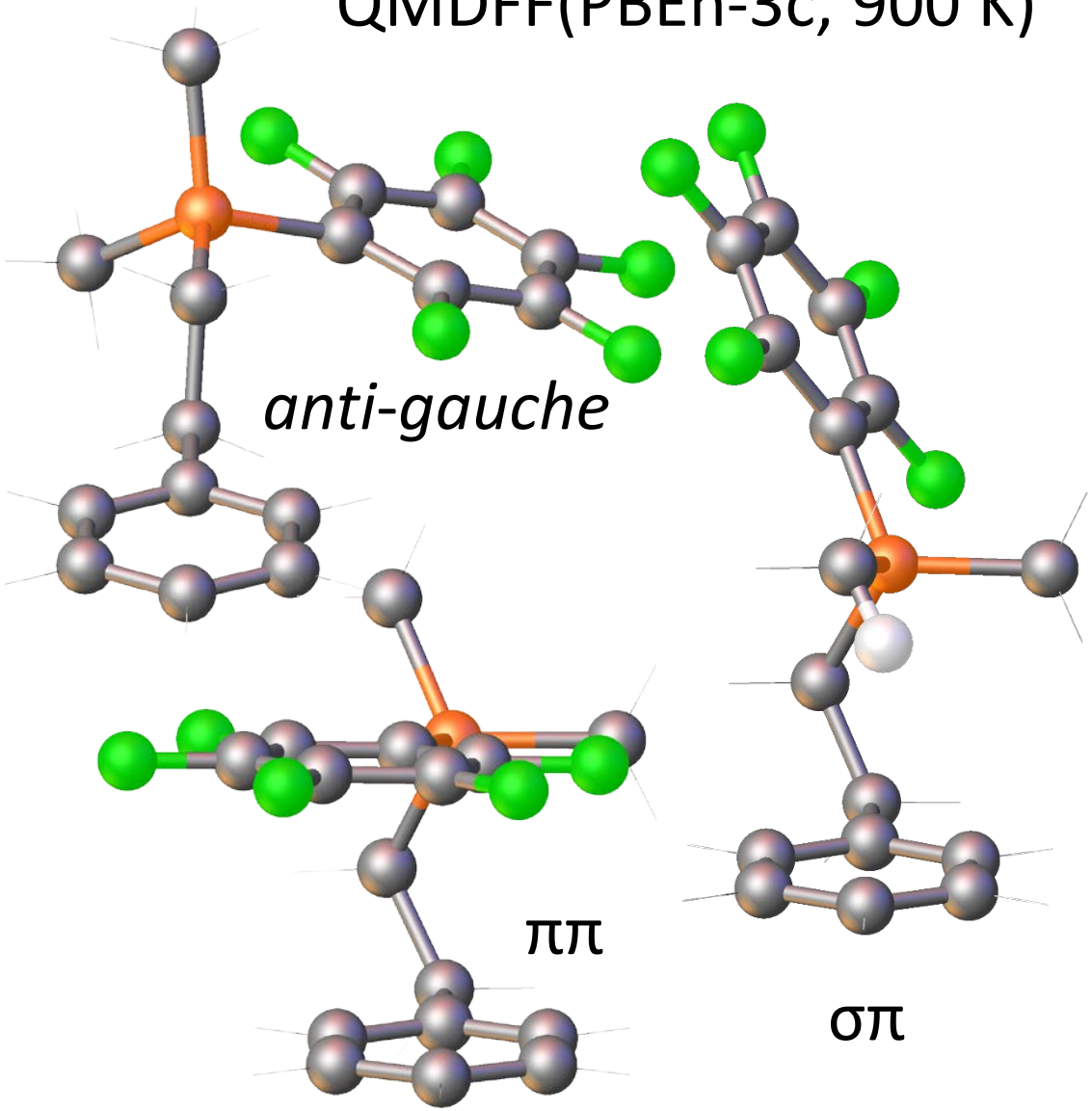


	***d* / Å**
C(1)–Si(1)	1.912(3)
Si(1)–C(9)	1.873(3)
C(9)–C(10)	1.528(4)
C(10)–C(11)	1.523(3)

	∢ / °
C(1)–Si(1)–C(9)	109.4(1)
Si(1)–C(9)–C(10)	112.9(2)
C(9)–C(10)–C(11)	116.1(2)

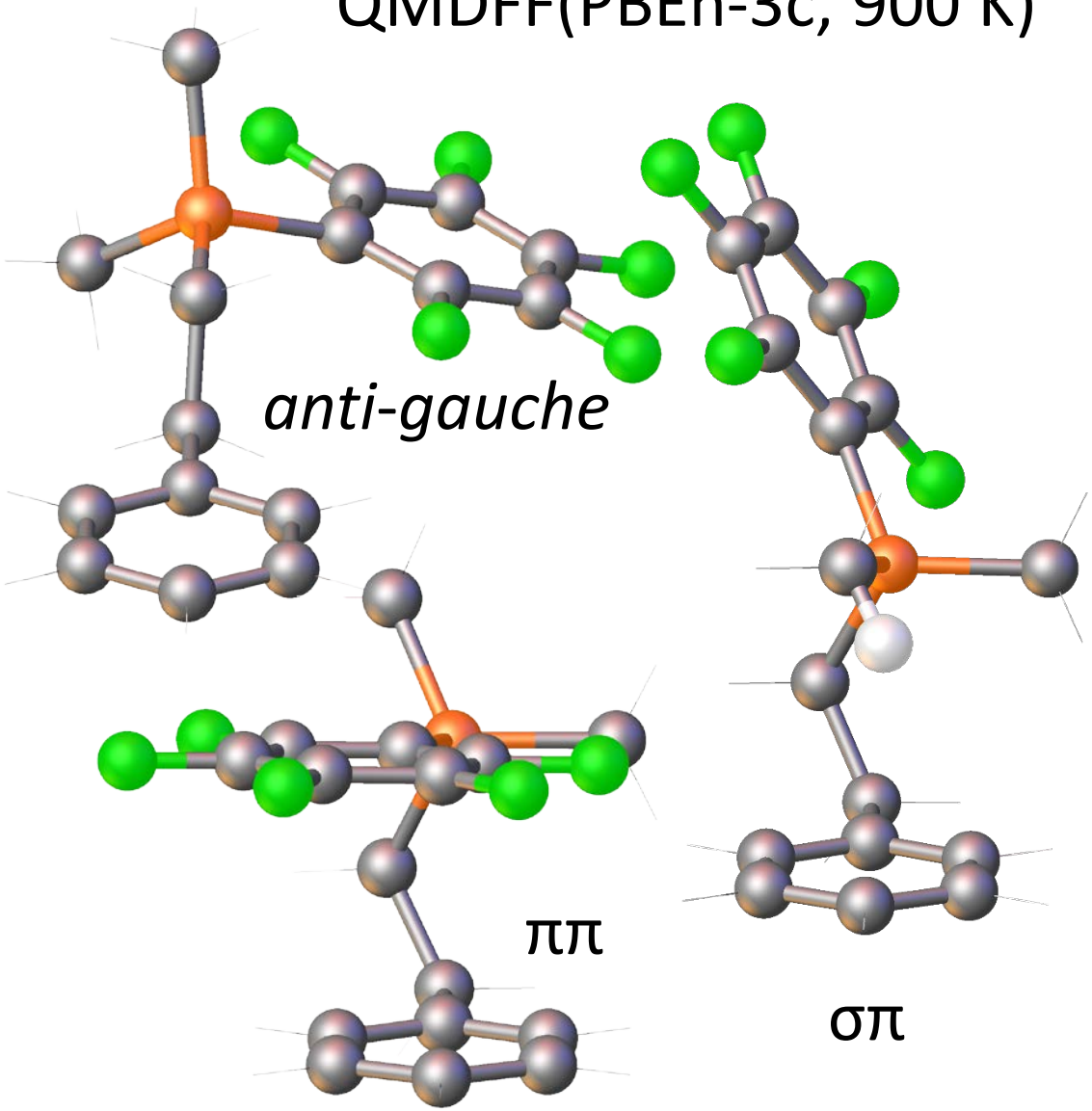
QC

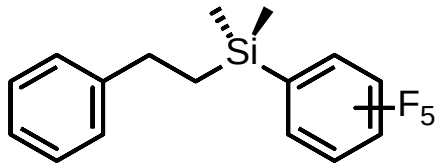
QMDFF(PBEh-3c, 900 K)



QC

QMDFF(PBEh-3c, 900 K)

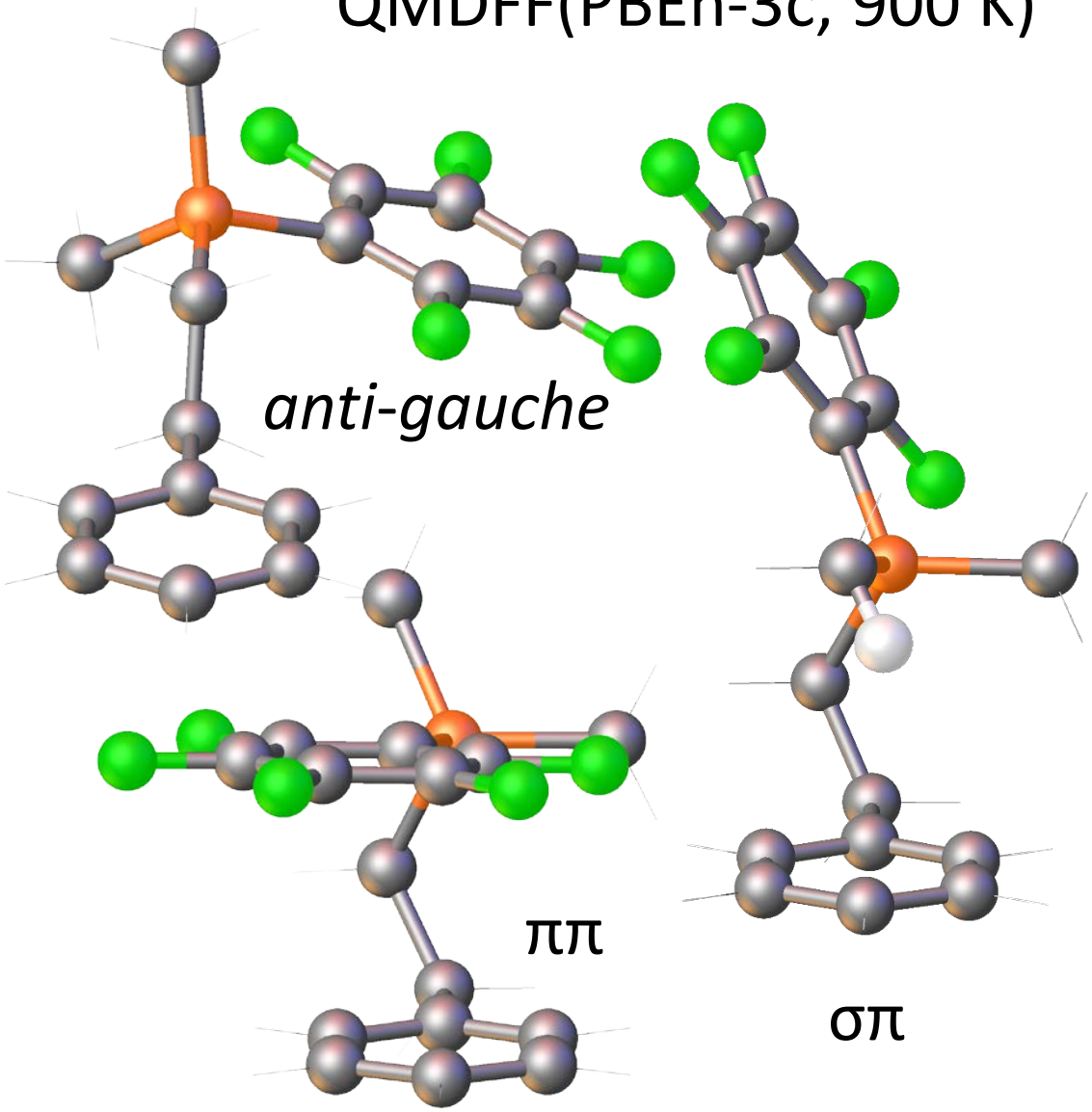


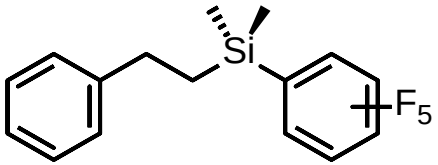
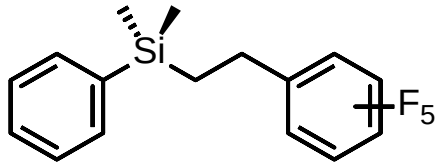
Δ*E* / kJ mol^{-1}	
ag	17.7
σπ	13.9
ππ	0
$d_{centroids}$ (ππ)	3.57 Å
$d_{centroid–H}$ (σπ)	2.74 Å

TPSS-D3BJ(abc)/def2-TZVP

QC

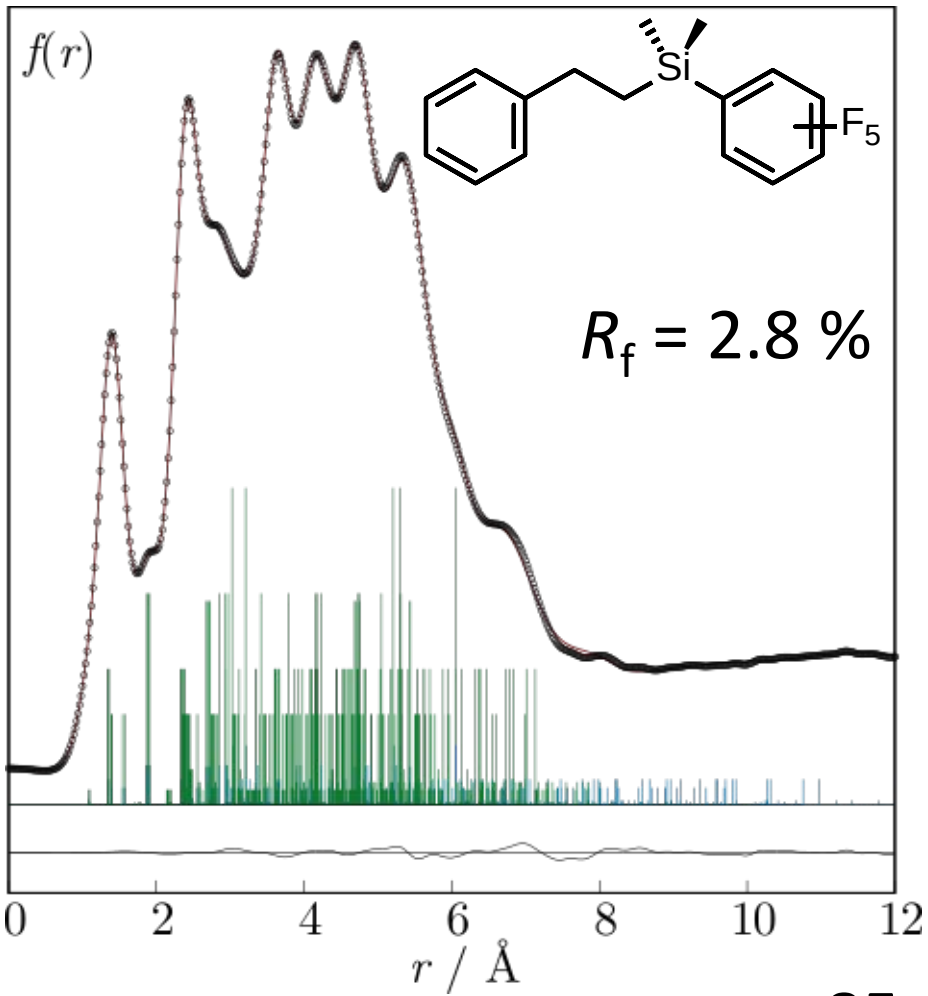
QMDFF(PBEh-3c, 900 K)



Δ*E* / kJ mol^{-1}		
ag	17.7	14.3
σπ	13.9	16.5
ππ	0	0
$d_{centroids}$ (ππ)	3.57 Å	3.53 Å
$d_{centroid–H}$ (σπ)	2.74 Å	2.84 Å

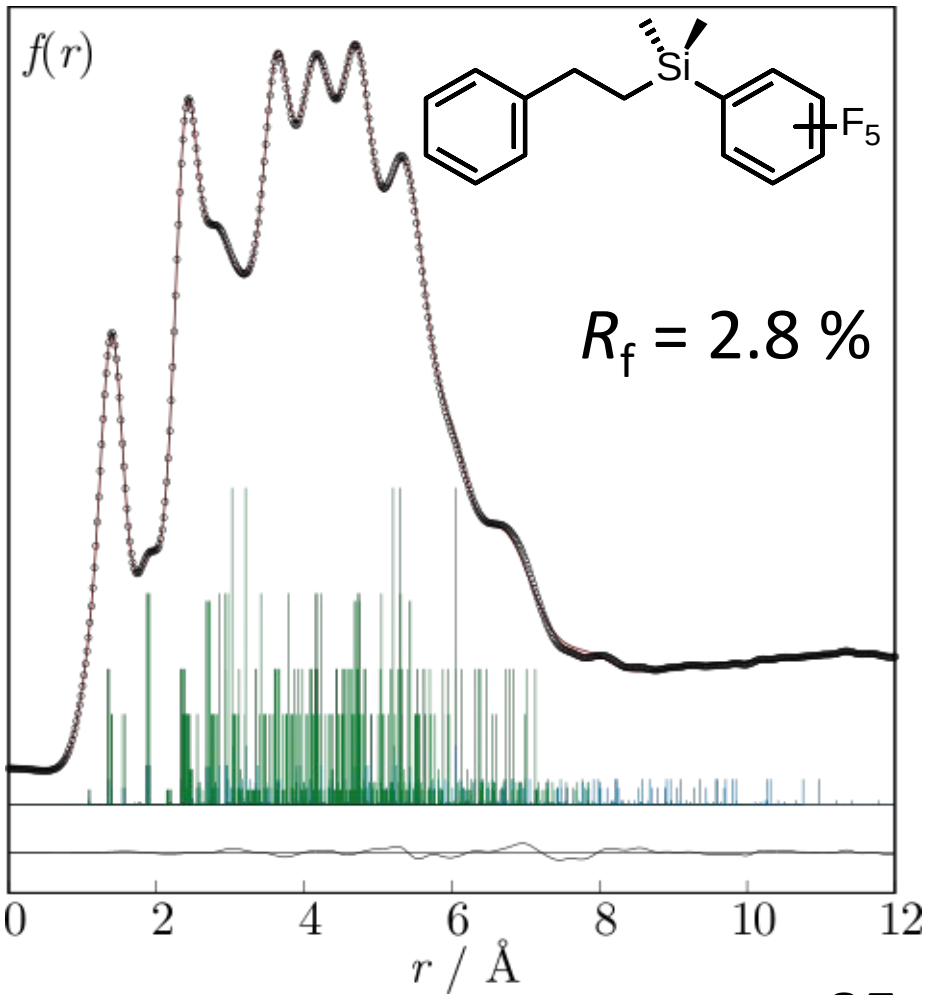
TPSS-D3BJ(abc)/def2-TZVP

GED

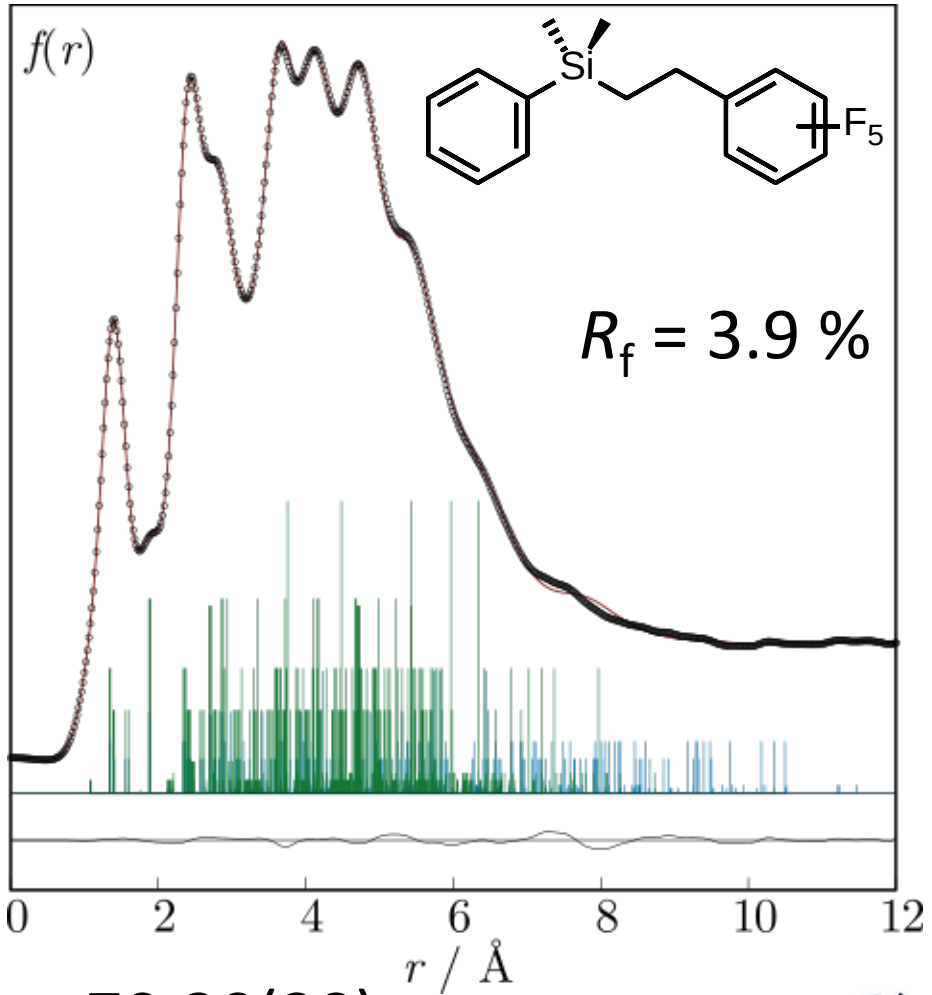


ππ:σπ = 85:15(26)

GED

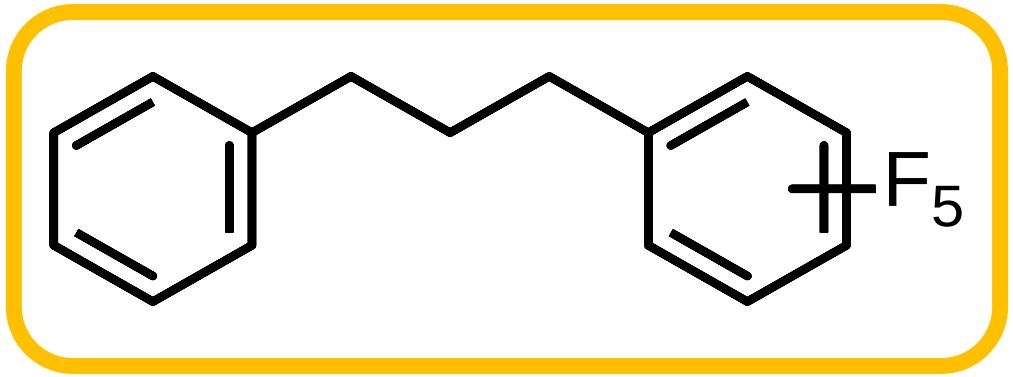


~~anti-gauche~~

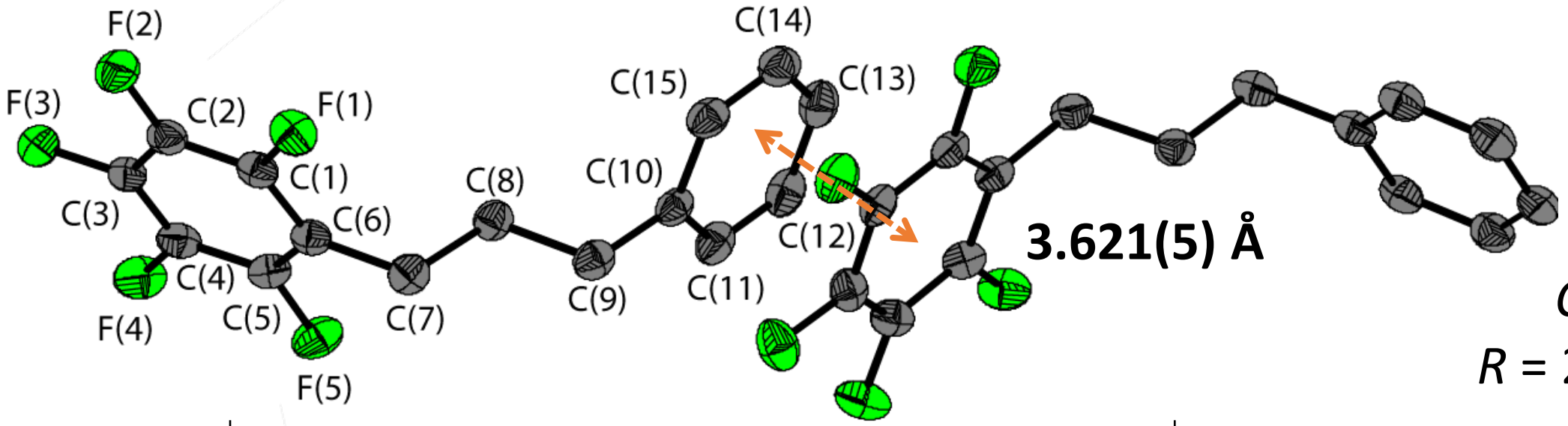


ππ:σπ = 85:15(26)

ππ:σπ = 70:30(30)


F5

XRD



Cc

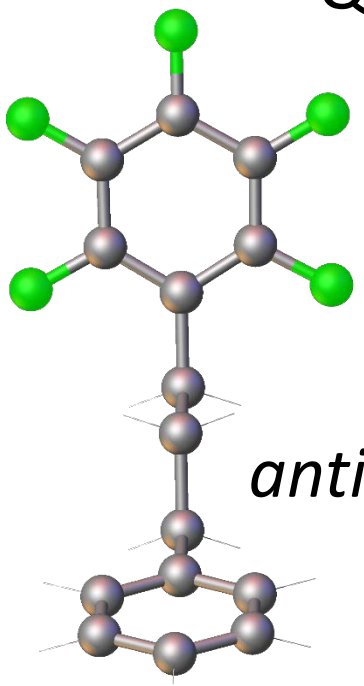
R = 2.9 %

	***d* / Å**
C(6)–C(7)	1.507(2)
C(7)–C(8)	1.531(2)
C(8)–C(9)	1.537(2)
C(9)–C(10)	1.511(2)

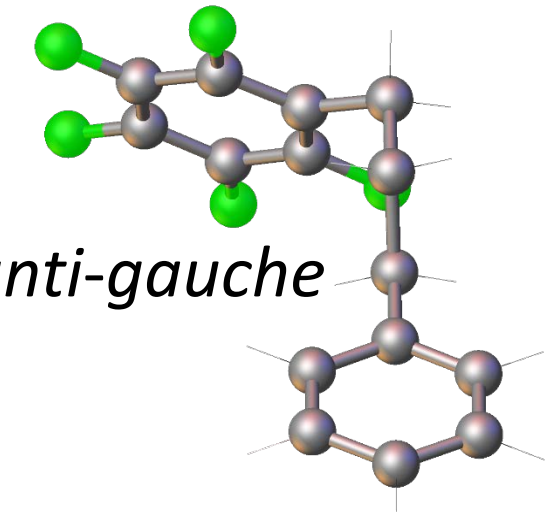
	∢ / °
C(6)–C(7)–C(8)	111.8(1)
C(7)–C(8)–C(9)	113.0(1)
C(8)–C(9)–C(10)	111.1(1)

QC

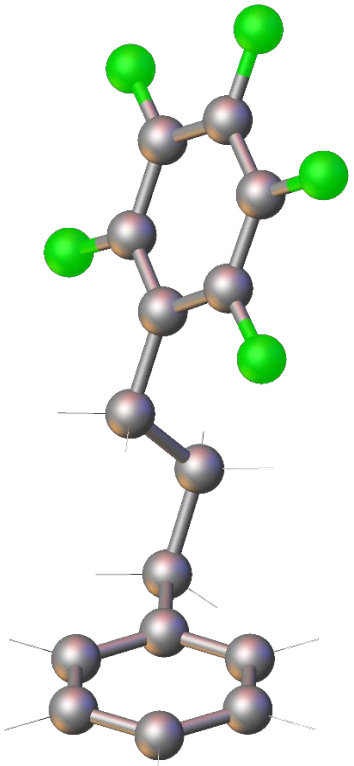
QMDFF(PBEh-3c, 900 K)



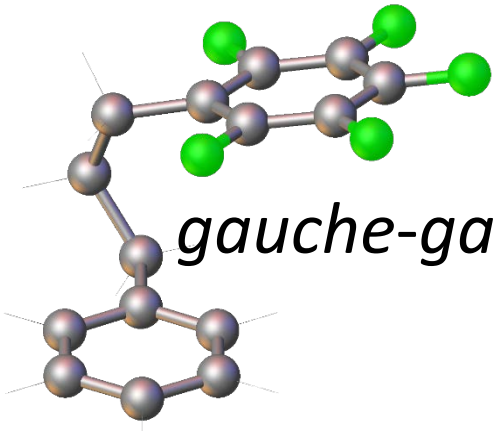
anti-anti



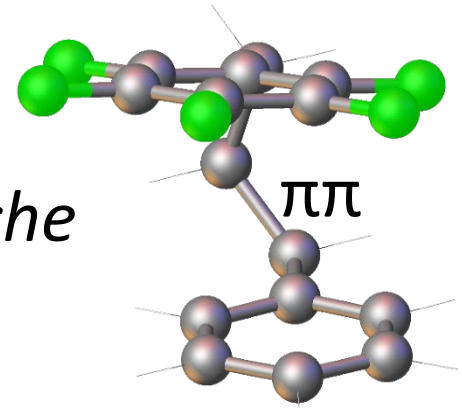
anti-gauche



gauche-anti



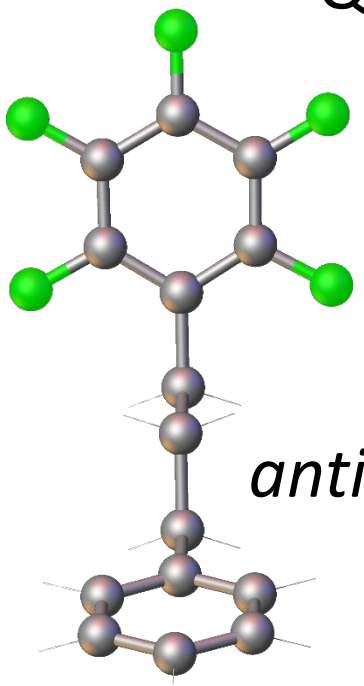
gauche-gauche



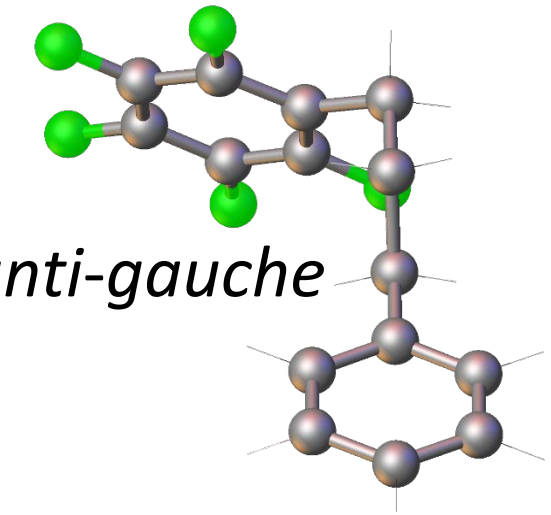
ππ

QC

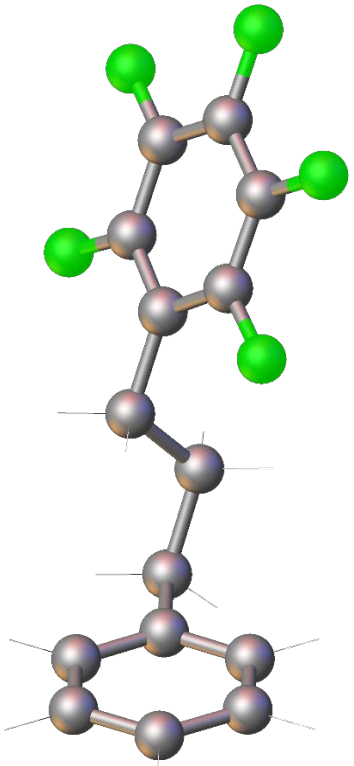
QMDFF(PBEh-3c, 900 K)



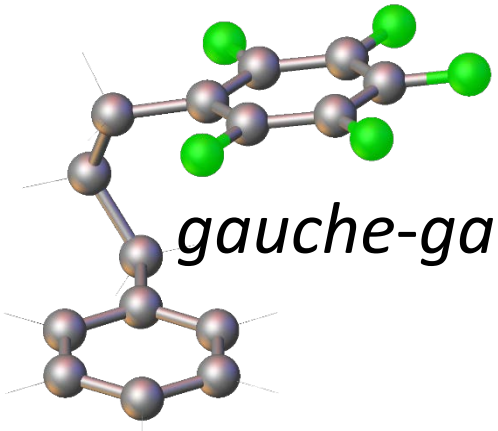
anti-anti



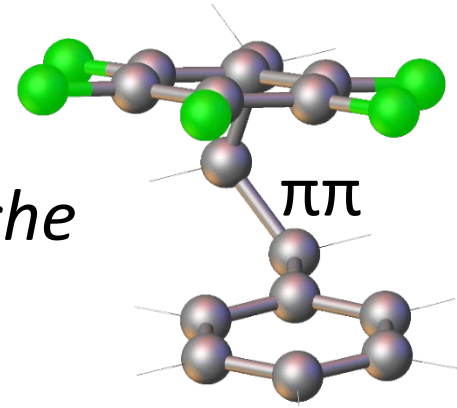
anti-gauche



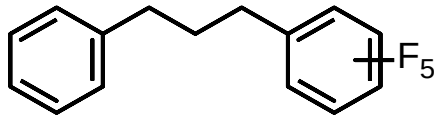
gauche-anti



gauche-gauche

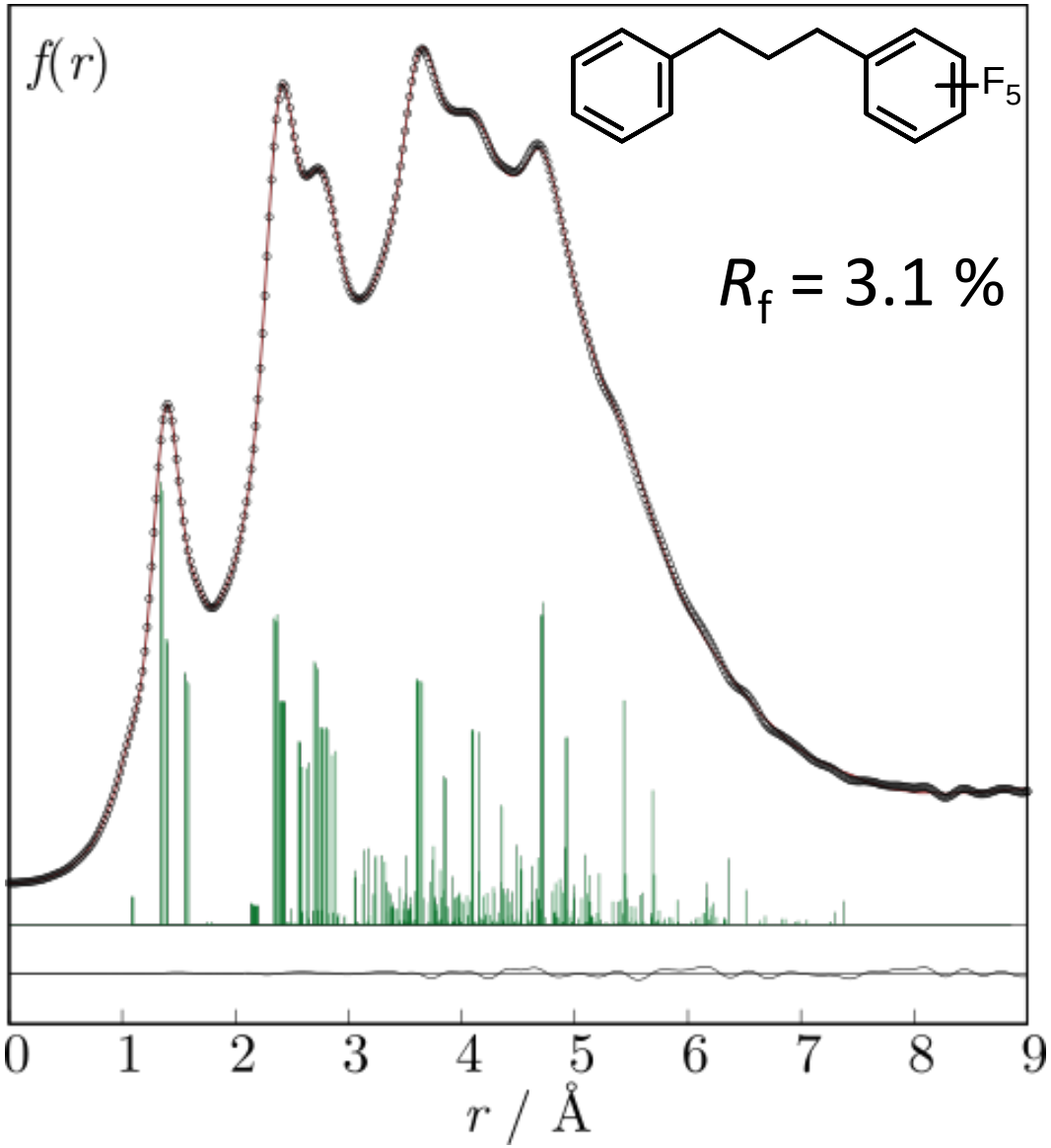


ππ

Δ*E* / kJ mol^{-1}	
aa	10.7
ag	10.1
ga	10.1
gg	9.4
ππ	0
$d_{centroids}$ (ππ)	3.57 Å

TPSS-D3BJ(abc)/def2-TZVP

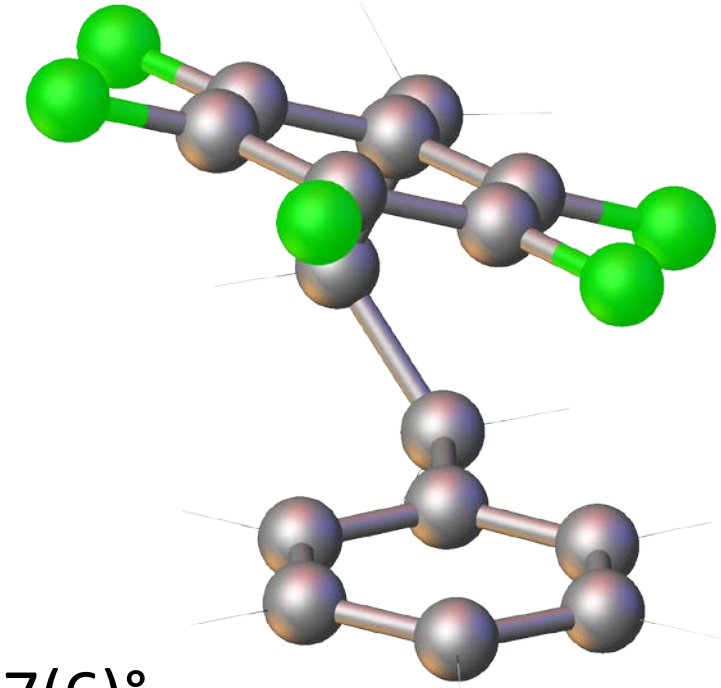
GED



best fit:
100 % ππ

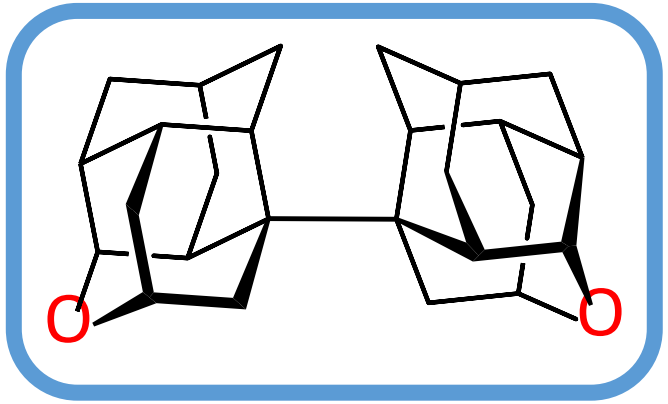
$d_{centroids}$ = 3.47(2) Å

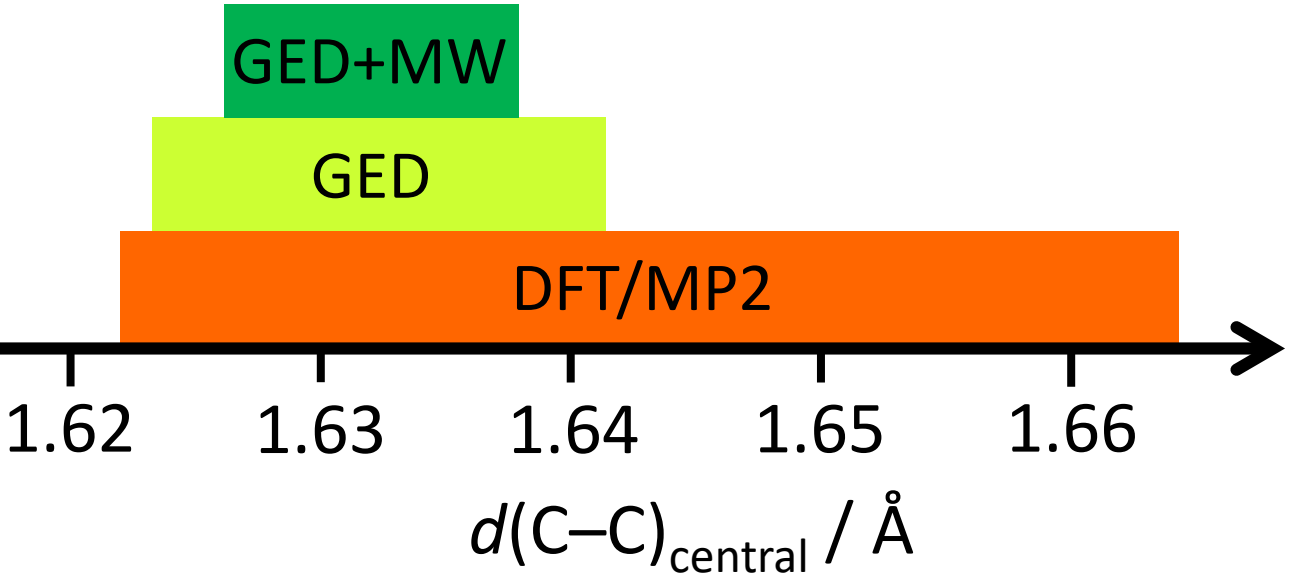
C_6 planes tilted by 17(6)°

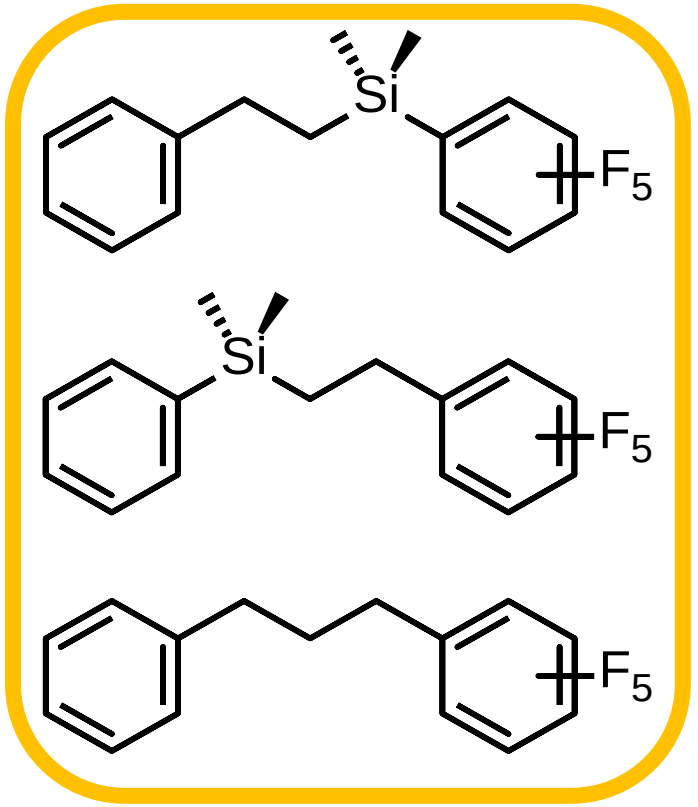


~~*anti-gauche*~~ ~~*anti-anti*~~ ~~*gauche-anti*~~

summary

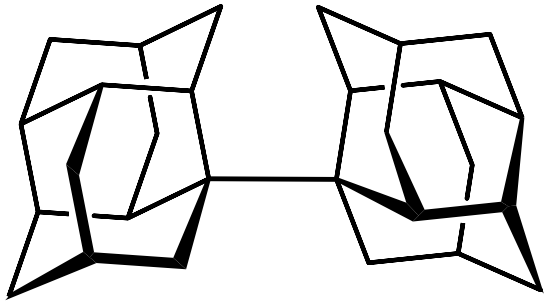


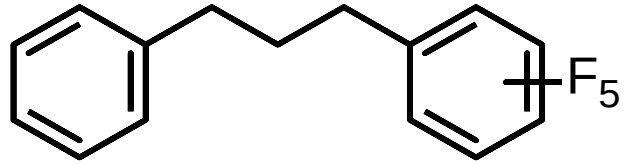




conformational landscape
dominated by
π–π interactions

acknowledgements





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