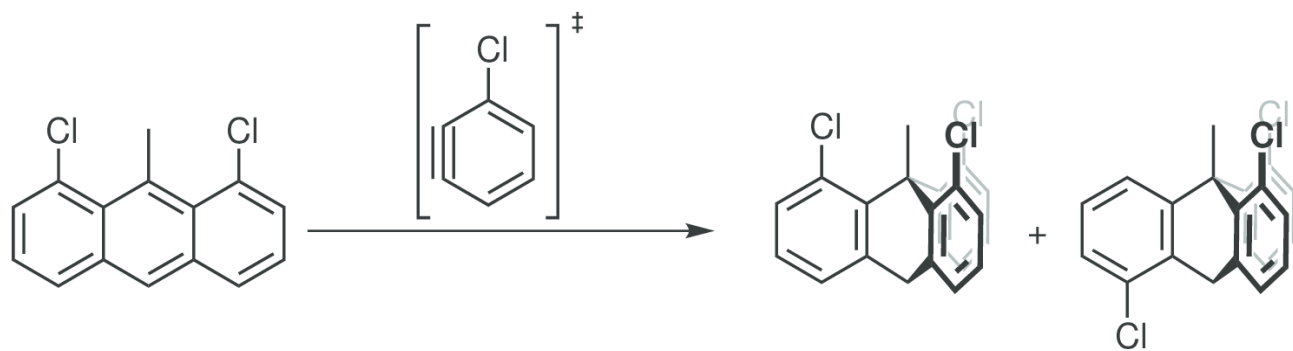
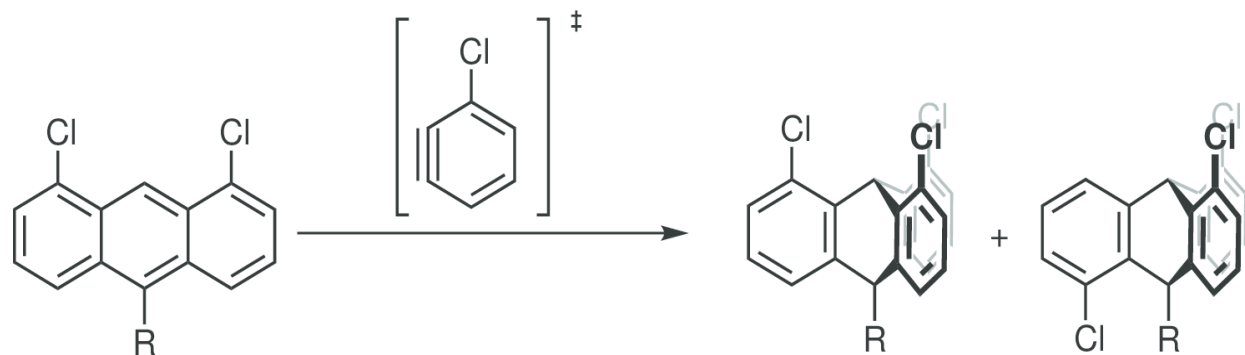


Theoretische Besonderheiten von Reaktionen

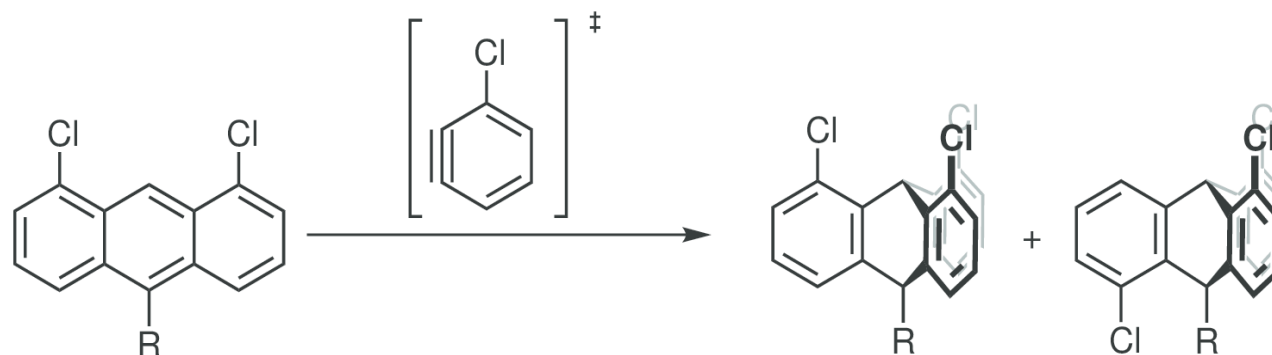
anthracene + benzyne \rightarrow triptycene

Yury V. Vishnevskiy
Bielefeld, 29. April 2014

Die Reaktionen



Die Reaktionen



R	% syn	% anti
H	23	77
Me	37	63
<i>n</i> -Bu	40	60
<i>i</i> -Pr	30	70
<i>t</i> -Bu	0	100
Cy	21	79
Ph	25	75
TMS	86	14
H (9-Me)	40	60

Fragen:

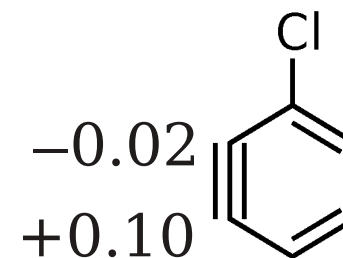
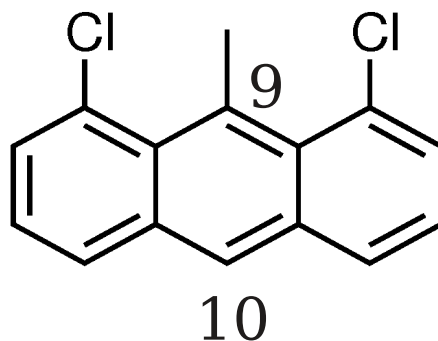
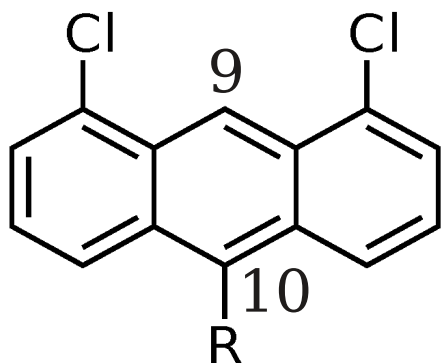
syn vs. anti

t-Bu

TMS vs. *t*-Bu

Versuch 1: Ladungen

NBO Ladungen



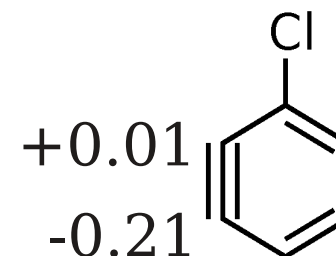
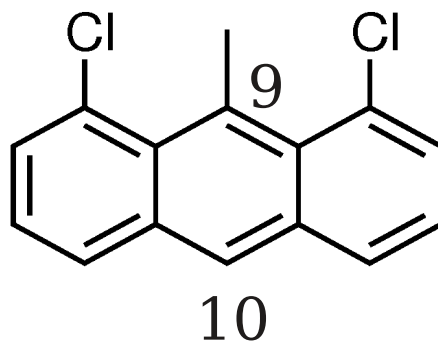
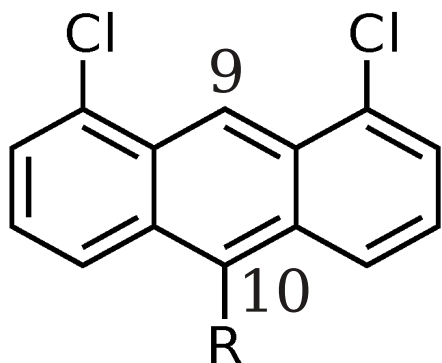
R	q(9)	q(10)	% syn	% anti
H	-0.18	-0.18	23	77
Me	-0.18	+0.03	37	63
<i>n</i> -Bu	-0.18	+0.03	40	60
<i>i</i> -Pr	-0.18	+0.03	30	70
<i>t</i> -Bu	-0.18	+0.04	0	100
Cy	-0.18	+0.03	21	79
Ph	-0.18	+0.01	25	75
TMS	-0.17	-0.44	86	14
H (9-Me)	+0.04	-0.18	40	60

H: eher schlecht

Me, *n*-Bu, *i*-Pr, *t*-Bu, Cy, Ph, TMS: eher gut

10-H-9-Me: schlecht

AIM Ladungen



R	q(9)	q(10)	% syn	% anti
H	+0.01	-0.00 ₄	23	77
Me	+0.01	-0.00 ₁	37	63
<i>n</i> -Bu	+0.01	-0.00 ₉	40	60
<i>i</i> -Pr	+0.01	-0.01 ₄	30	70
<i>t</i> -Bu	+0.01	-0.02 ₀	0	100
Cy	+0.01	-0.01 ₄	21	79
Ph	+0.01	-0.00 ₉	25	75
TMS	+0.01	-0.65 ₀	86	14
H (9-Me)	+0.01	-0.00 ₂	40	60

H, Me, *n*-Bu, *i*-Pr, *t*-Bu, Cy, Ph: eher schlecht

TMS: schlecht

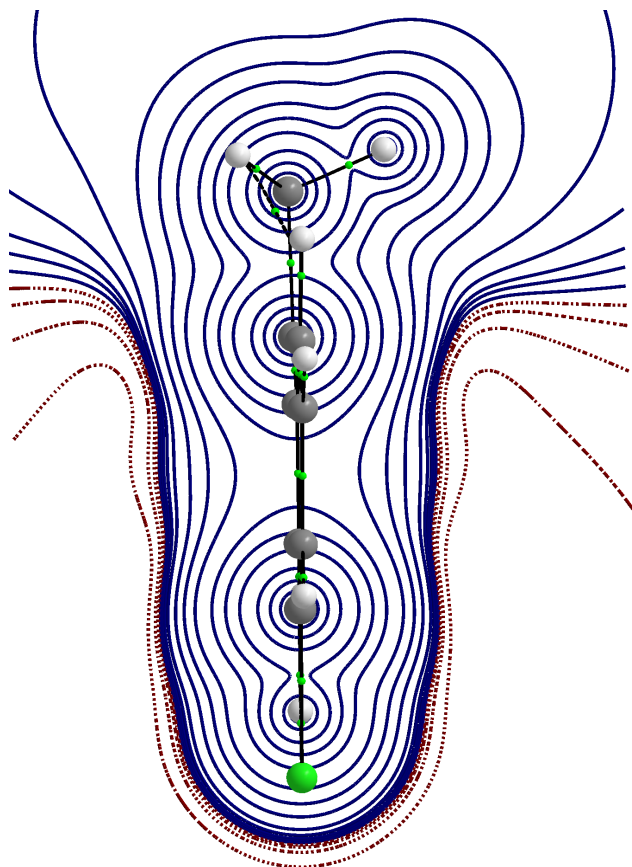
10-H-9-Me: eher gut

B3LYP/6-31G(d,p)

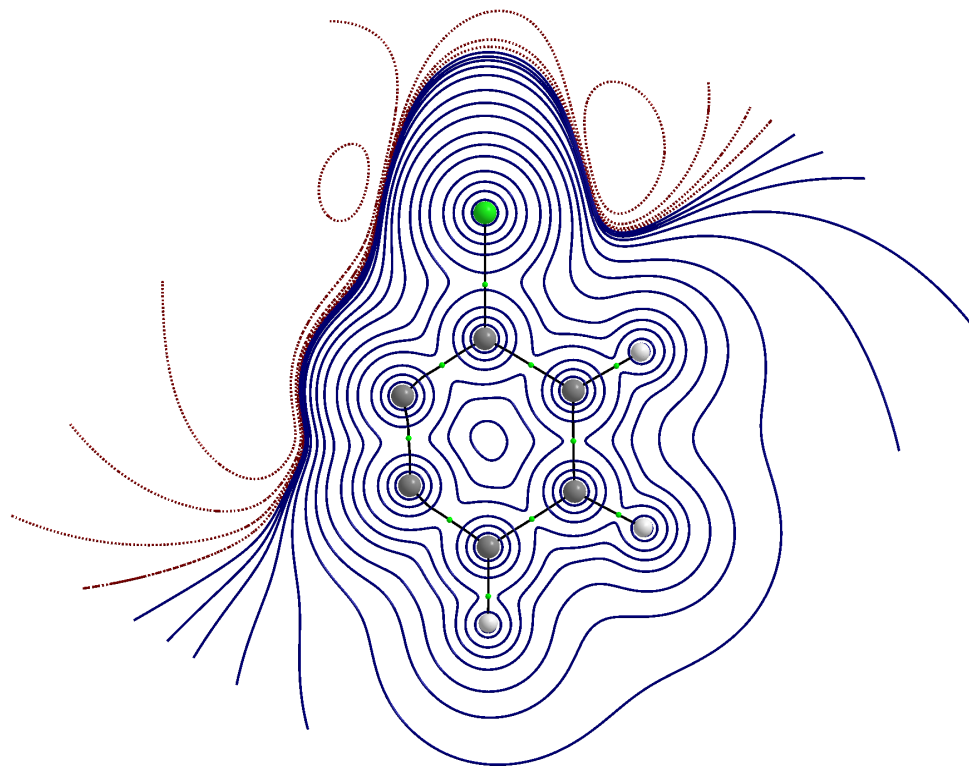
Versuch 2: Elektrostatische Potentiale

Elektrostatistische Potentiale

anti (60% im Experiment)

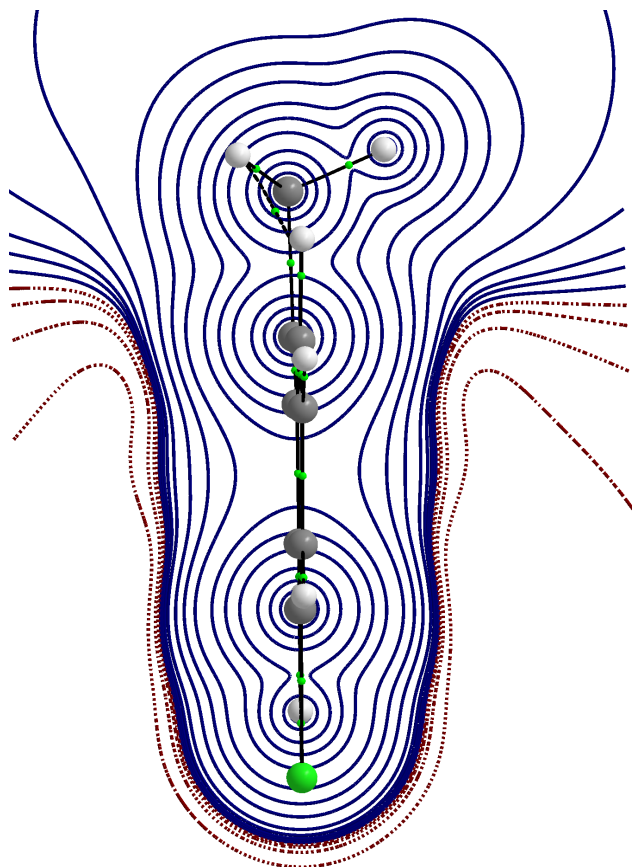


1,8-Dichlor-10-methylantracene

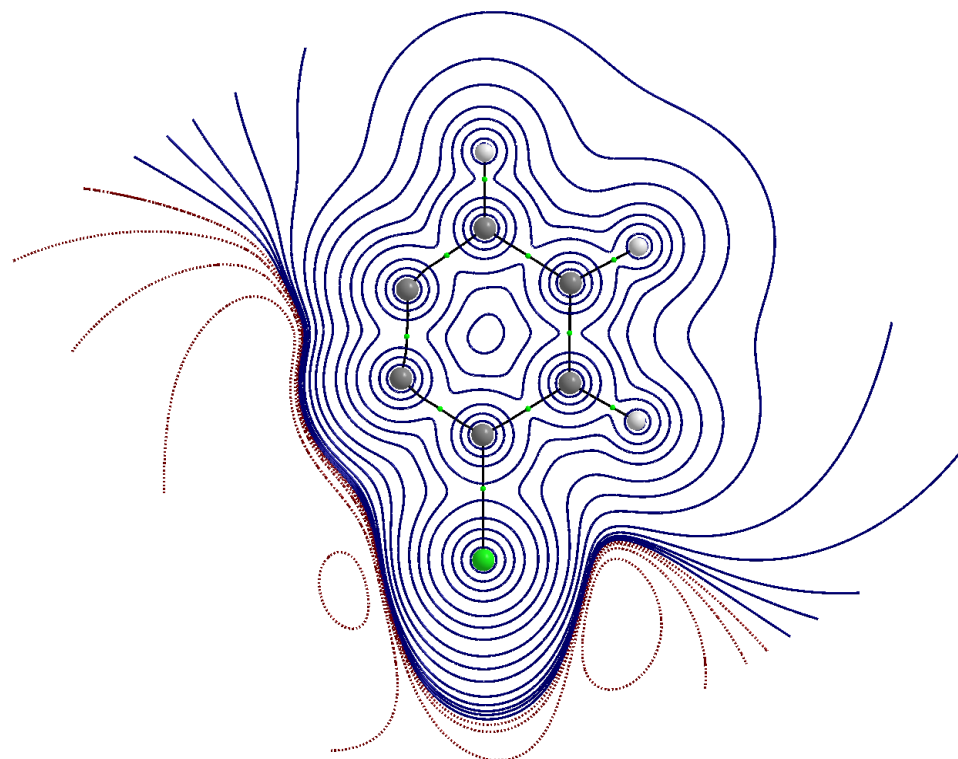


6-Chlorbenzyl

syn (40% im Experiment)



1,8-Dichlor-10-methylantracene

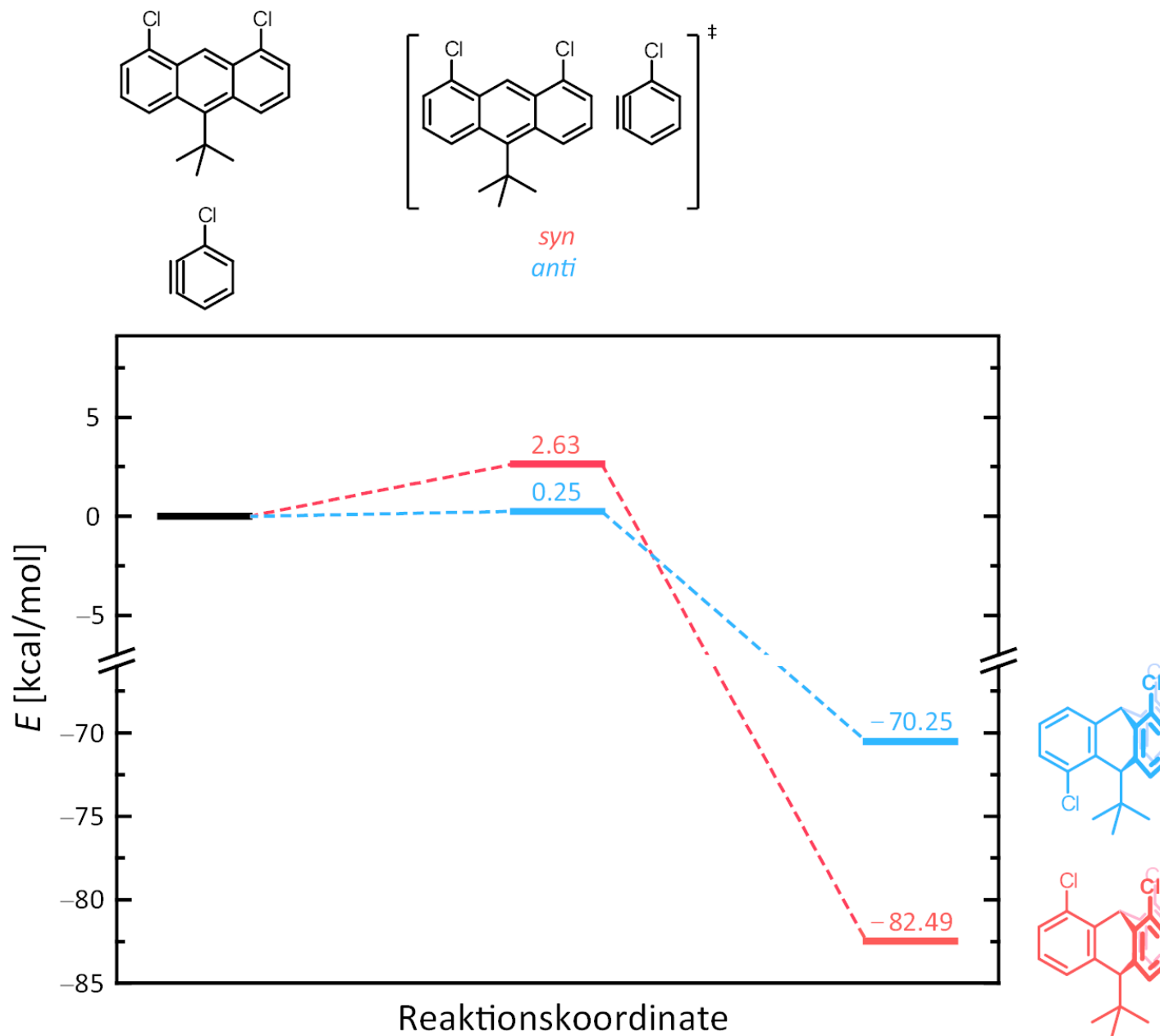


6-Chlorbenzyl

EP Erklärung: nicht überzeugend

Versuch 3: Übergangszustände

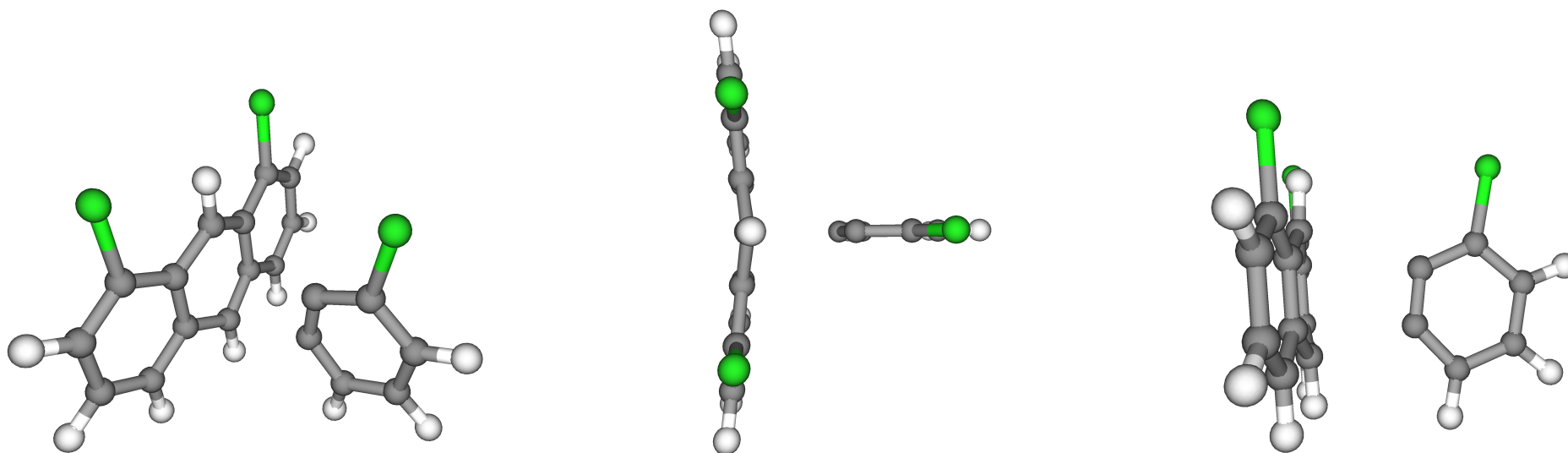
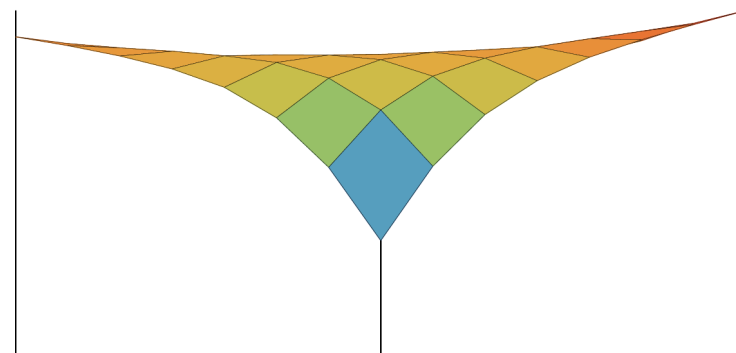
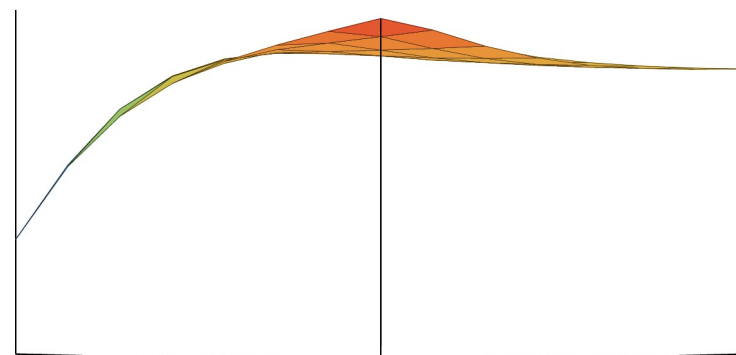
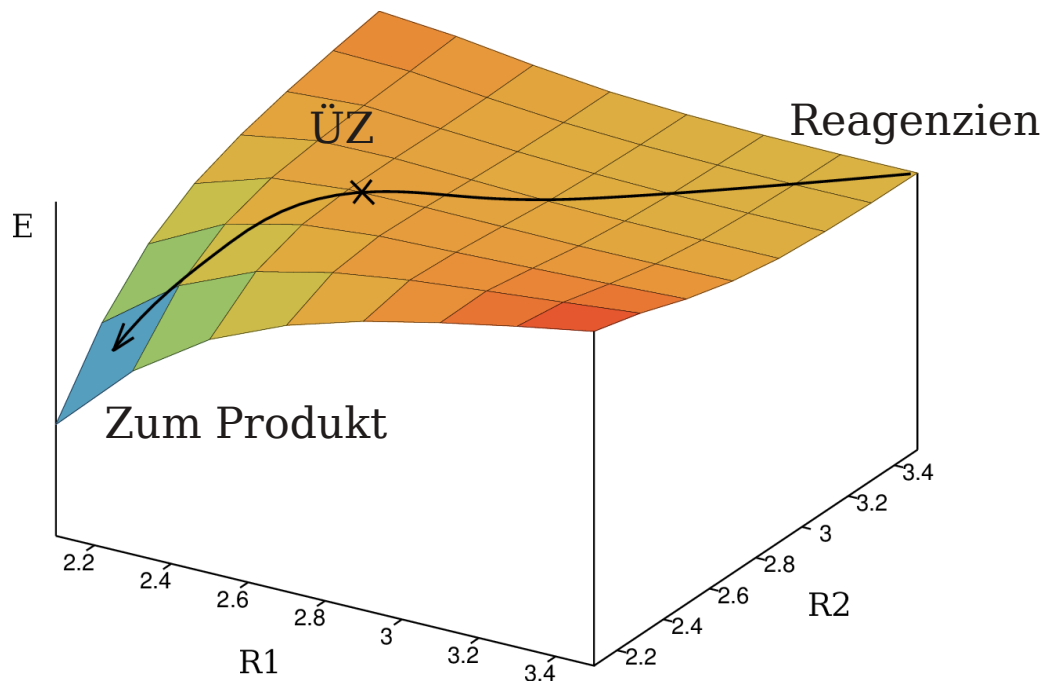
Kinetik vs. Thermodynamik



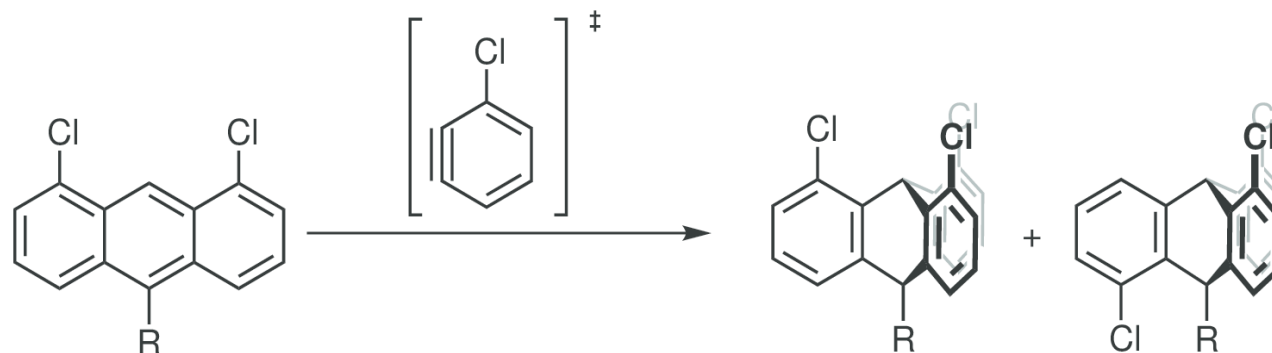
DFT Screening: 9-H,10-H

Methode	Barriere zu triptycene, kcal/mol		Kommentar
	1,8,13-triclor	1,8,16-triclor	
B3LYP/6-31G(d,p)	1.79	0.79	Stimmt zum Experiment
B3LYP/6-31G(d,p) BSSE	4.76	3.78	Stimmt zum Experiment
B3LYP/6-31+G(d,p)	-	-	Divergenz
B3LYP/6-31+G(d,p) BSSE	-	-	Divergenz
B3LYP/6-31++G(d,p)	2.82	1.91	Stimmt zum Experiment
B3LYP/6-31++G(d,p) BSSE	4.17	-	Divergenz
B3LYP/cc-pVTZ	4.22	3.35	Stimmt zum Experiment
B3LYP/cc-pVTZ BSSE	4.81	3.98	Stimmt zum Experiment
PBE0/cc-pVTZ	0.39	-	Barriere ist zu klein
PBE0/cc-pVTZ BSSE	0.90	0.03	Stimmt zum Experiment
PBE0/pc-2	0.35	-	Barriere ist zu klein
PBE0/pc-2 BSSE	0.76	-	Barriere ist zu klein
PBE0-D3/cc-pVTZ	-	-	Barriere ist zu klein
PBE0-D3/cc-pVTZ BSSE	-	-	Barriere ist zu klein
M11/cc-pVTZ	-	-	Barriere ist zu klein
M11/cc-pVTZ BSSE	-	-	Barriere ist zu klein

1,8,13-Trichlortriptycene: ÜZ



Barrieren

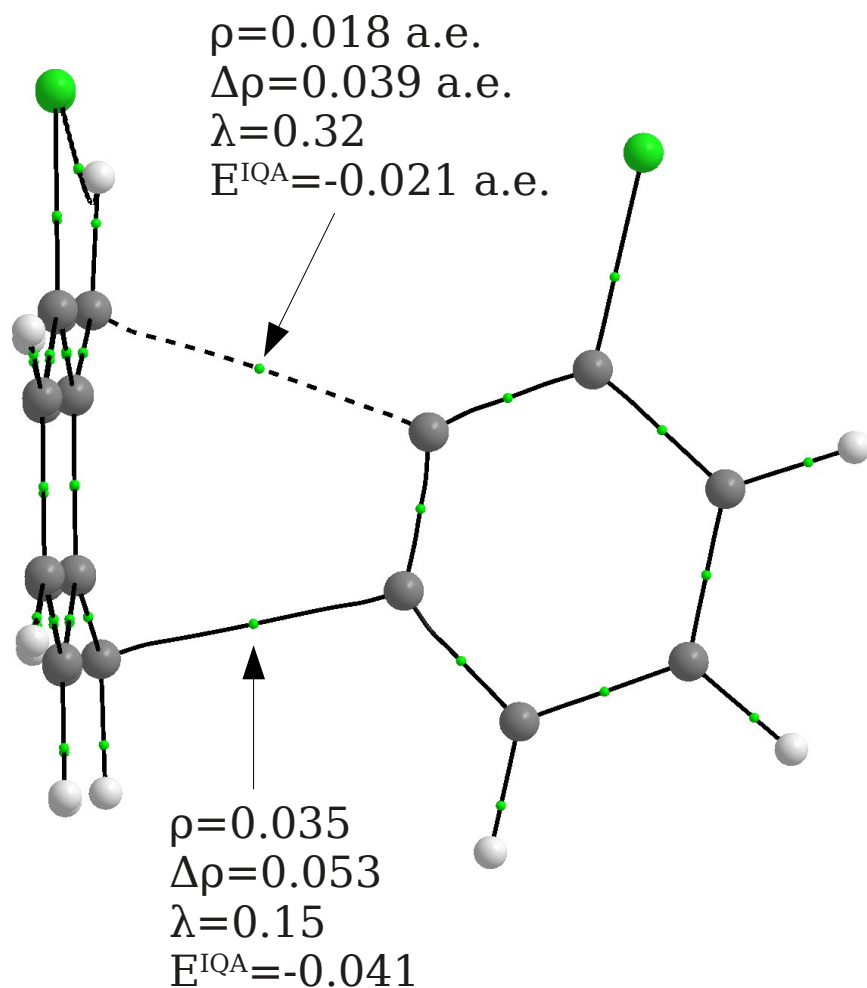


R	syn		anti	
	% im Experiment	Barriere, kcal/mol	% im Experiment	Barriere, kcal/mol
H	23	4.76	77	3.78
Me	37	3.75	63	2.28
<i>t</i> -Bu	0	2.63	100	0.25
Ph	25	6.29	75	3.39
TMS	86	3.62	14	1.84
H (9-Me)	40	1.95	60	1.89

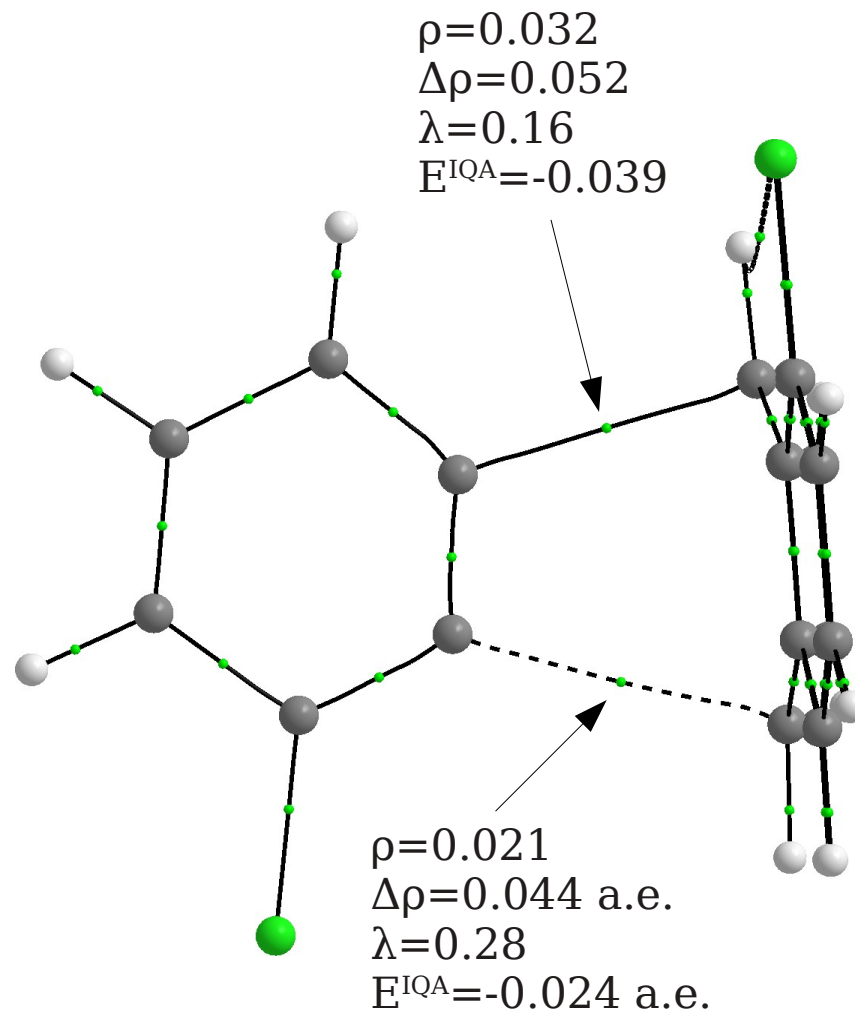
Alles gut außer mit R=TMS

Analysen der Energien

AIM (IQA) Analyse



Bspw.:
 $E^{IQA}(\text{Cl}\dots\text{Cl})=+0.007$
 $E^{IQA}(\text{C-C})=-0.35$



Bspw.:
 $E^{IQA}(\text{Cl}\dots\text{Cl})=+0.005$
 $E^{IQA}(\text{C-C})=-0.35$

$$E_{Mol}^{IQA} = \sum_i E_i^{IQA} + \sum_{i>j} E_{i,j}^{IQA}$$

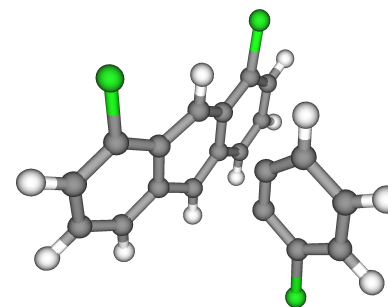
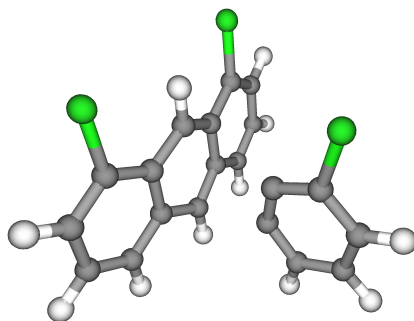
NBO Analyse (NEDA)

$$E_{Mol}^{NEDA} = E^{EL} + E^{CT} + E^{CORE} \quad \text{(Electrical + Charge Transfer + Core) Wechselwirkung}$$

$$E^{EL} = E^{ES} + E^{POL} + E^{SE} \quad \text{(Electrostatic + Polarization + Self-Energy)}$$

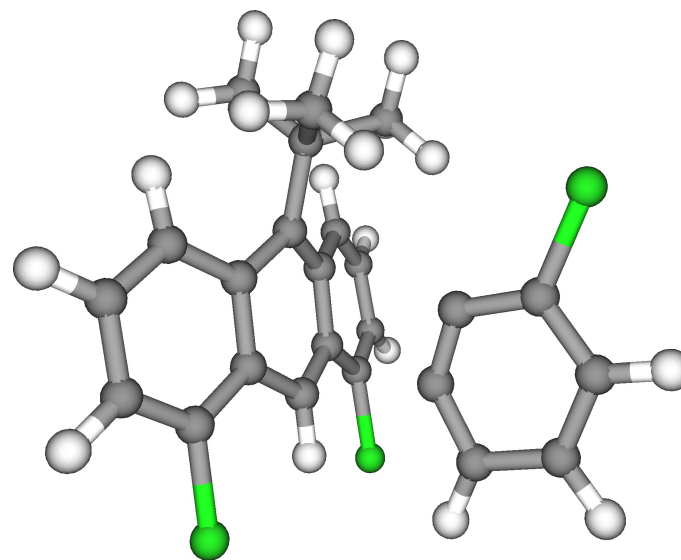
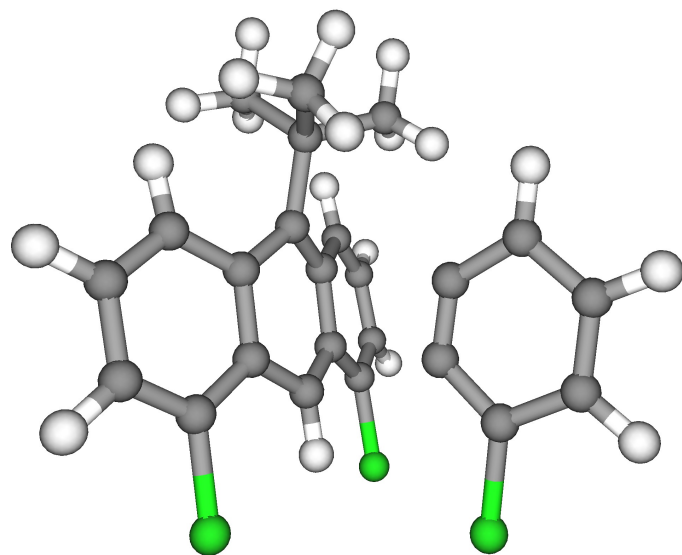
$$E^{CORE} = E^{XC} + E^{DEF} - E^{SE} \quad \text{(Pauli Exchange + Deformation - Self-Energy)}$$

1,8,13- und 1,8,16-Trichlortriptycene:



Komponente	<i>syn</i> (23% im Experiment)	<i>anti</i> (77% im Experiment)
E^{EL}	-39.39	-40.30
E^{CT}	-50.26	-49.45
E^{CORE} (E^{XC})	88.55 (-20.46)	87.72 (-20.53)
E^{NEDA} (Total), kcal/mol	-1.10	-2.03

NEDA für R=*t*-Bu



Komponente	<i>syn</i> (0% im Experiment)	<i>anti</i> (100% im Experiment)
E^{EL}	-26.37	-24.24
E^{CT}	-32.70	-29.67
E^{CORE} (E^{XC})	59.49 (-15.21)	52.61 (-12.94)
E^{NEDA} (Total), kcal/mol	0.42	-1.30

ÜZ zum *anti* ist stabiler wegen Deformationsenergie!

R=TMS: Methoden Screening

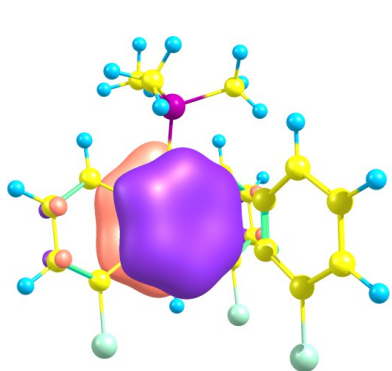
Methode	ΔE (ÜZ), kcal/mol	
	<i>syn</i> (86%)	<i>anti</i> (14%)
B3LYP/6-31G(d,p)	1.78	0.0
B3LYP/cc-pVTZ	1.57	0.0
B3LYP/6-31+G(d,p)	1.73	0.0
B3LYP/6-31G(d,p) im Lösungsmittel	1.68	0.0
M06-2X/cc-pVTZ	1.58	0.0
RHF/6-311G(d,p)	3.55	0.0
RHF/cc-pVTZ	3.62	0.0
MP2/cc-pVTZ // RHF/cc-pVTZ	0.0	5.05
CISD/6-31G(d,p) // B3LYP/cc-pVTZ	0.46	0.0
CASSCF(4,4)/6-31G(d)	0.11	0.0
XMCQDPT2(4,4)/6-31G(d) // CASSCF(4,4)/6-31G(d)	0.52	0.0
CASSCF(8,8)/6-31G(d)	0.97	0.0
XMCQDPT2(8,8)/6-31G(d) // CASSCF(8,8)/6-31G(d)	0.0	0.08

Weitere Tests:

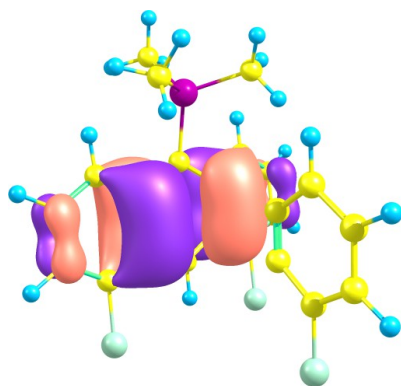
1. Ist ÜZ Triplet Biradikal? Nein, laut UB3LYP/6-31G(d,p).
2. Ist ÜZ Singlet Biradikal? Nein, UB3LYP/6-31G(d,p).
3. Stören andere elektronische Zustände? Nein, SA-CASSCF(8,8)/6-31G(d,p).

R=TMS, CASSCF(8,8) Orbitale

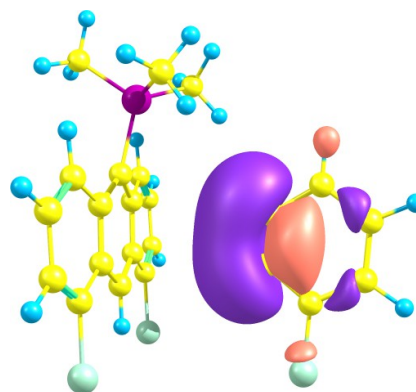
Besetzte π -Orbitale:



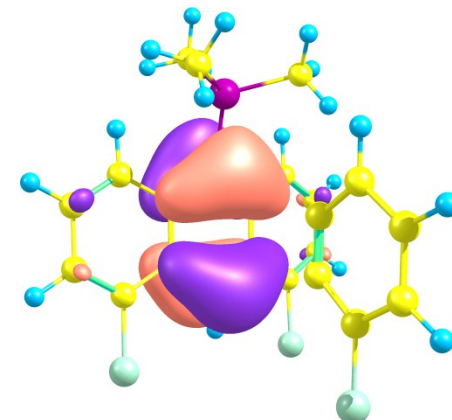
$n=1.97\ e$



1.93

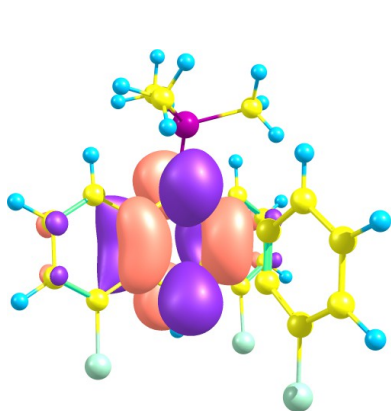


1.79

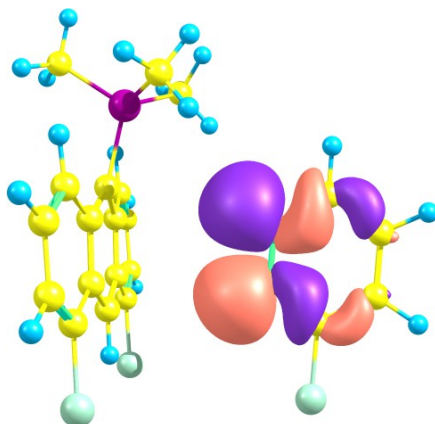


1.89

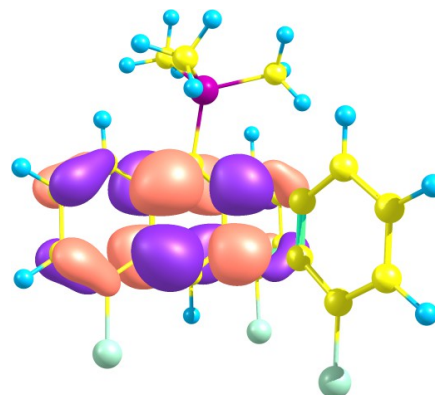
“Nicht besetzte” π^* -Orbitale:



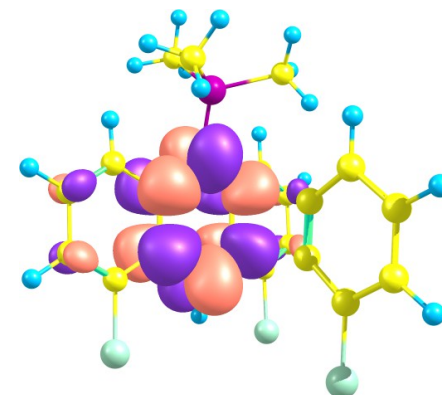
$n=0.11\ e$



0.21

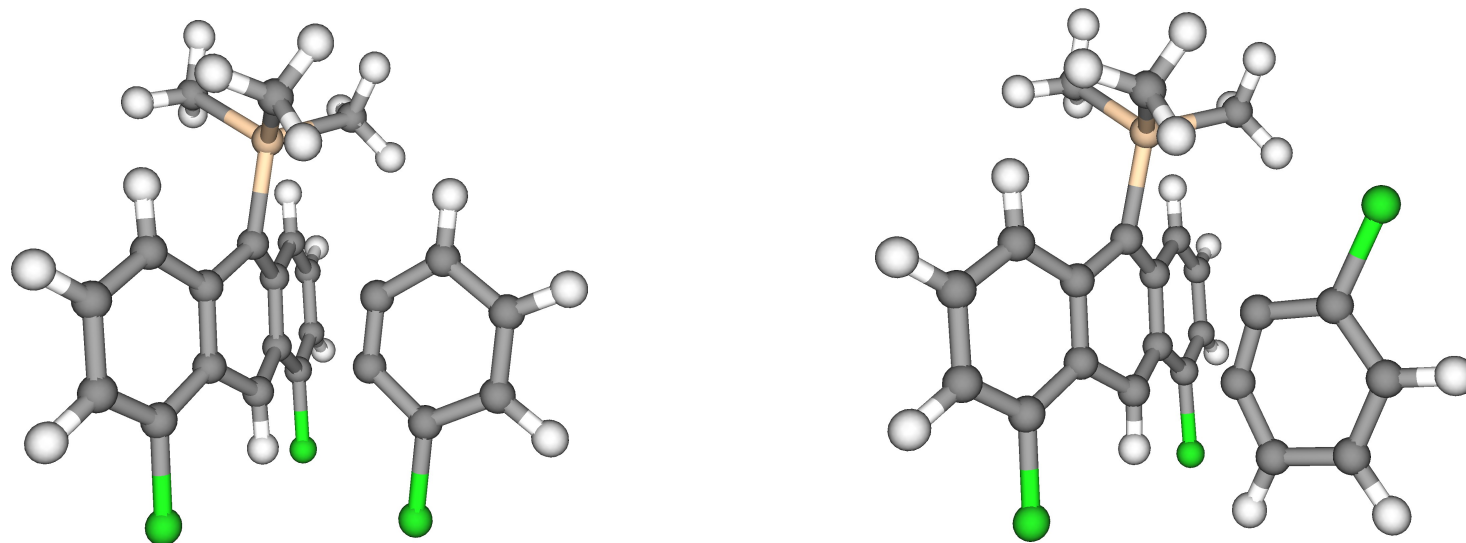


0.07



0.03

CASSCF: statische Korrelation spielt keine wichtige Rolle.
Falsche ÜZ:



MP2/cc-pVTZ // RHF/cc-pVTZ
XMCQDPT2/6-31G(d) // CASSCF(8,8)/6-31G(d)

Es gibt Hoffnung, dass dynamische Korrelation sehr wichtig ist.

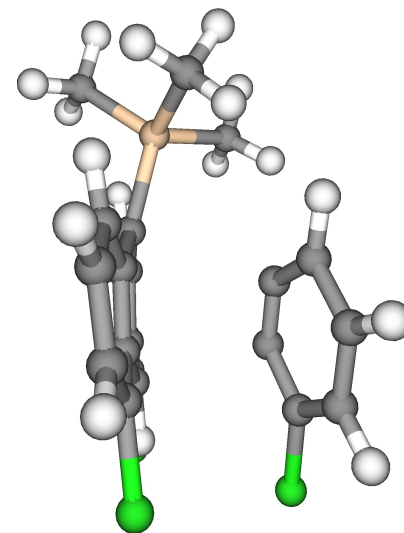
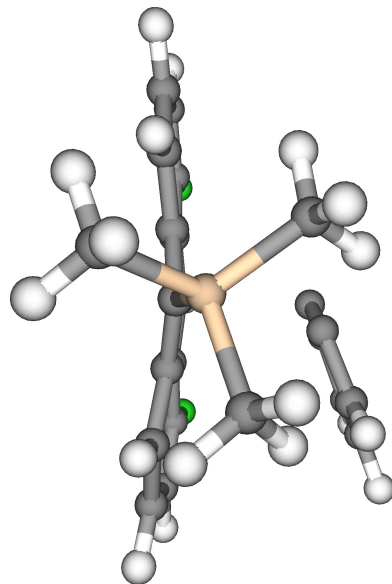
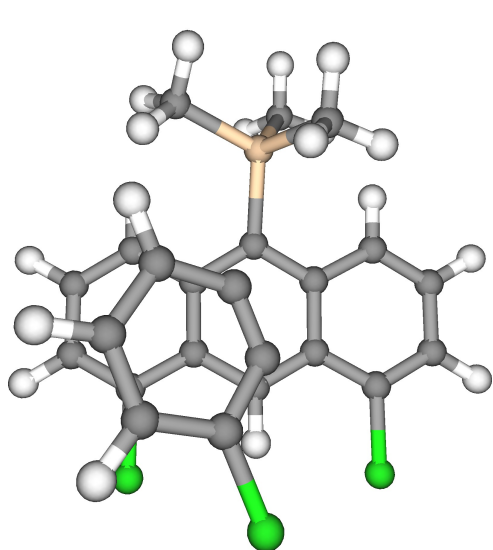
Polarisierbarkeit:

1,8-Dichlor-10-TMS-Anthracene: 237.0 Bohr³

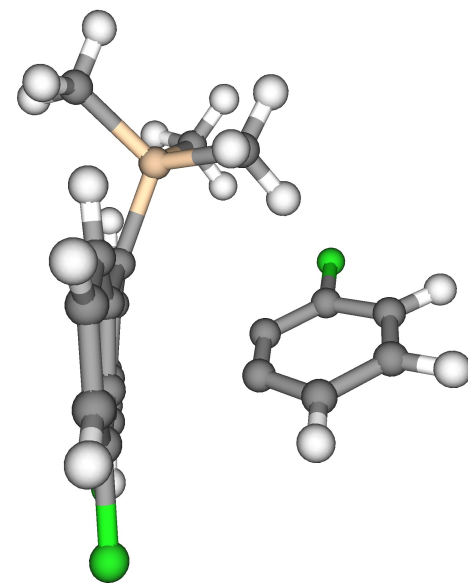
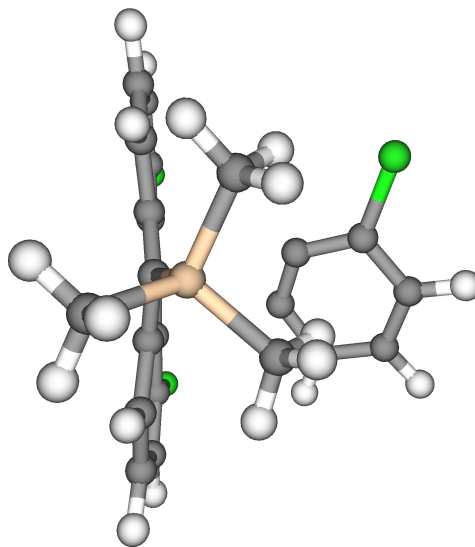
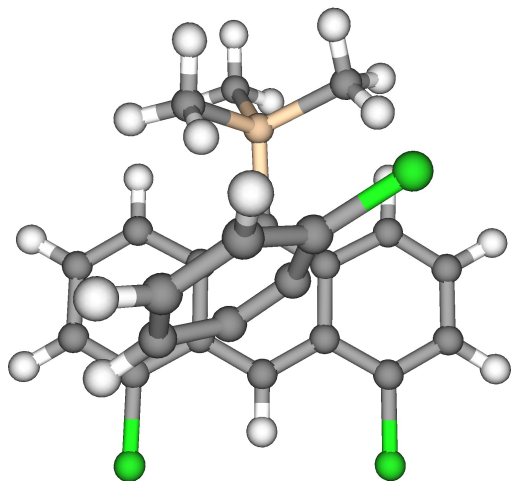
1,8-Dichlor-10-*t*Bu-Anthracene: 224.5 Bohr³

R=TMS, ÜZ aus MP2

ÜZ zum 1,8,13-Trichlor-10-TMS-Triptycene (*syn*, 86% im Experiment) ist 1.48 kcal/mol stabiler!



ÜZ zum 1,8,16-Trichlor-10-TMS-Triptycene (*anti*):



Zusammenfassung

1. Ladungen sind nicht nützlich für Erklärung der Reaktionen.
2. Elektrostatische Potentiale geben höchstens nicht entscheidende qualitative Ergebnisse.
3. Richtige Übergangszustände müssen gerechnet werden.
4. ÜZ Stabilitäten sind schwierig mit mechanistischen Modellen zu erklären.
5. Im Falle $R=TMS$, ist der ÜZ zum *anti*-Isomer mit dem π -Stacking stabilisiert.

~360 Rechnungen wurden gemacht.

Danke für die Aufmerksamkeit!