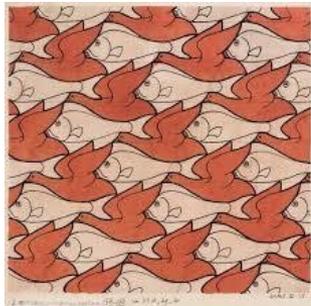
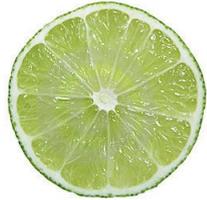
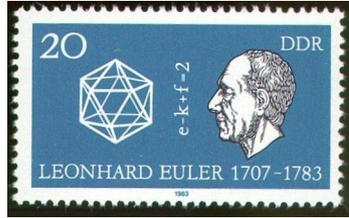


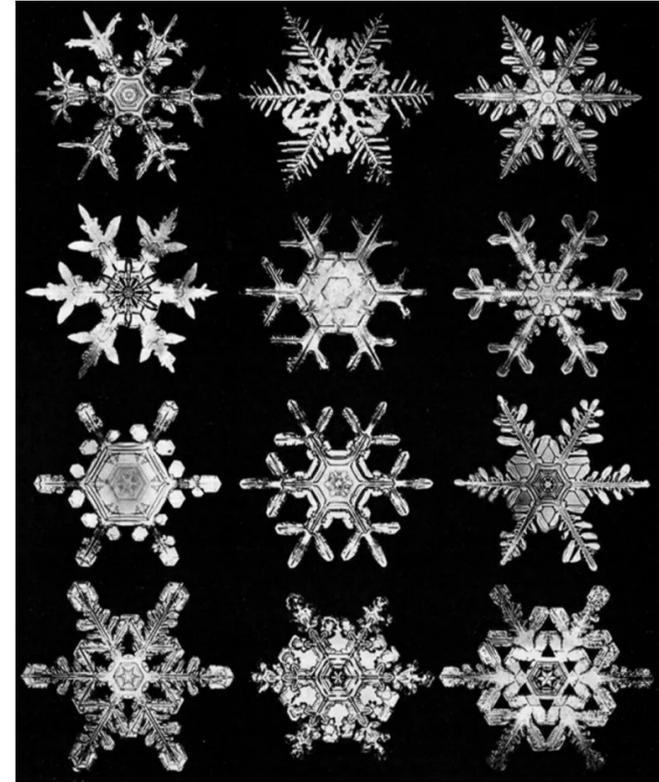
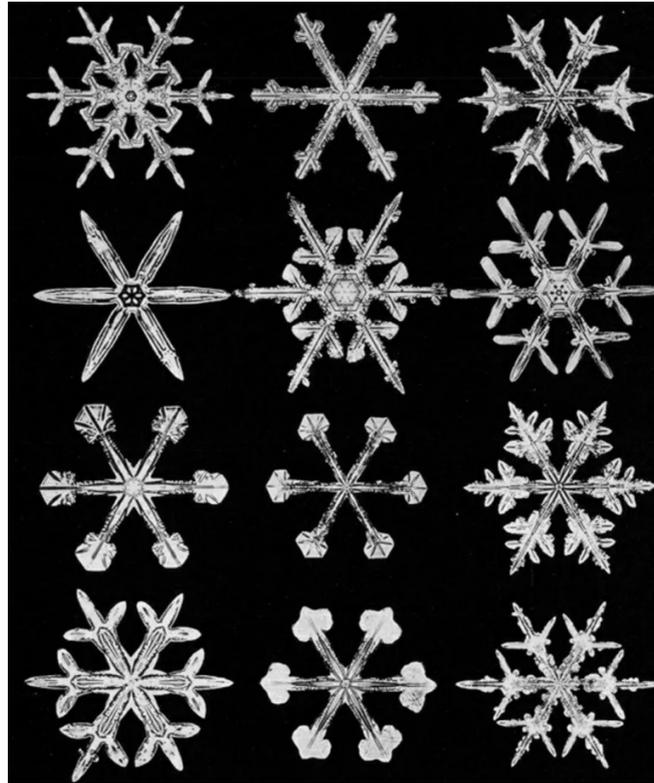
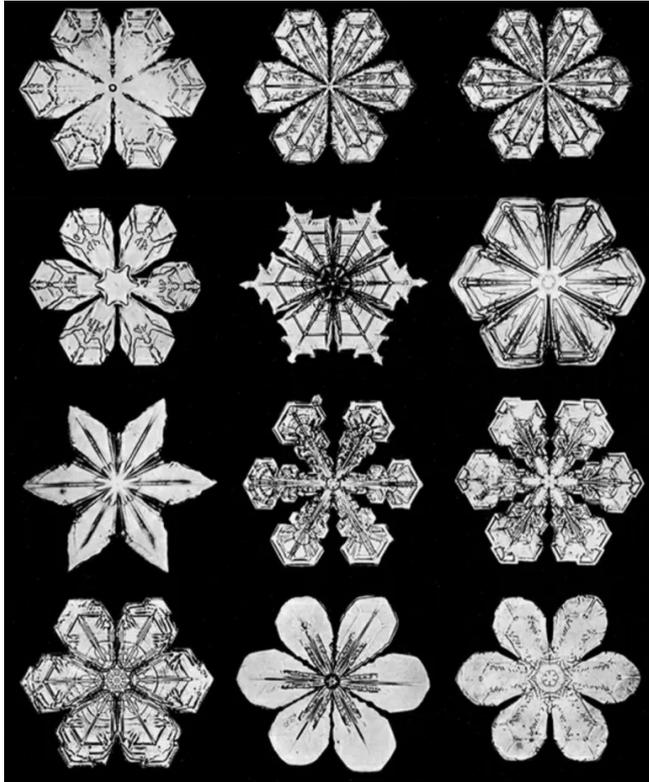
Strukturaufklärung in der molekularen anorganischen Chemie

2. Symmetrie

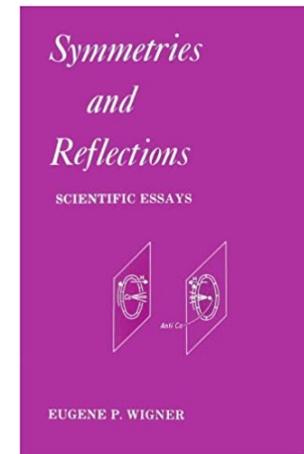
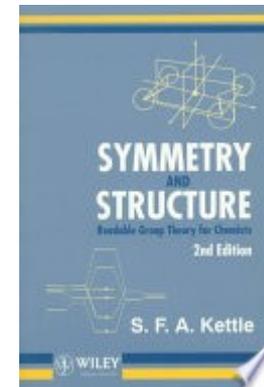
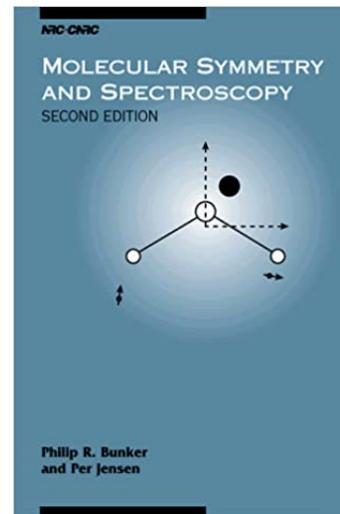
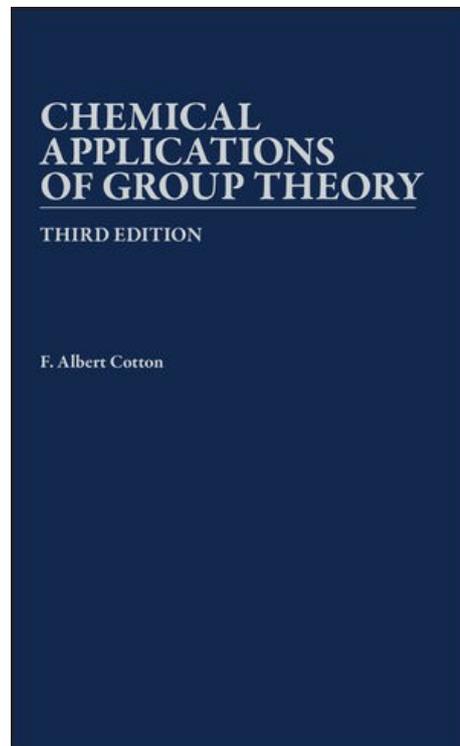
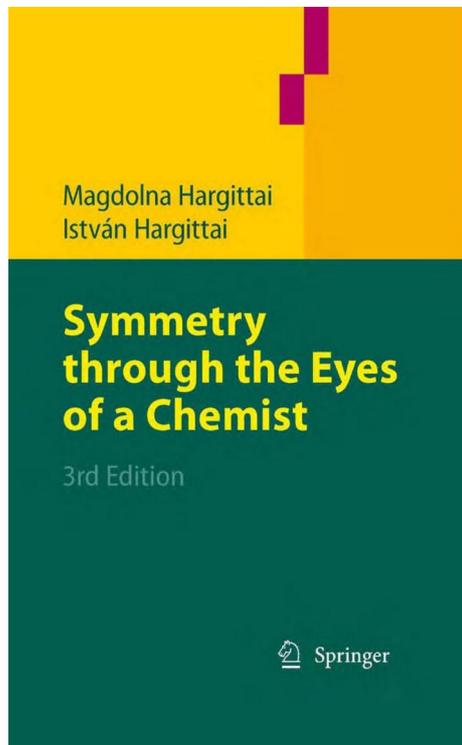
Symmetrie überall



Schneeflocken



Bücher

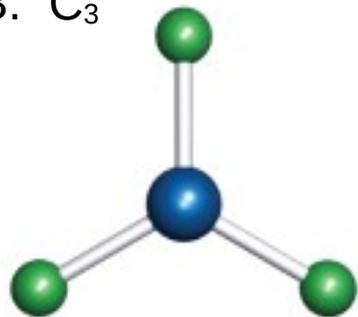


Symmetrioperationen und -elementen

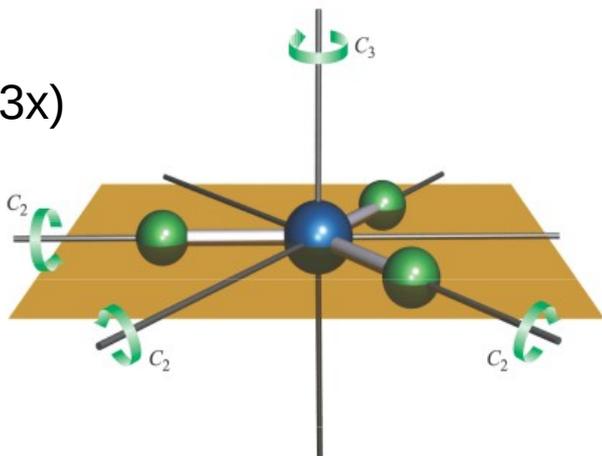
Symmetrioperation	Symmetrieelement	Schönflies-Symbol
Identitätsabbildung		E
n-zählige Drehung (um $2\pi/n$)	Drehachse	$C_n, n = 2, 3, 4, \text{ usw.}$
Punktspiegelung	Inversionszentrum	i
Spiegelung	Spiegelebene	σ
1. n-zählige Drehung (um $2\pi/n$) 2. Spiegelung	Drehspiegelachse	$S_n, n = 4, 6, 8, \text{ usw.}$

Drehung

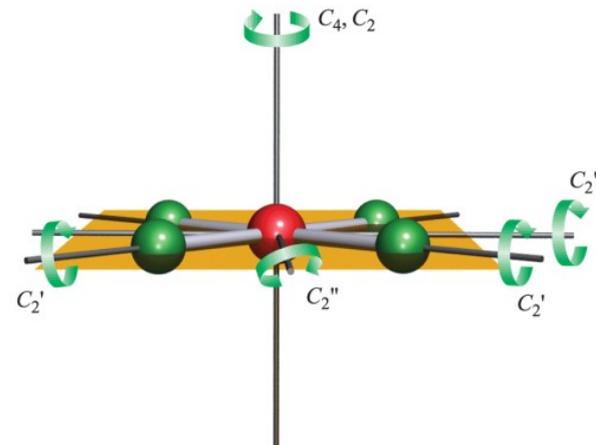
z. B. C_3



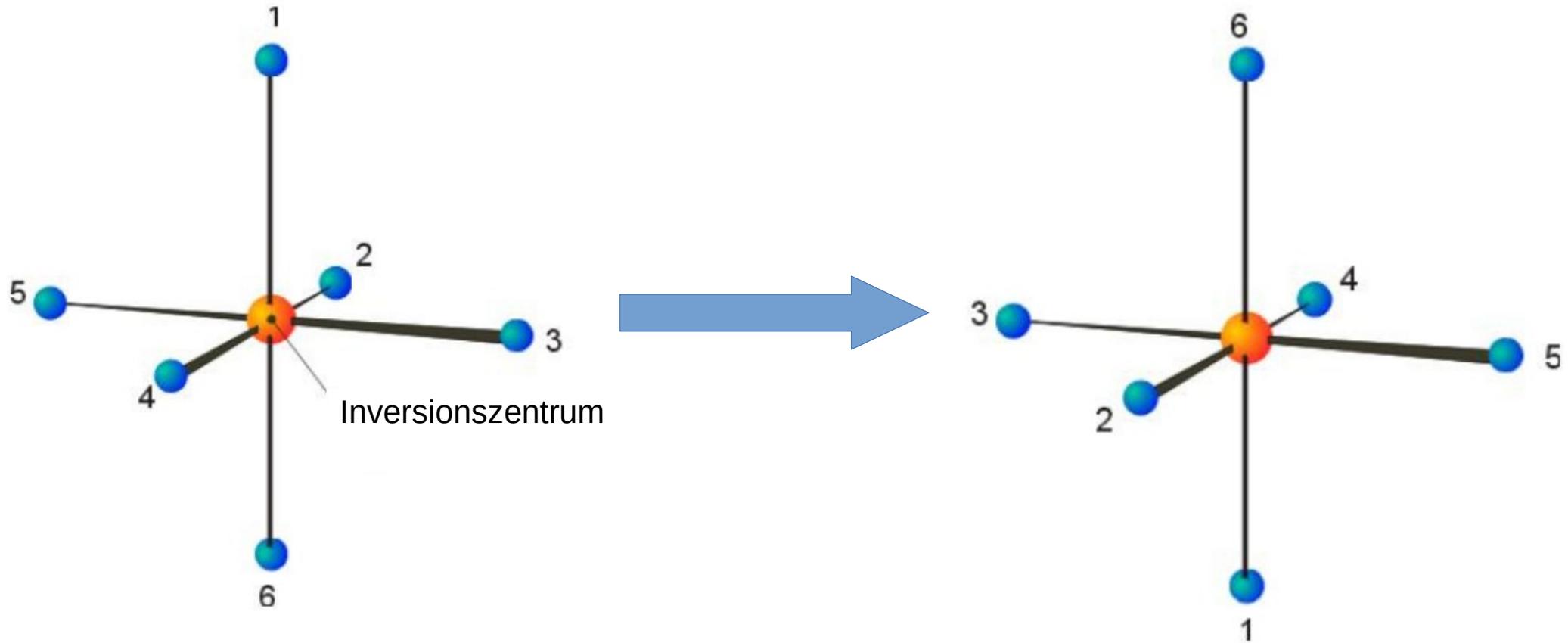
C_3 und C_2 (3x)



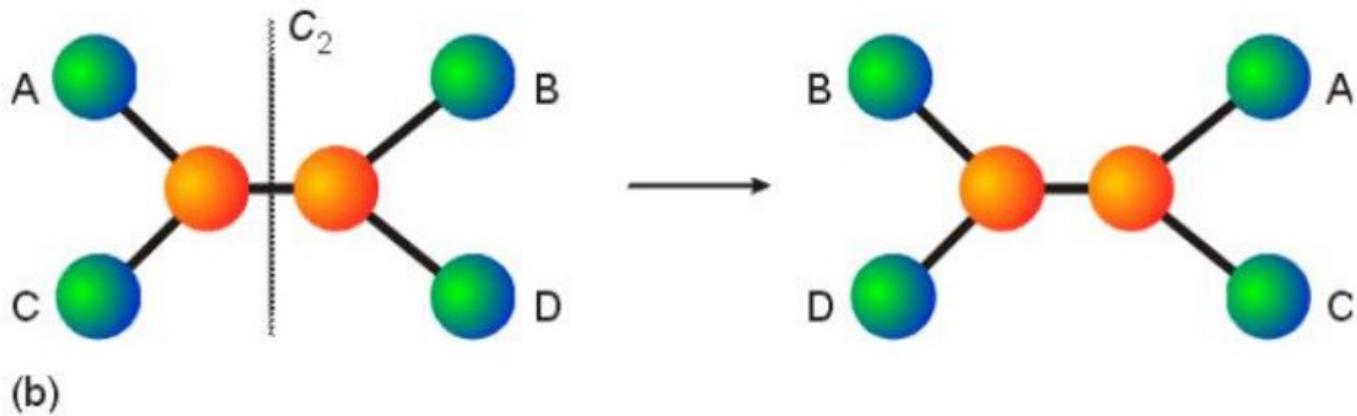
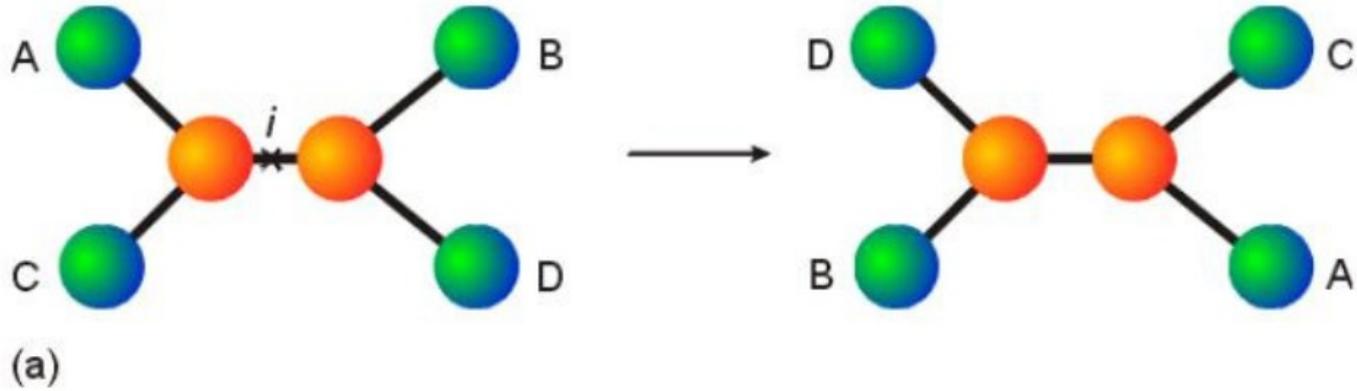
C_4 und C_2 (3x)



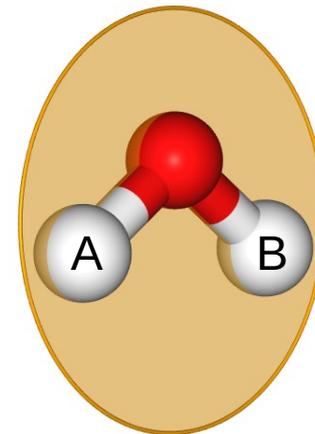
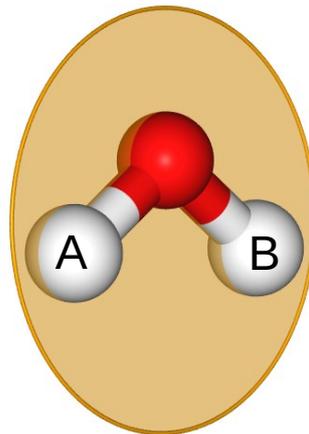
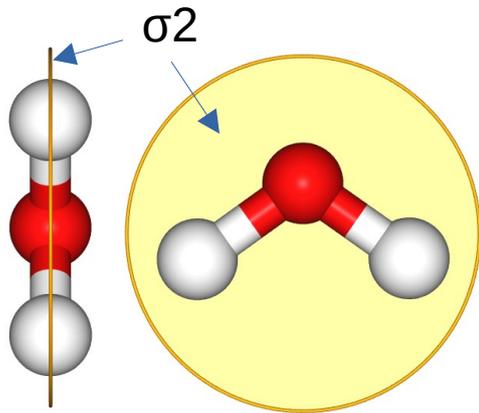
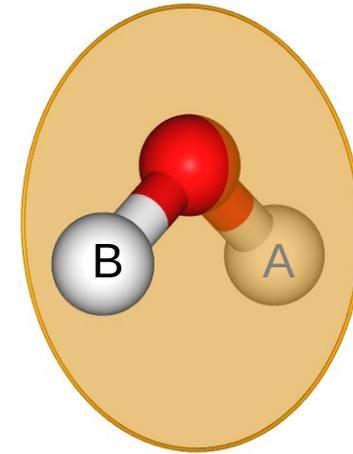
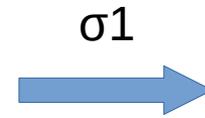
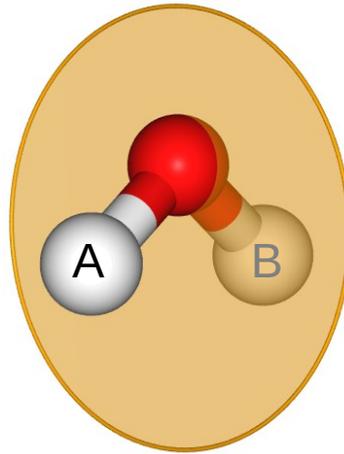
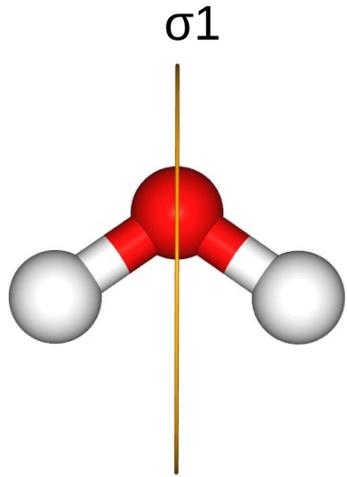
Punktspiegelung



Punktspiegelung vs. C_2

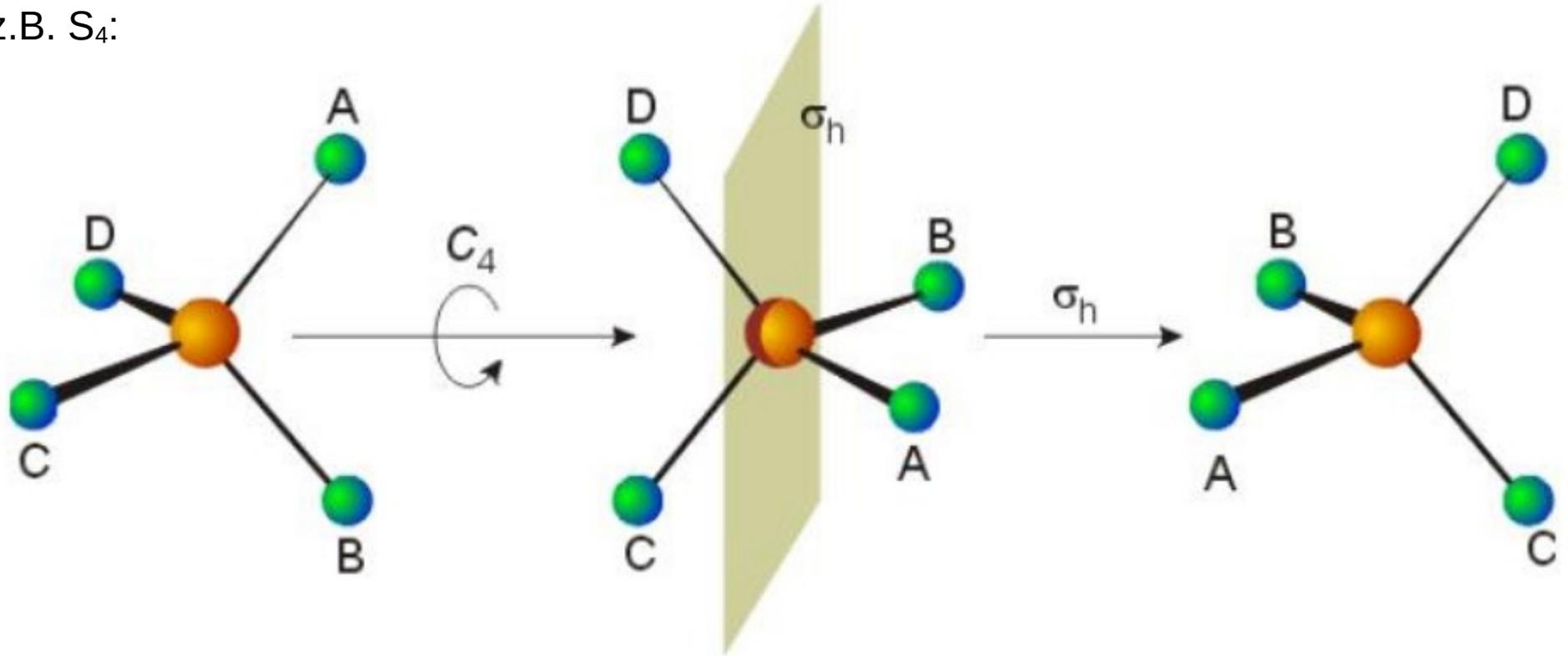


Spiegelung

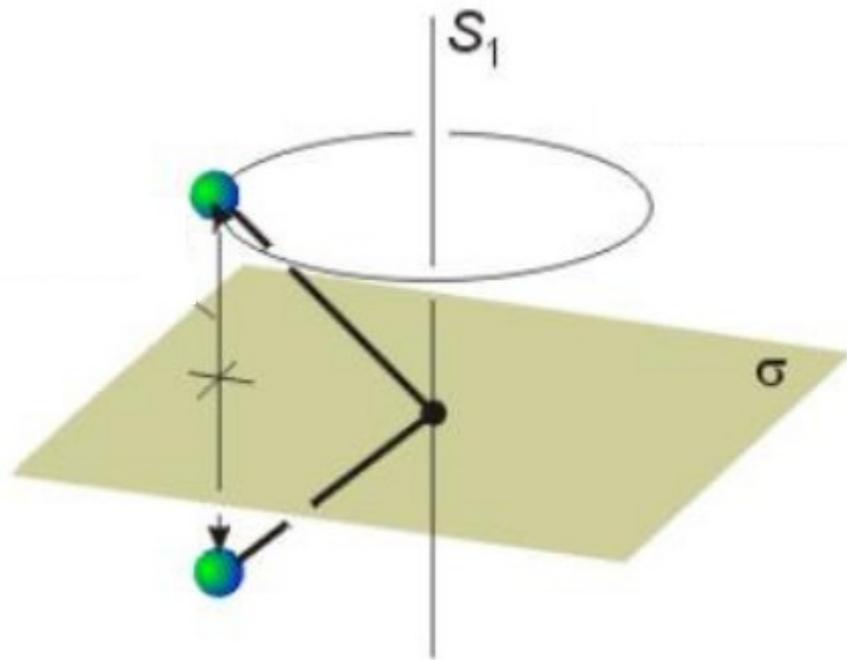


Drehung-Spiegelung

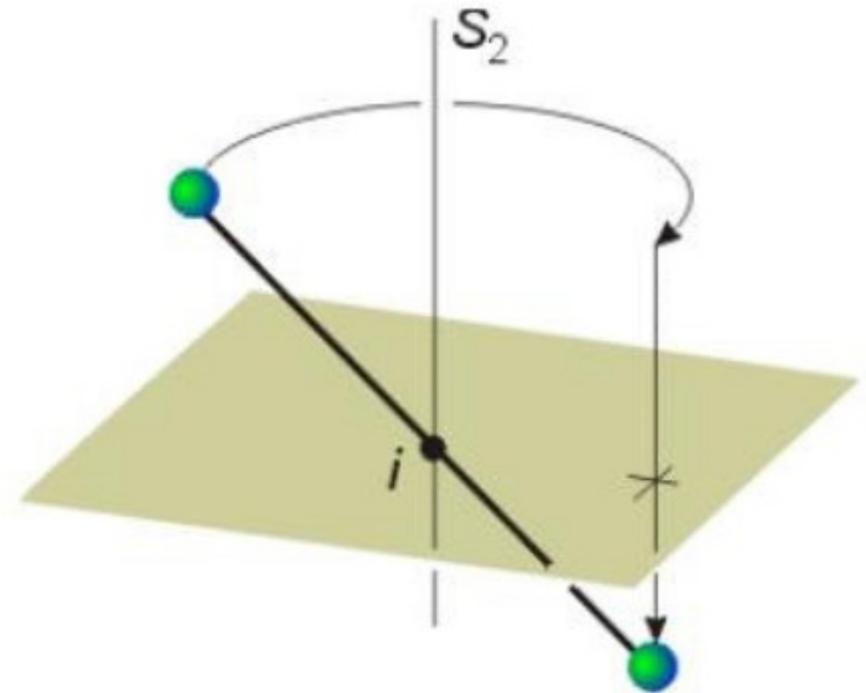
z.B. S_4 :



S_1 und S_2



$$S_1 = \sigma$$



$$S_2 = i$$

ALLE Punktgruppen

Typen	Gruppen	Zusammensetzung (nur Elemente!)
Drehgruppen	C_n	E, C_n ($n = 1, 2, 3, \dots$) [C_n generieren Operationen C_n^k]
	C_{nv}	E, C_n , n -mal- σ_v (v: vertical!) [NB: $n = \infty$]
	C_{nh}	E, C_n , σ_h (h: horizontal, senkrecht zur Achse!), S_n ($=\sigma_h C_n$), i ($n = 2, 4, 6, \dots$)
Dieder-	D_n	E, C_n , n -mal- C_2 senkrecht zur C_n
	D_{nd}	E, C_n , n -mal- C_2 sr.z. C_n , n -mal- σ_d (d: diagonal), S_{2n} , i ($n = 3, 5, \dots$)
	D_{nh}	E, C_n , n -mal- C_2 sr.z. C_n , n -mal- σ (v, d), σ_h , S_n , i ($n = 2, 4, \dots$) [NB: $n = \infty$]
Drehspiegel-	S_n	E, S_n , (+ aus Untergruppen) [NB: $S_1 \equiv C_s$, $S_2 = C_i$]
Tetraeder-	T	E, $4C_3$, $3C_2$
	T_d	E, $4C_3$, $3C_2$, $6\sigma_d$ (+ $6S_4$)
	T_h	E, $4C_3$, $3C_2$, $6\sigma_h$ (+ i , $4S_6$)
Oktaeder-	O	E, $4C_3$, $6C_2$, $3C_4$ (generieren $3C_2$ und Operationen C_4^{-1})
	O_h	E, $4C_3$, $6C_2$, $3C_4$ (s. Oben), $3\sigma_h$ (+ i , $3S_4$), $6\sigma_d$, $4S_6$
Ikosaeder-	I	E, $6C_5$ (generieren Operationen C_5^k), $10C_3$ (g. $10C_3^{-1}$), $15C_2$
	I_h	E, $6C_5$ (s. oben), $10C_3$ (s. oben), $15C_2$, 15σ , $6S_{10}$ (g. Op.), $10S_6$ (g. Op.)

Punktgruppen sind mat. Gruppen!

0. Es gibt ein Punkt, der durch alle Symmetrieeoperationen der Punktgruppe wieder auf sich selbst abgebildet wird!
1. Zwei Elementen **a** und **b** der Gruppe G sind durch Multiplikation ein Element **c**, das ebenfalls zur Gruppe G gehört, zugeordnet: $\mathbf{a \cdot b = c}$

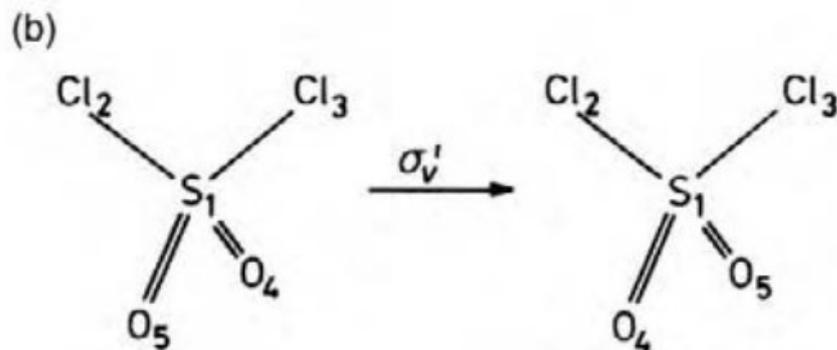
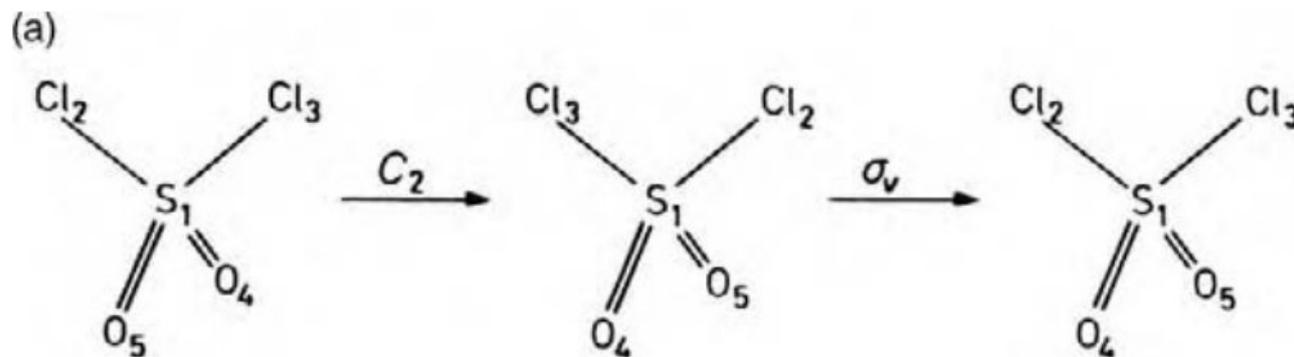
Hier: Element \equiv Symmetrieeoperation!

Multiplikationstafel für C_{2v} :

C_{2v}	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

Multiplizieren

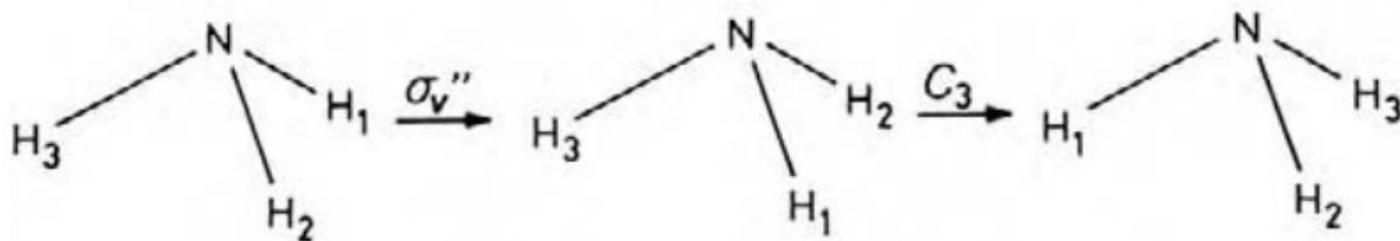
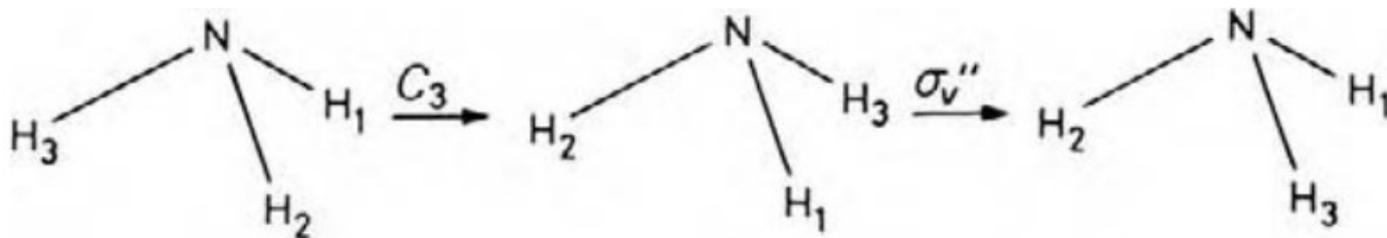
$$\sigma_v \cdot C_2 = \sigma'_v$$



Aber...

... die Elemente einer Gruppe G sind allgemein nicht kommutativ (, es sei denn...)

$a \cdot b \neq b \cdot a$ z.B.:



G Eigenschaften, Fortsetzung

2. Die Gruppe G beinhaltet das sogenannte Einselement \mathbf{e} .
Es gilt: $\mathbf{a} \cdot \mathbf{e} = \mathbf{e} \cdot \mathbf{a} = \mathbf{a}$

3. Die Elemente einer Gruppe sind immer assoziativ:
 $(\mathbf{a} \cdot \mathbf{b}) \cdot \mathbf{c} = \mathbf{a} \cdot (\mathbf{b} \cdot \mathbf{c})$

Z.B. in C_{2v} :

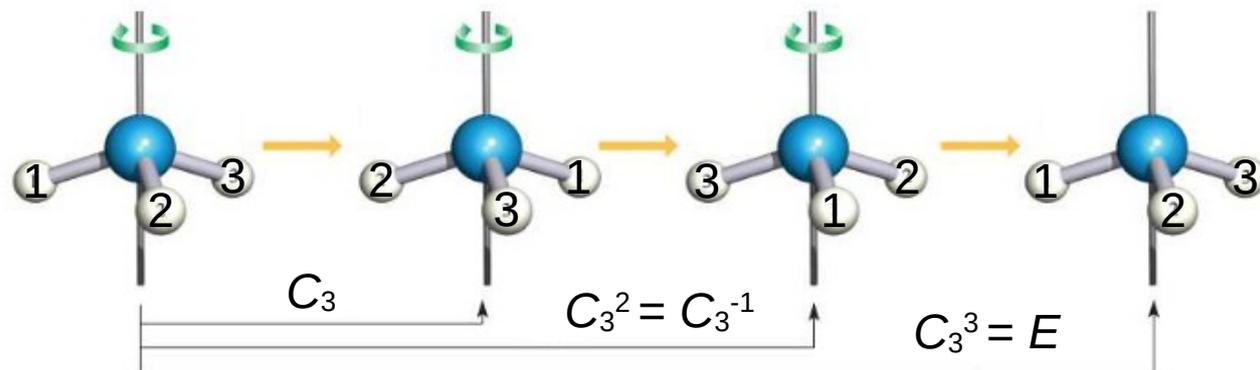
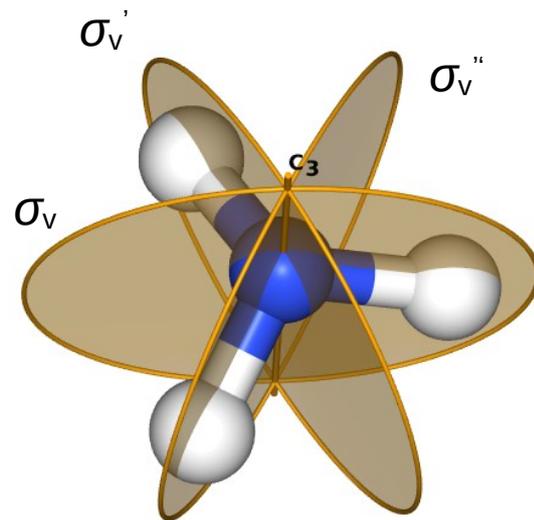
$$C_2 \cdot \sigma_v \cdot \sigma_v' = C_2 \cdot (\sigma_v \cdot \sigma_v') = (C_2 \cdot \sigma_v) \cdot \sigma_v'$$

4. Zu jedem Element \mathbf{a} existiert ein inverses Element \mathbf{a}^{-1} .
Es gilt: $\mathbf{a} \cdot \mathbf{a}^{-1} = \mathbf{a}^{-1} \cdot \mathbf{a} = \mathbf{e}$

Symmetrieelemente vs. -operationen

Multiplikationstafel für C_{3v} :

C_{3v}	E	C_3	C_3^2	σ_v	σ'_v	σ''_v
E	E	C_3	C_3^2	σ_v	σ'_v	σ''_v
C_3	C_3	C_3^2	E	σ''_v	σ_v	σ'_v
C_3^2	C_3^2	E	C_3	σ'_v	σ''_v	σ_v
σ_v	σ_v	σ'_v	σ''_v	E	C_3	C_3^2
σ'_v	σ'_v	σ''_v	σ_v	C_3^2	E	C_3
σ''_v	σ''_v	σ_v	σ'_v	C_3	C_3^2	E

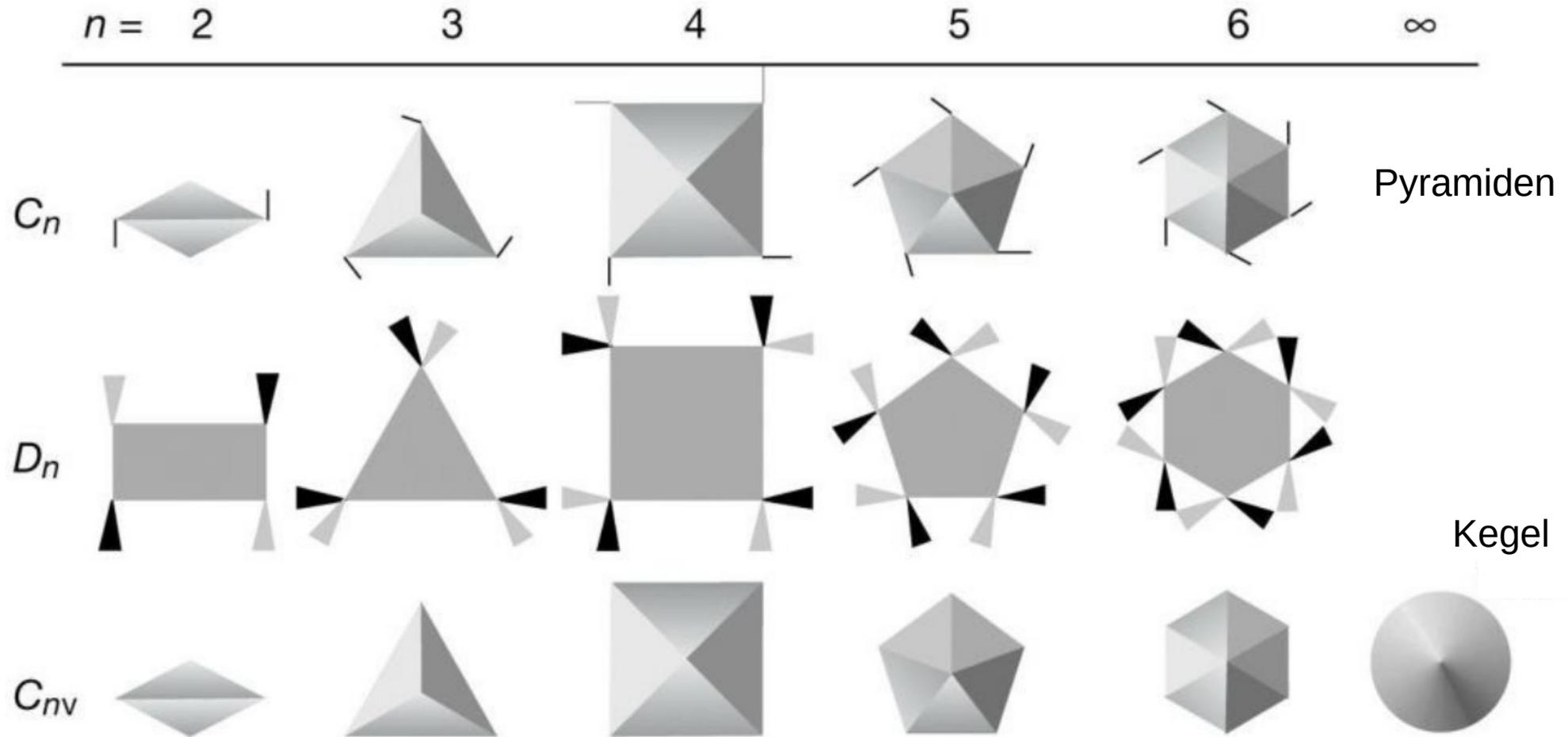


Element: C_3

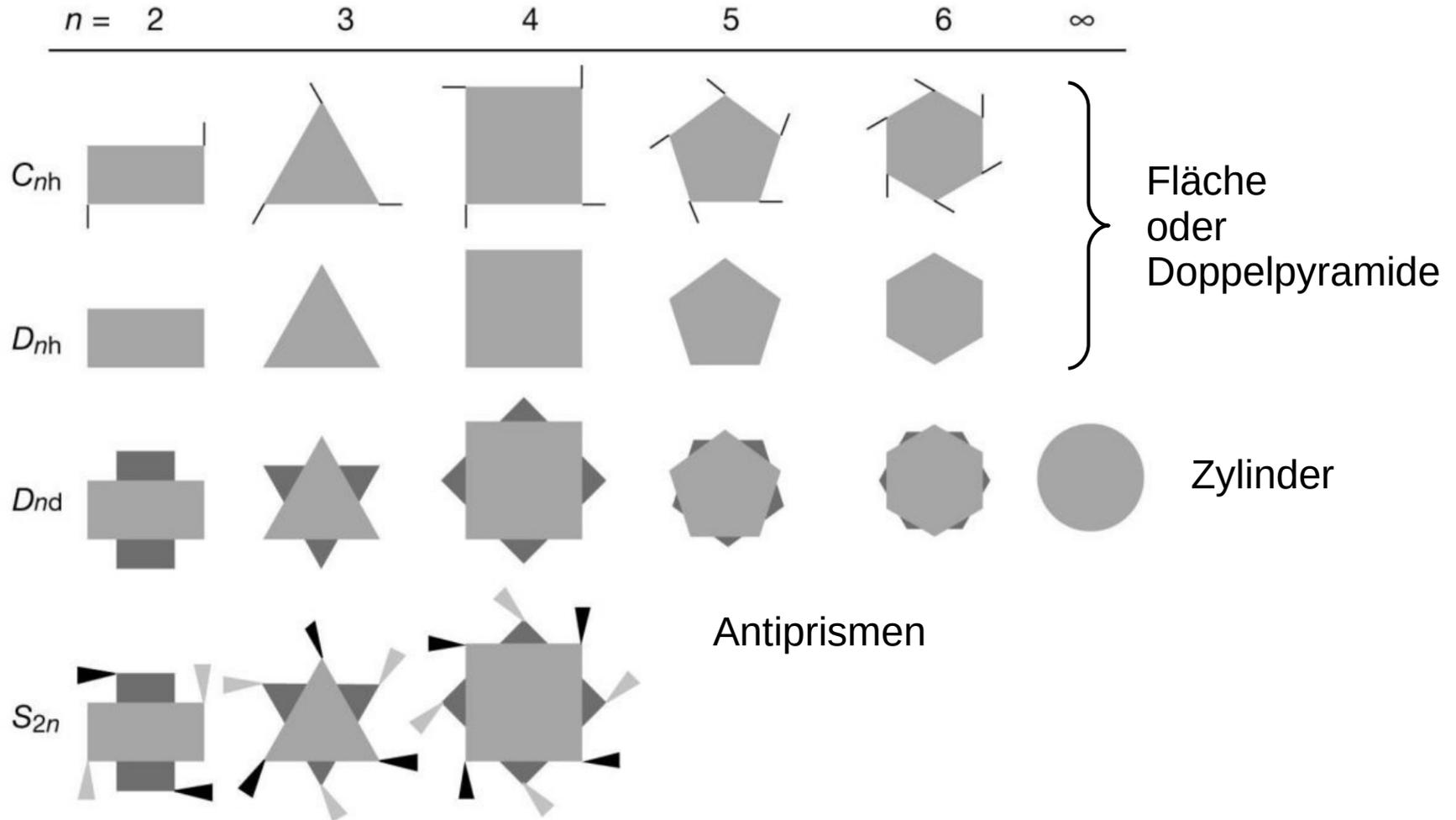
Operationen:

$$C_3 \cdot C_3 = C_3^2 (= C_3^{-1})$$

Geometrische Formen I

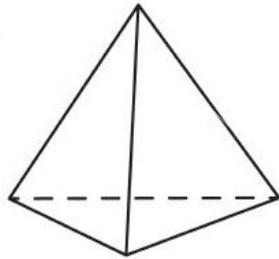


Geometrische Formen II

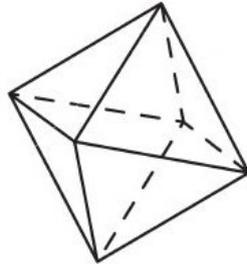


Platonischer Körper

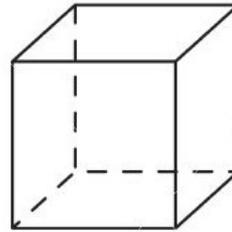
Tetraeder



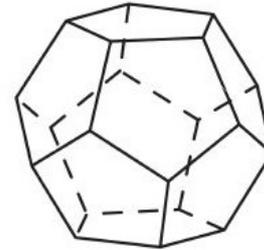
Oktaeder



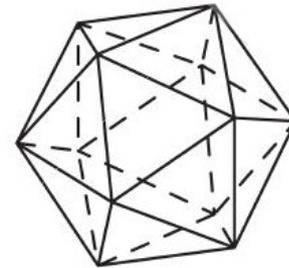
Hexaeder



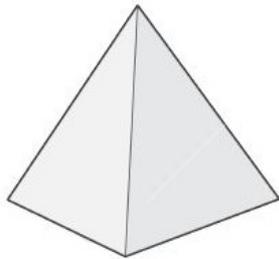
Dodekaeder



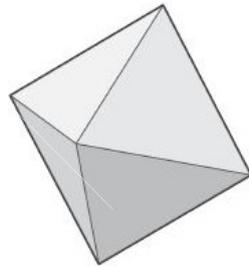
Ikosaeder



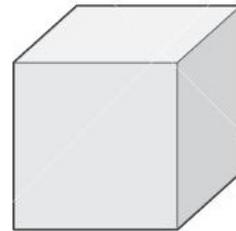
Dual



T_d

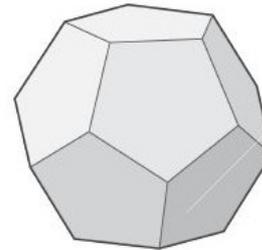


O_h

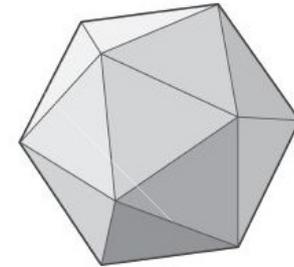


O_h

Dual



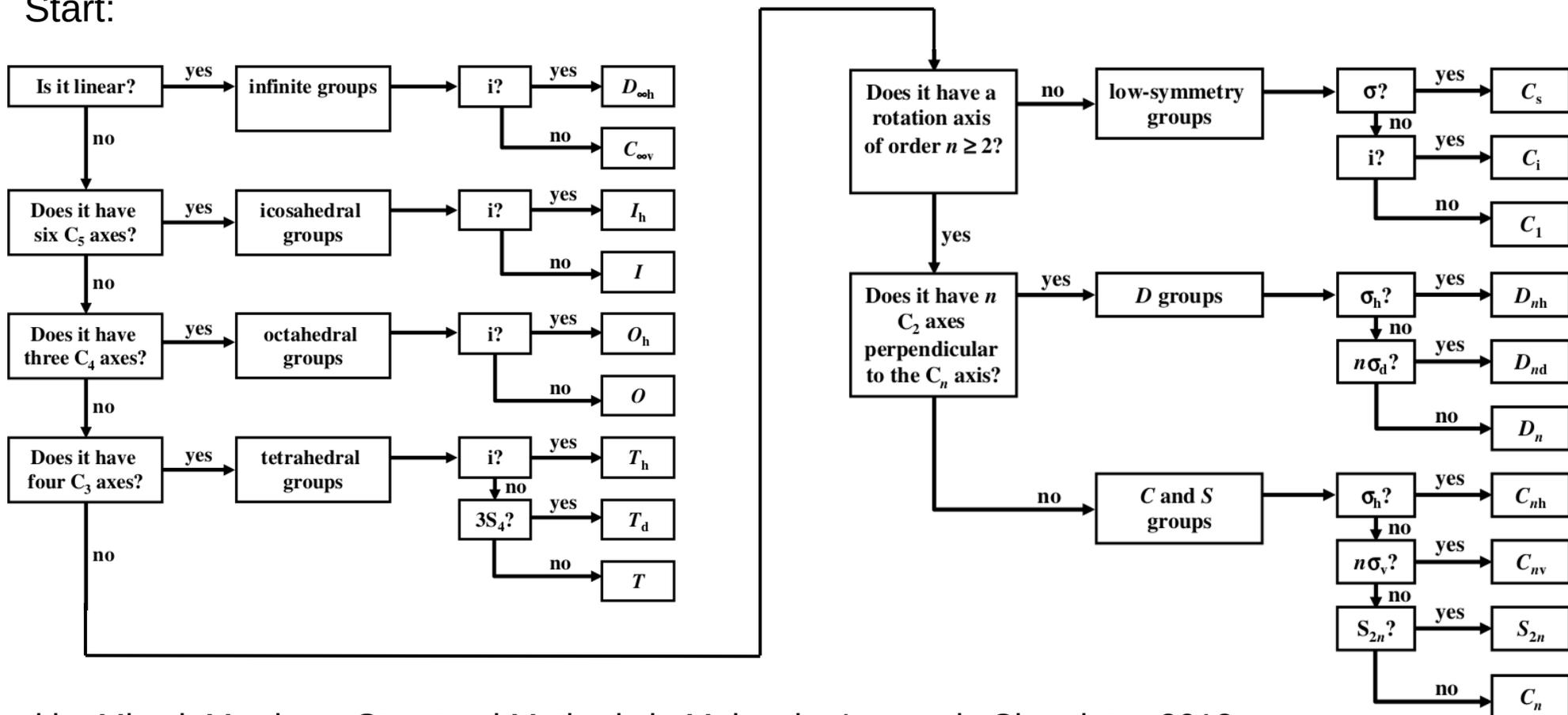
I_h



I_h

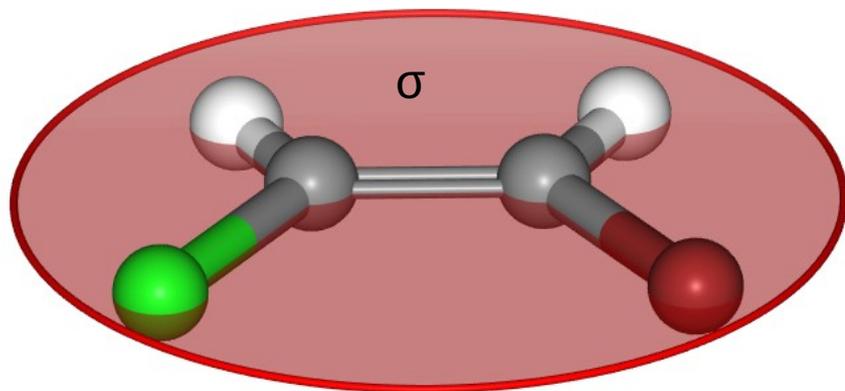
Fließschema II (besser)

Start:

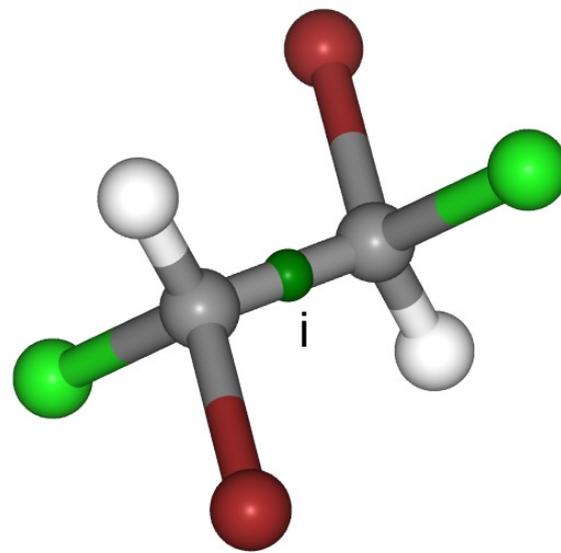


Beispiele

C_s, C_i

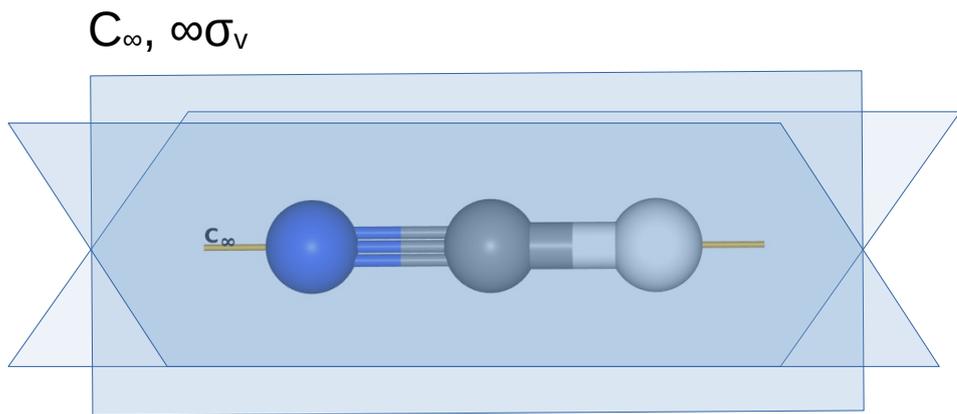


C_s : ClHC=CHBr

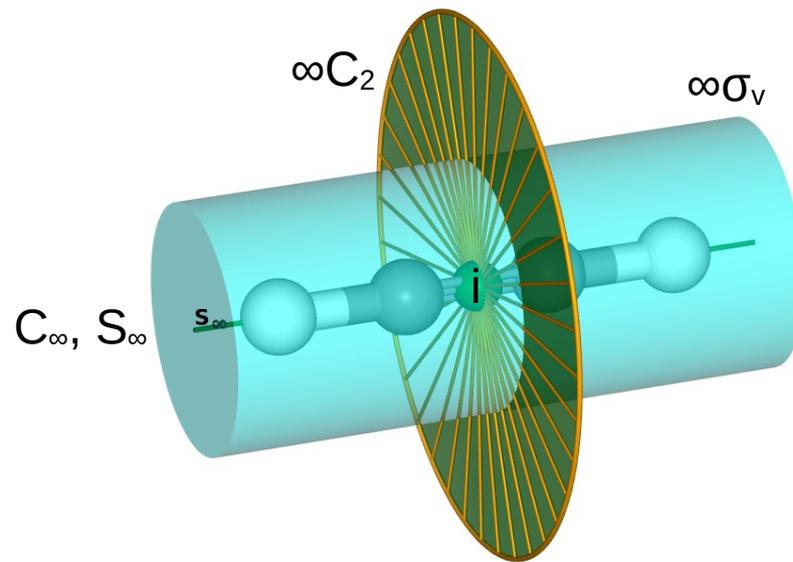


C_i : BrClHC-CHClBr

$C_{\infty v}, D_{\infty h}$

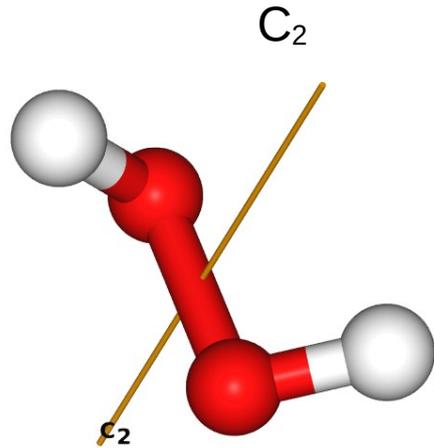


$C_{\infty v}$: N#C-H

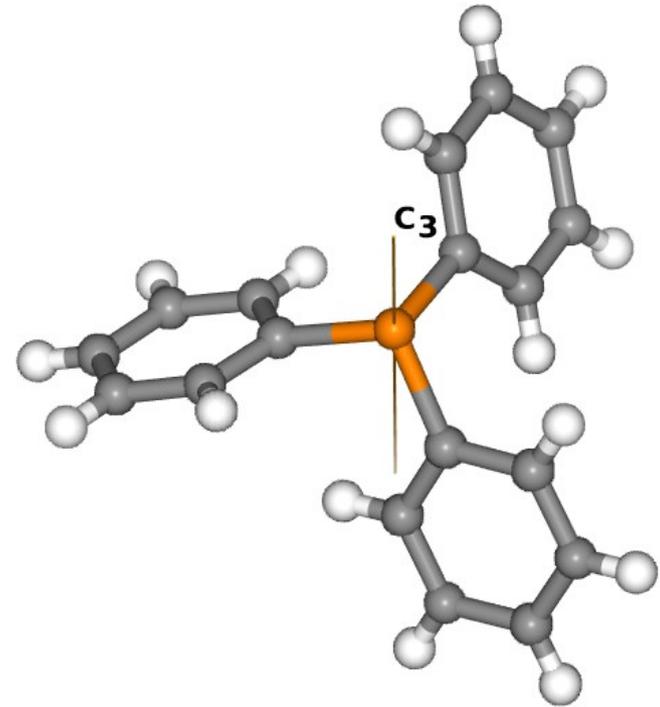


$D_{\infty h}$: H-C#C-H

C_n



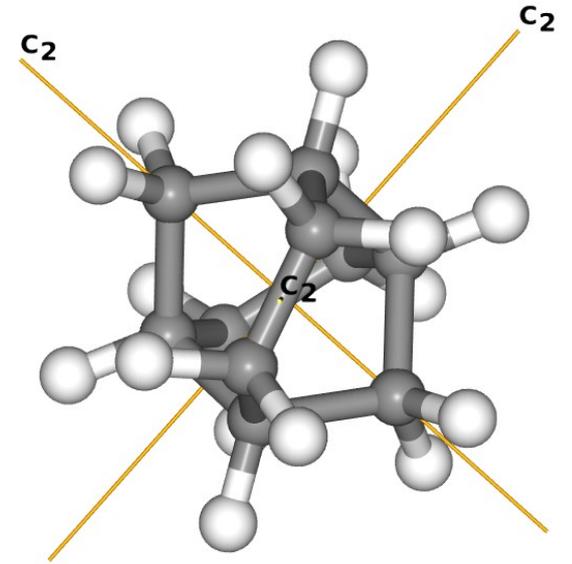
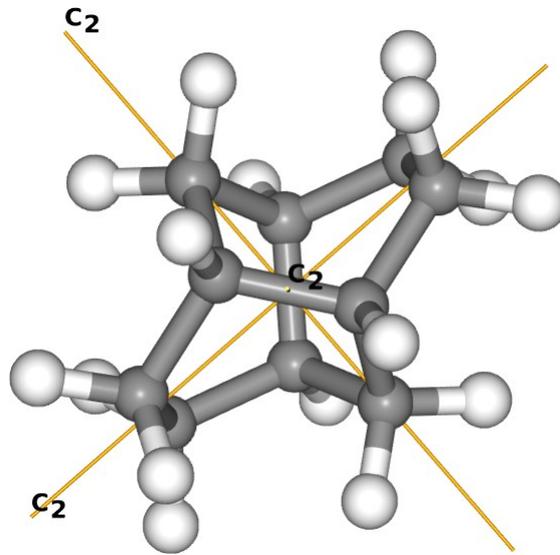
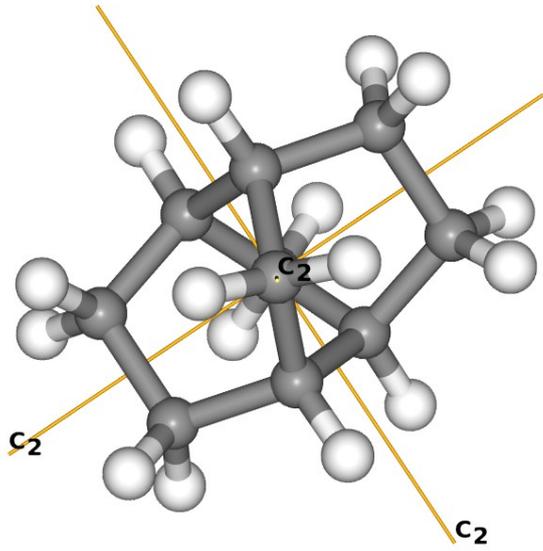
C₂: HO-OH



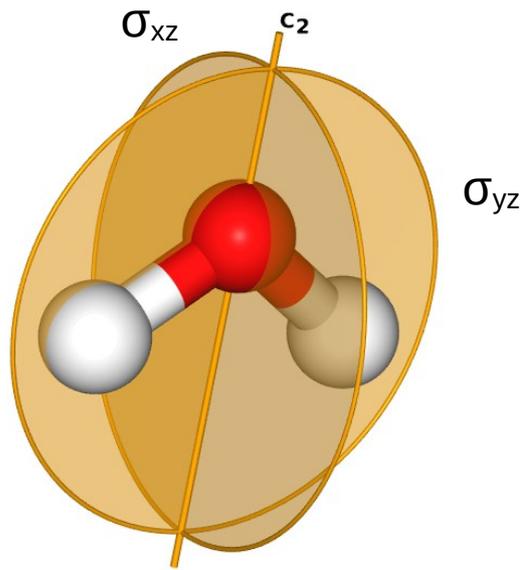
C₃: Triphenylphosphin

D_n

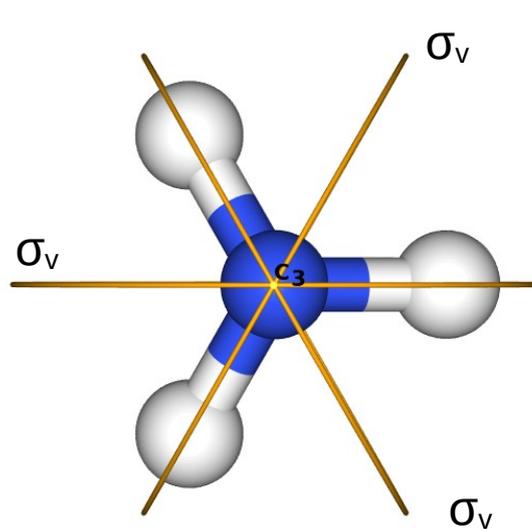
D_2 : Twistan



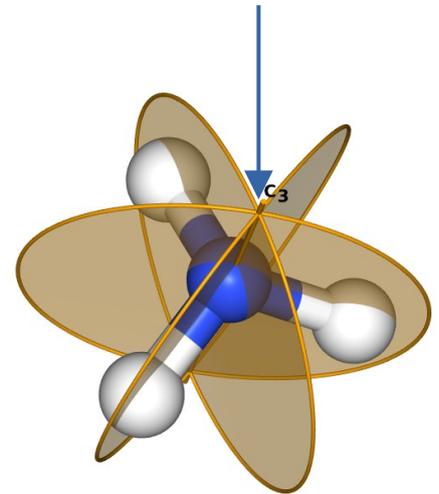
C_{nv}



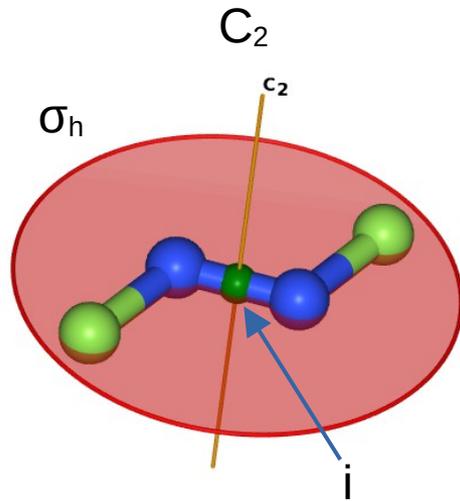
C_{2v} : H_2O



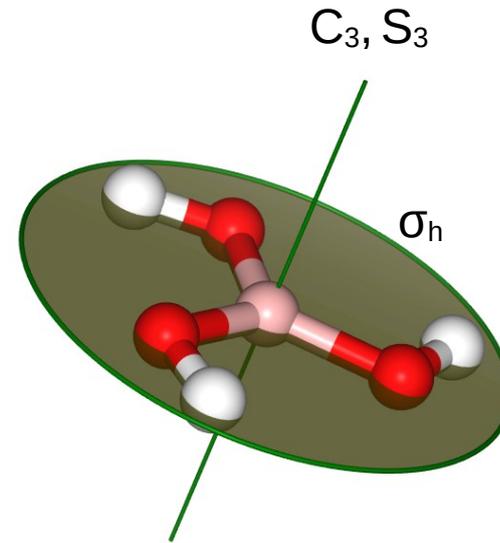
C_{3v} : NH_3



C_{nh}

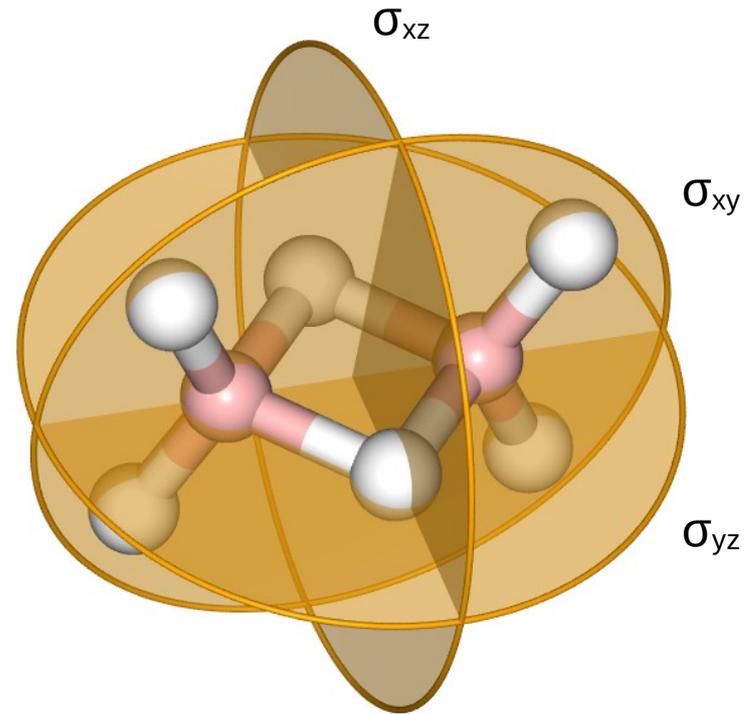
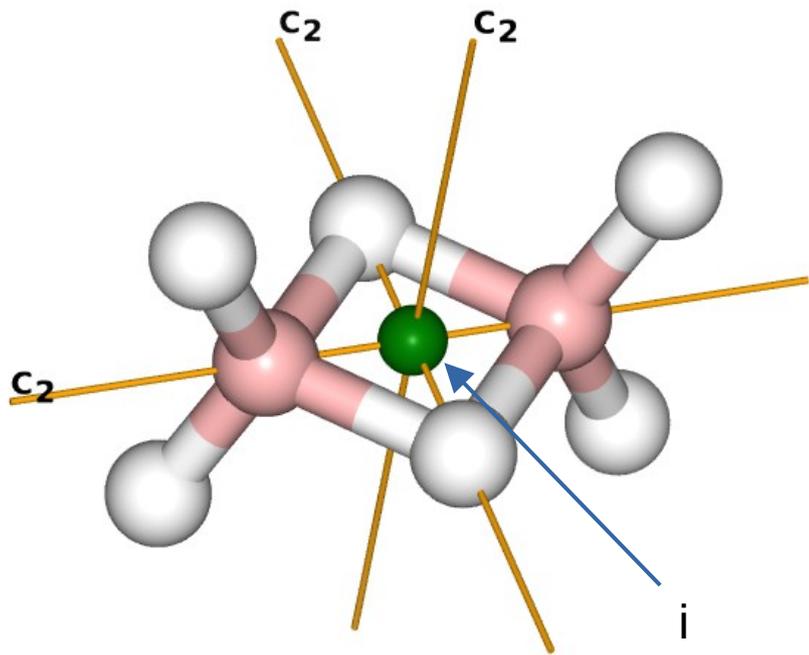


C_{2h} : FN=NF



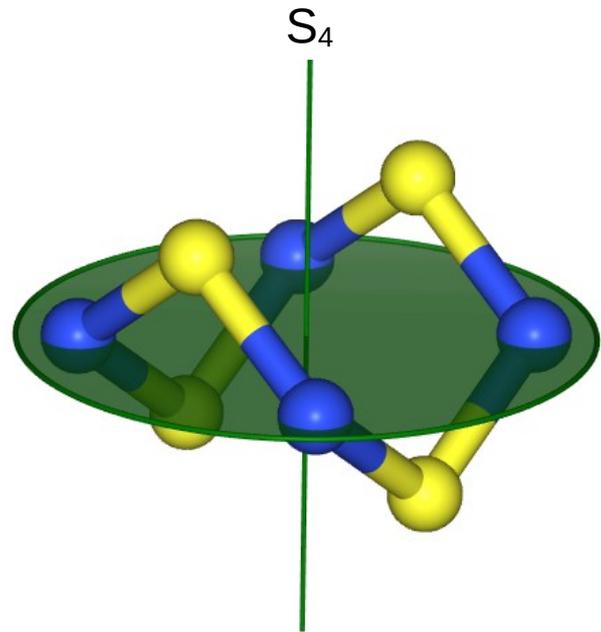
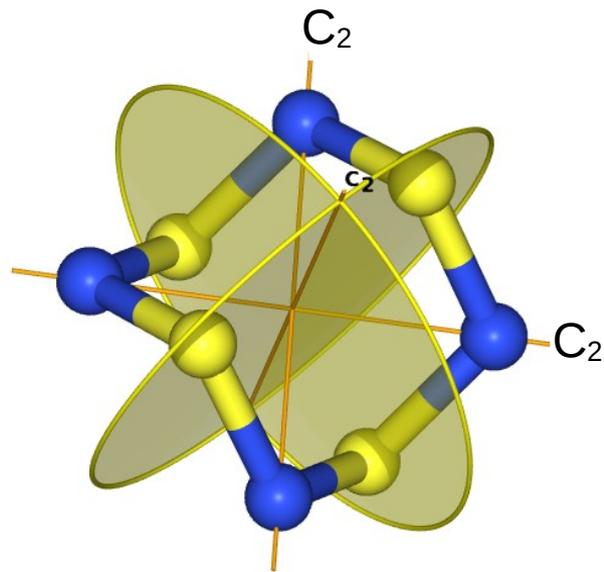
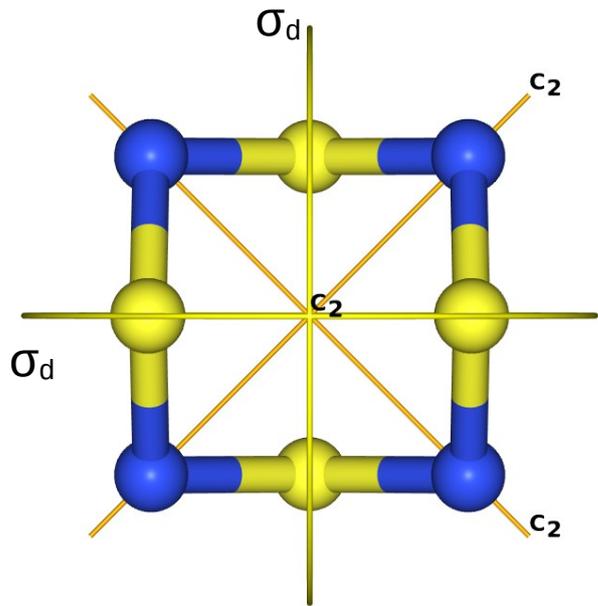
C_{3h} : Borsäure

D_{nh}



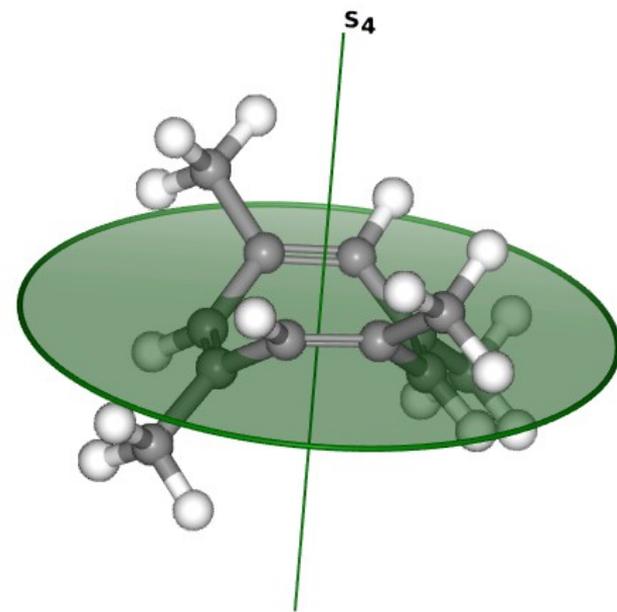
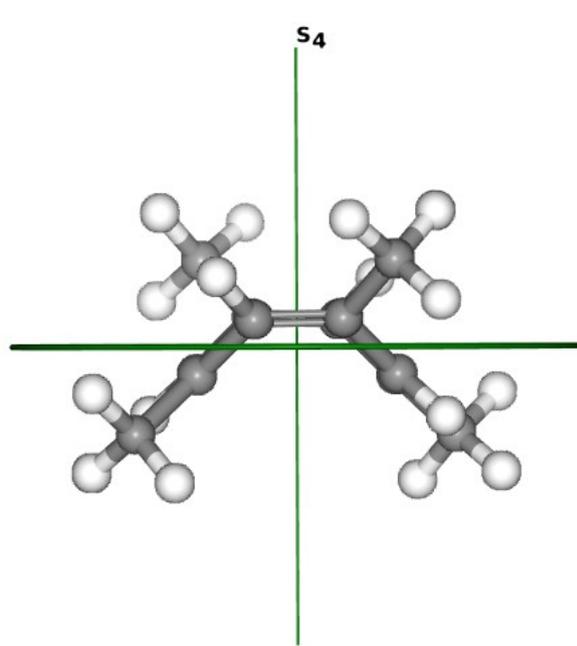
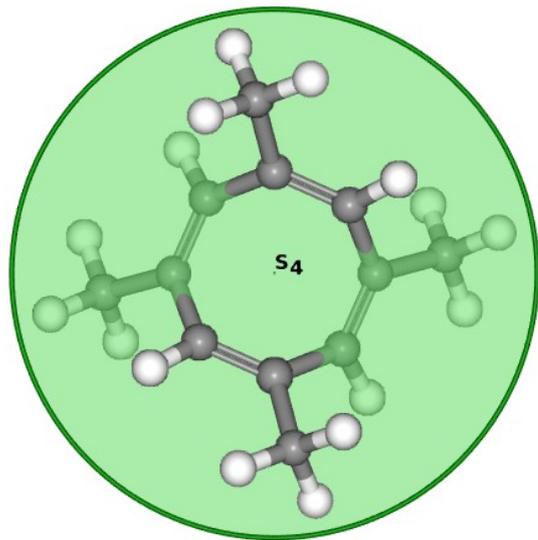
D_{2h} : Diboran

D_{nd}



D_{2d} : S_4N_4

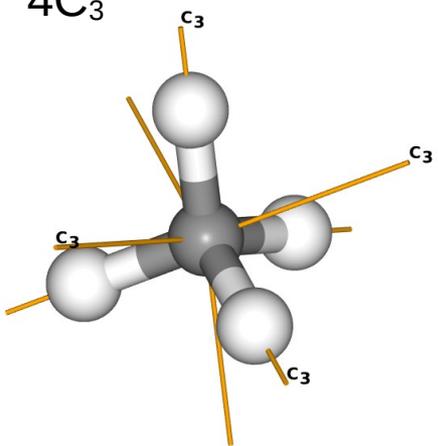
S_n



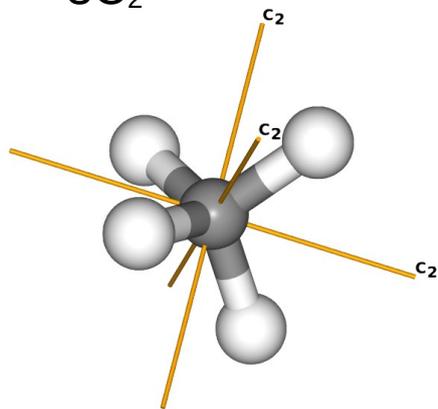
S_4 : Tetramethyl-Cot

T_d

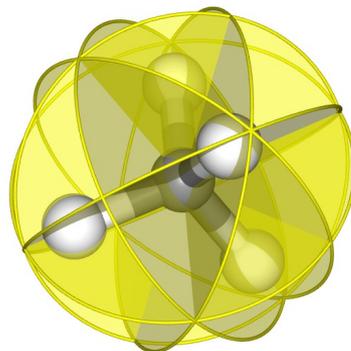
$4C_3$



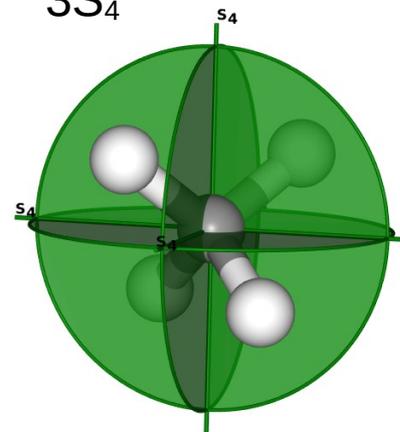
$3C_2$



$6\sigma_d$

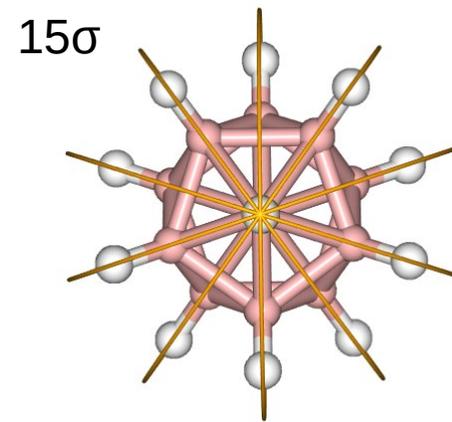
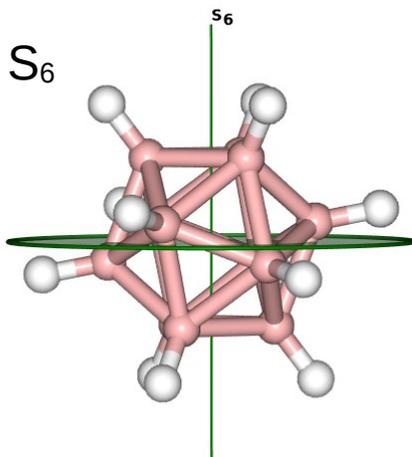
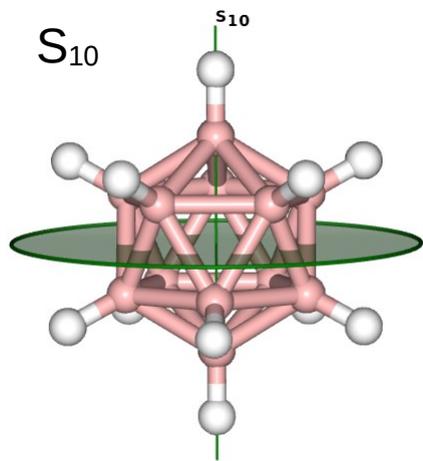
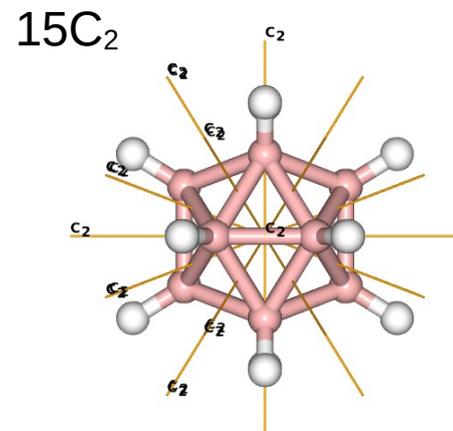
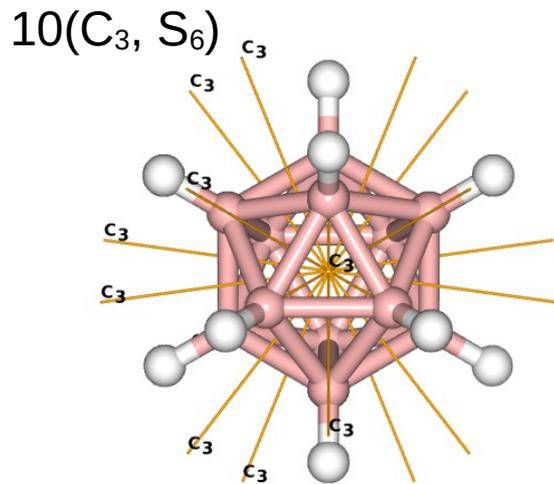
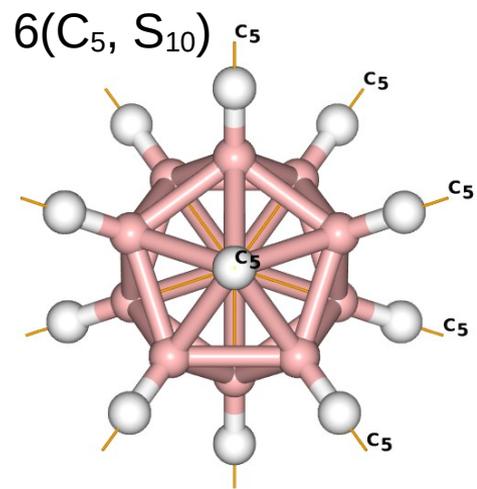


$3S_4$



T_d : Methan

I_h

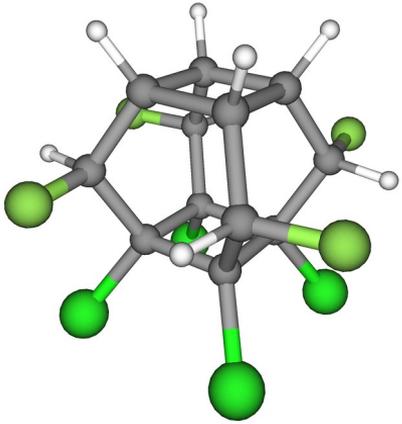


$I_h: [B_{12}H_{12}]^{2-}$

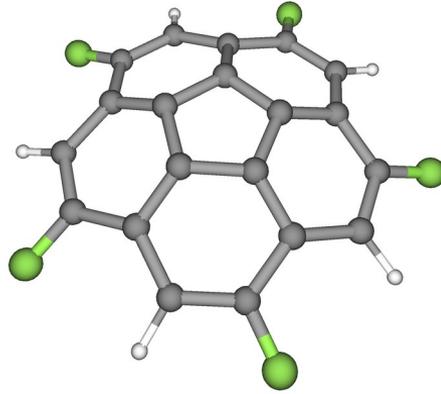
Kompliziertere
und
realistische (*sic!*)
Beispiele

C_n

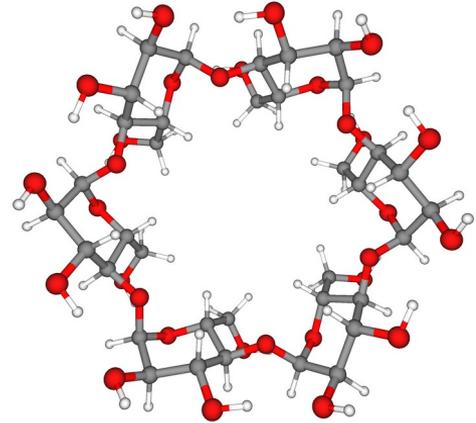
C_4 : [4]asteran



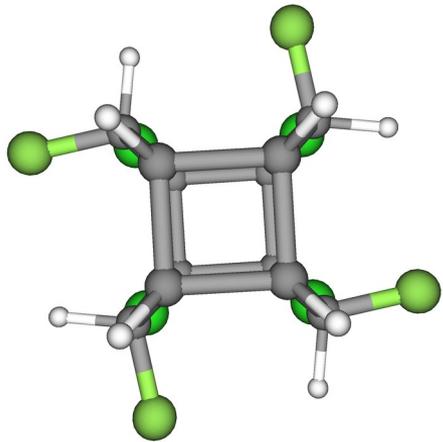
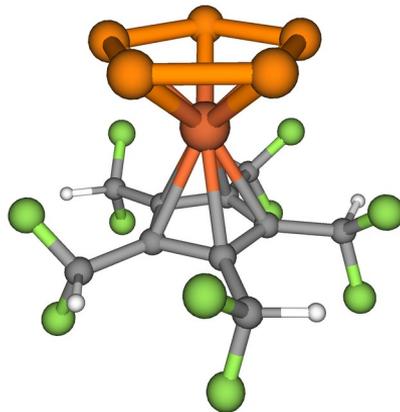
C_5 : F-Corannulen



C_6 : α -Cyclodextrin

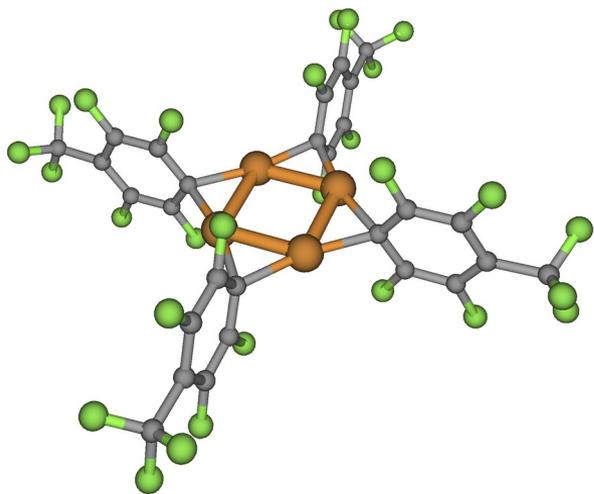


C_5 : [Cp(CHF₂)₅]Fe(P₅)

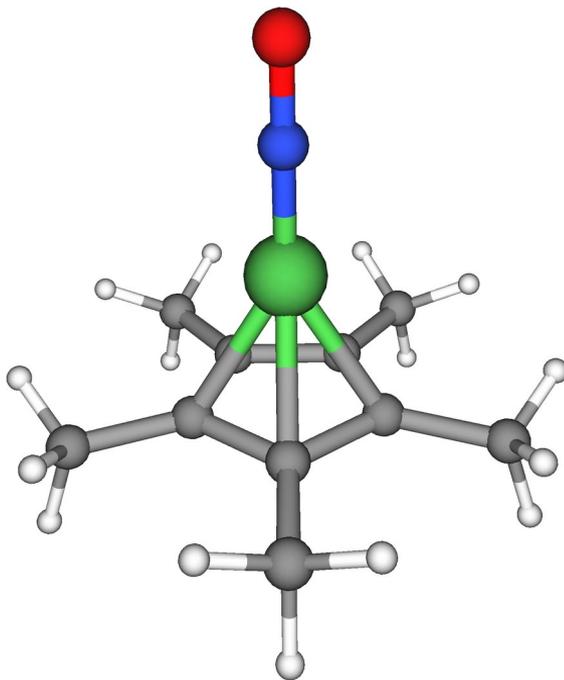


C_{nv}

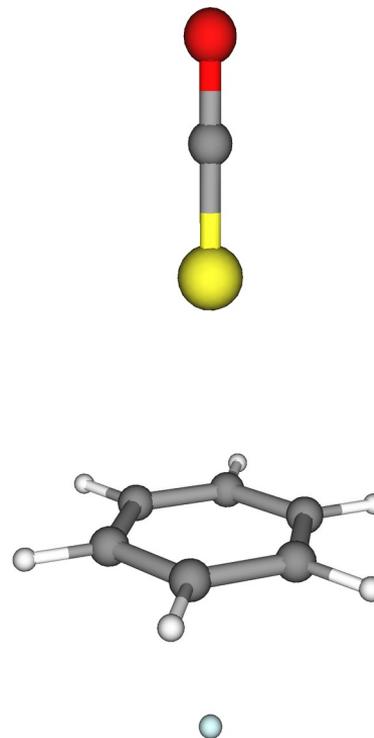
C_{4v} : $Cu_4(C_7F_7)_4$



C_{5v} : $(C_5Me_5)Ni-N=O$



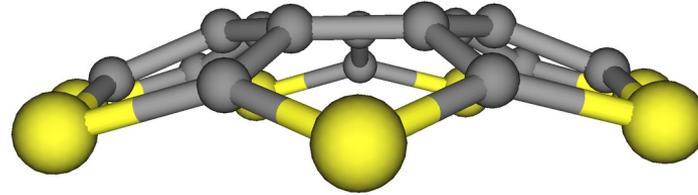
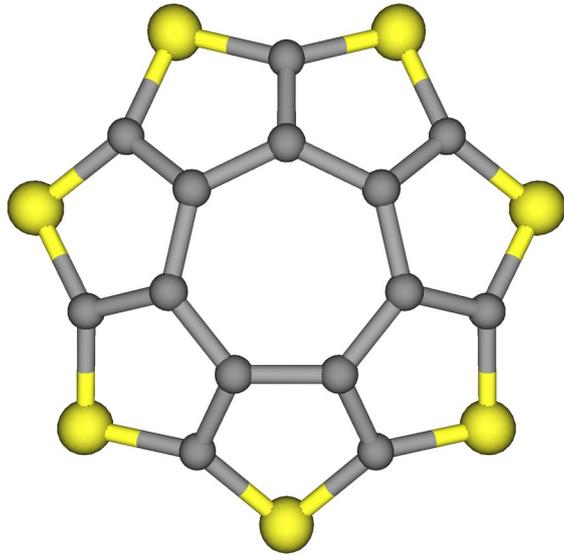
C_{6v} : $He...C_6H_6...S=C=O$



C_{7v}

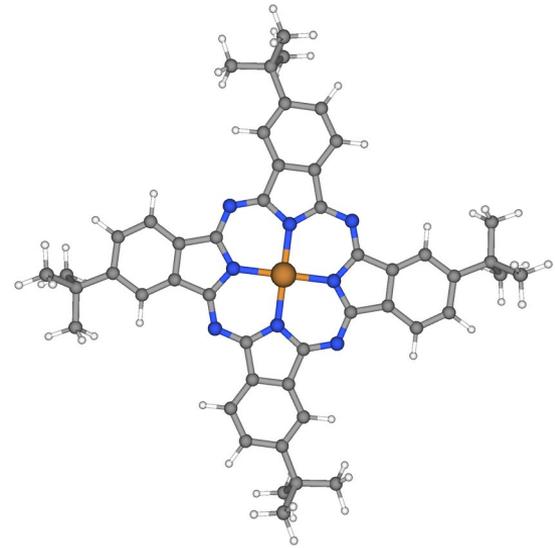
$C_{14}S_7$, eine Form von Kohlenstoffsulfid

C_{7v} @ PBE0-D3BJ/def2-TZVP

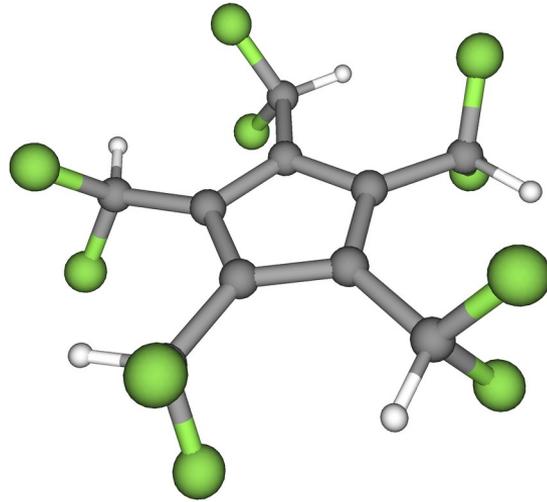


C_{nh}

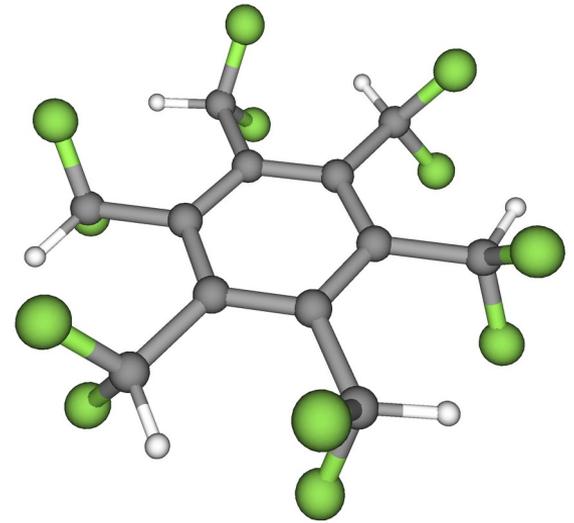
C_{4h} : Cu-Phthalocyanin



C_{5h} : Auf Basis von
Cyclopentadienyl Anion

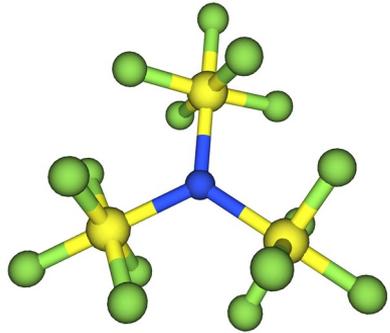


C_{6h} : $C_6(CHF_2)_6$

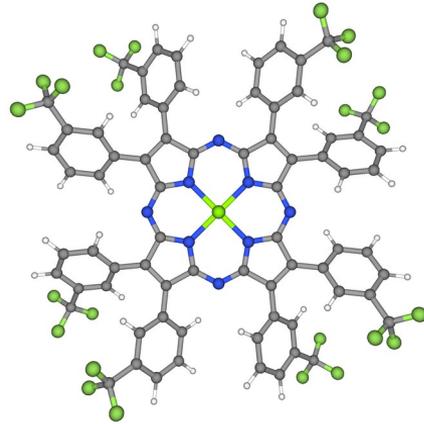


D_n

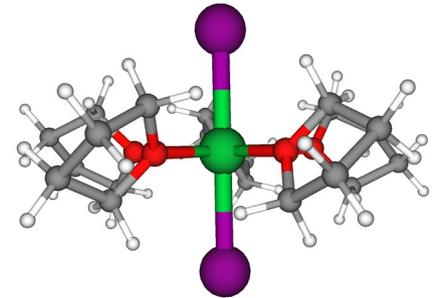
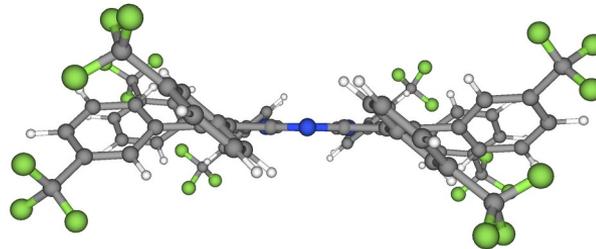
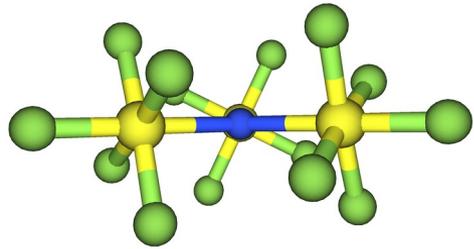
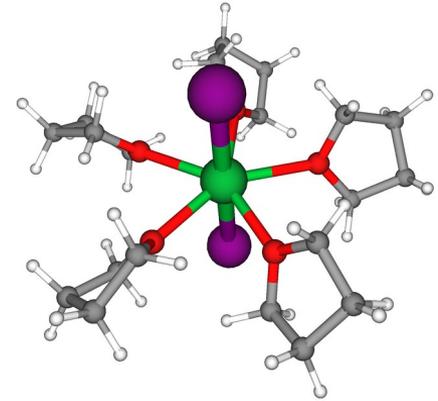
D_3 : $N(SF_5)_3$



D_4 : Mg-Porphyrizin

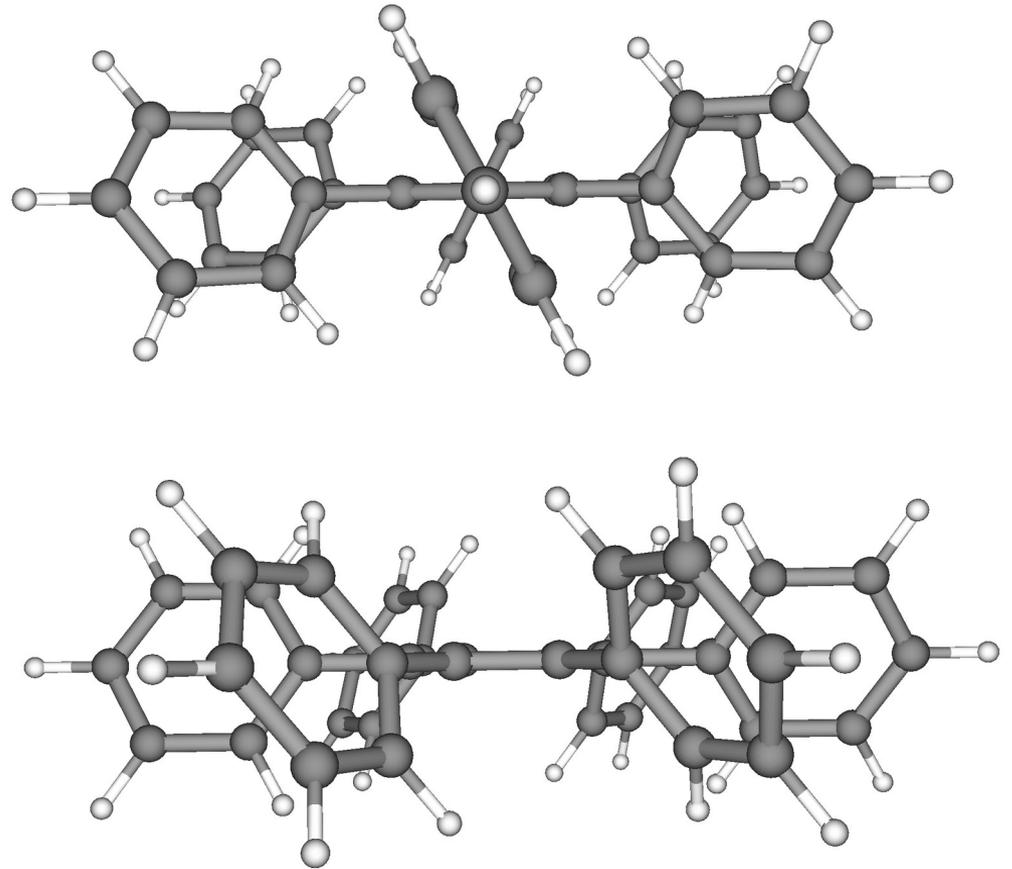
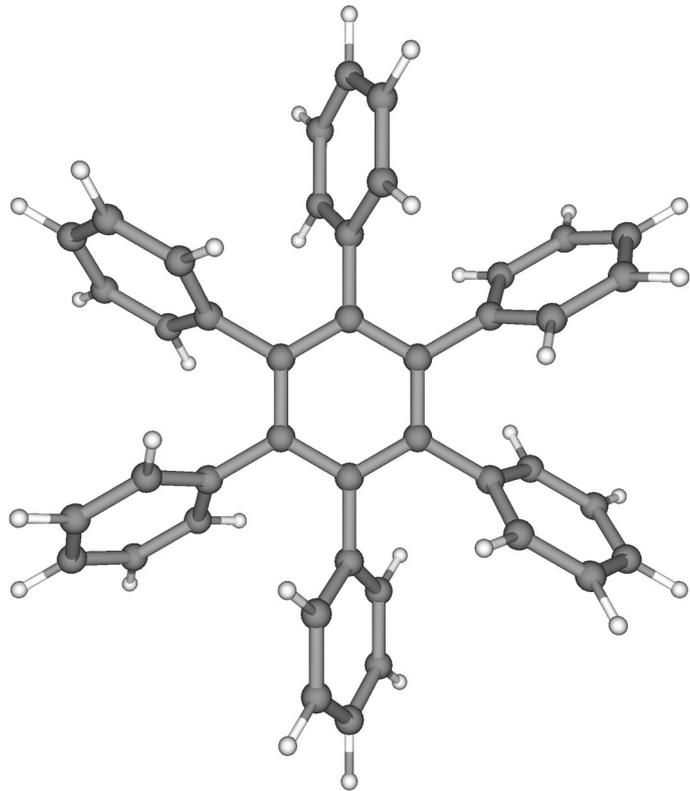


D_5 : $I_2Yb(thf)_5$



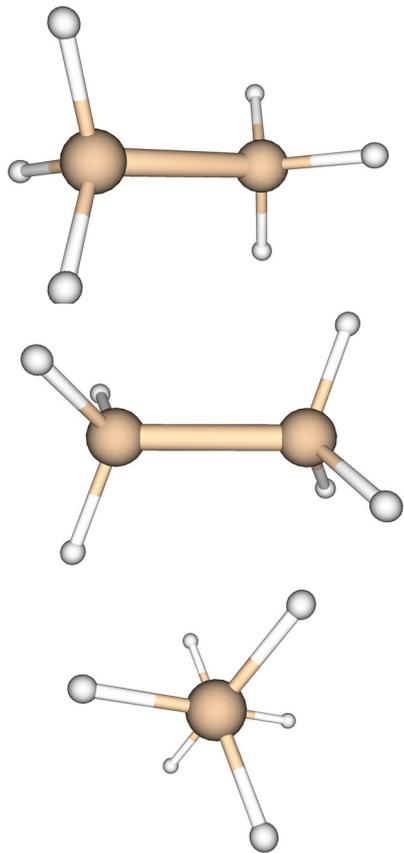
D_6

D_6 : Hexaphenylbenzol

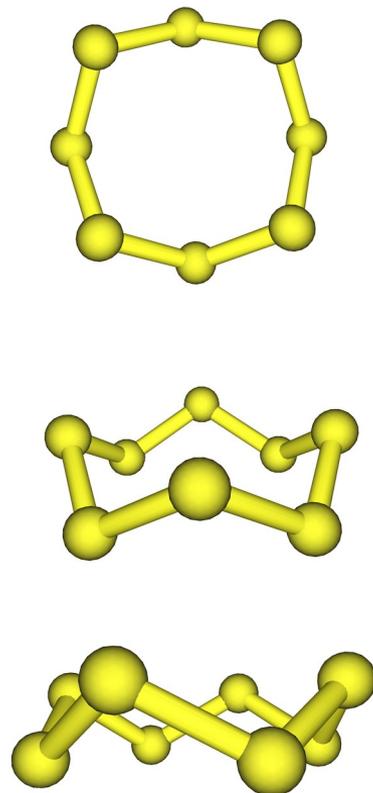


D_{nd}

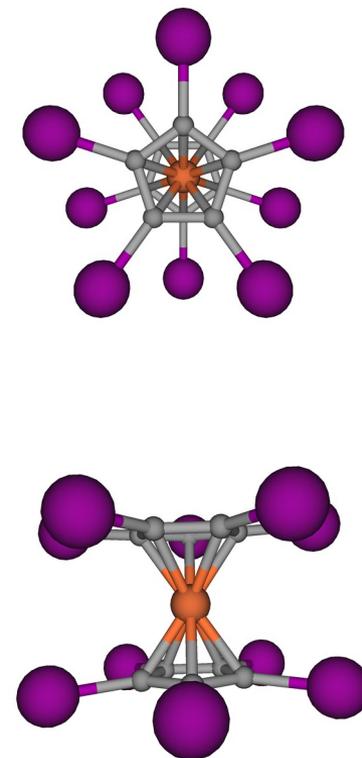
D_{3d} : Si_2H_6



D_{4d} : S_8

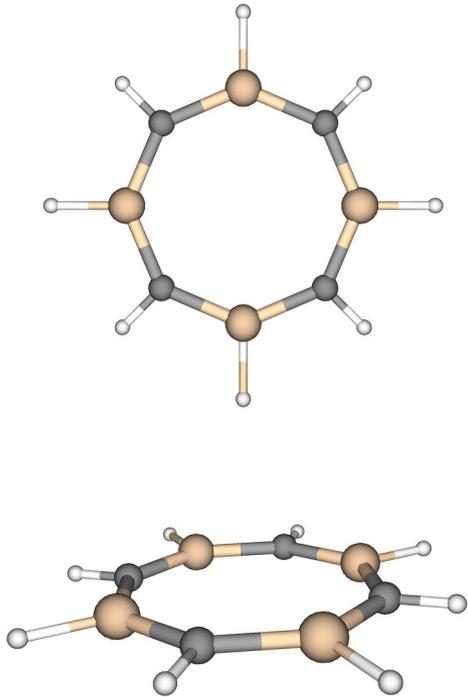


D_{5d} : $\text{Fe}(\text{C}_5\text{I}_5)_2$

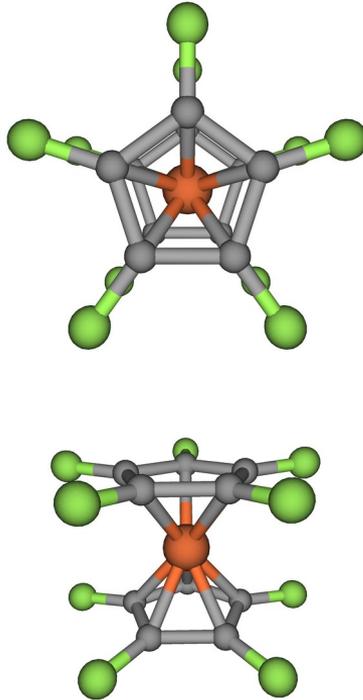


D_{nh}

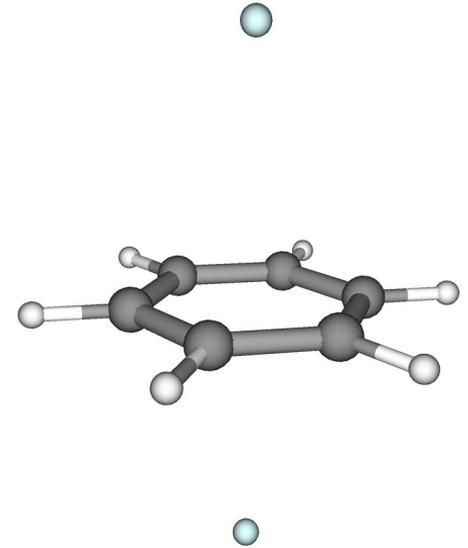
D_{4h} : Si-cot



D_{5h} : Fe(C₅F₅)₂



D_{6h} : He...C₆H₆...He



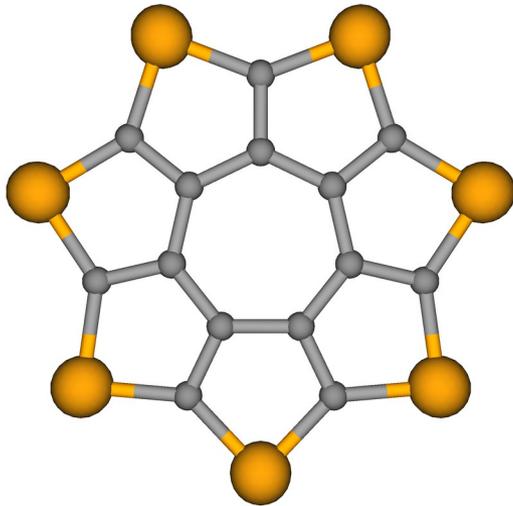
Auch D_{6h} : C₆H₆, C₆F₆, ... C₆I₆, usw.

D_{7h}

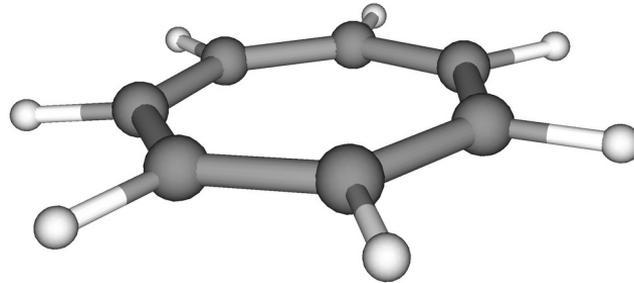
$C_{14}Se_7$

eine Form von Kohlenstoffselepid

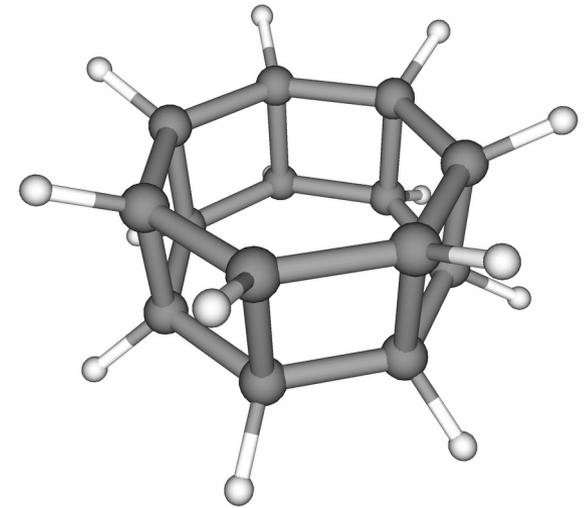
D_{7h} @ PBE0-D3BJ/def2-TZVP



Tropylium Kation $C_7H_7^+$

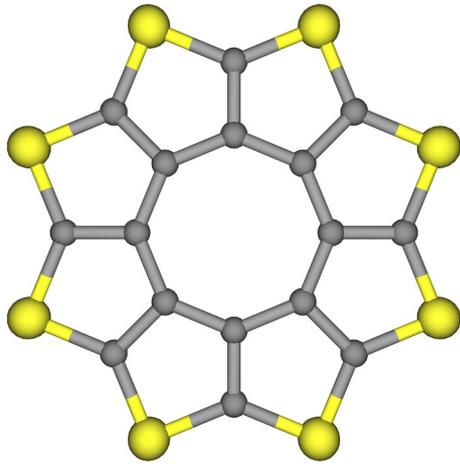


[7]Prisman

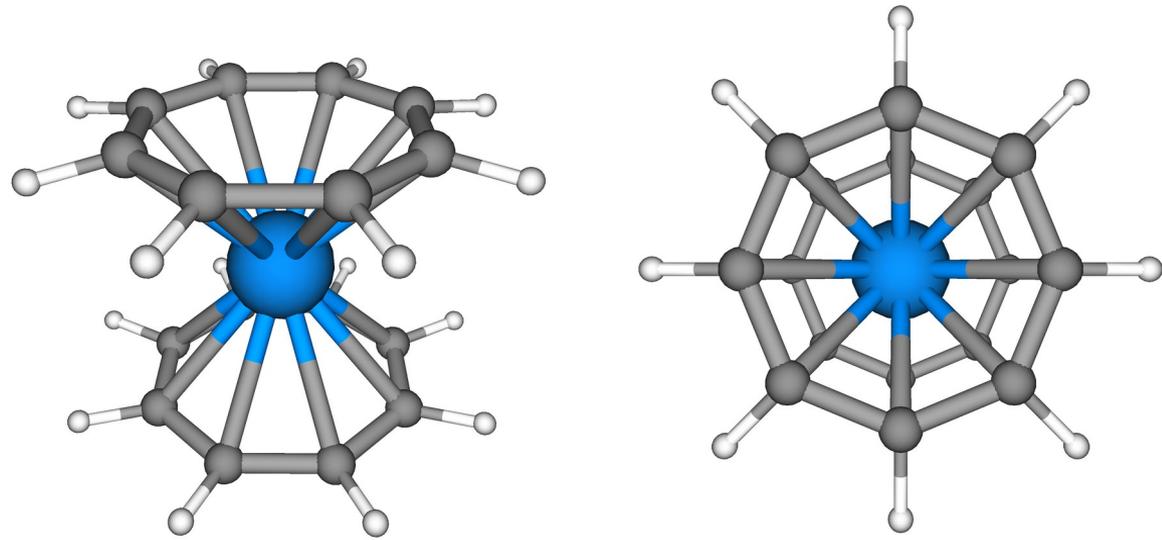


D_{8h}

$C_{16}S_8$ „Sulflower“



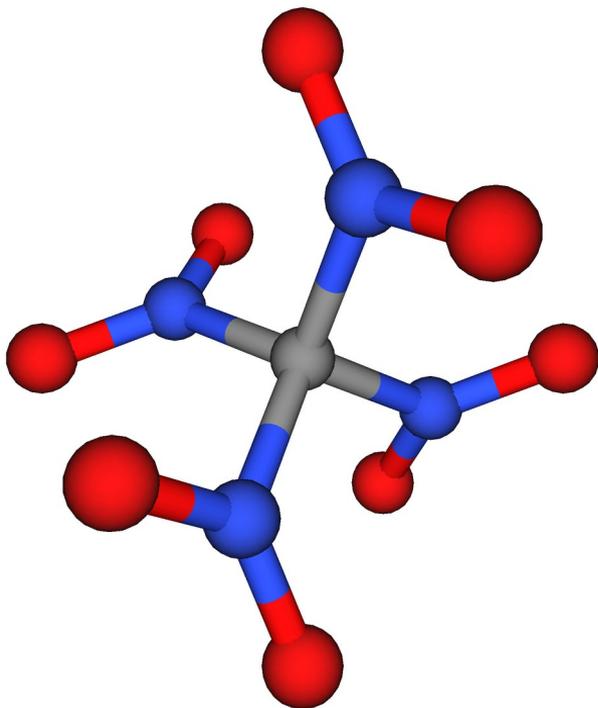
Uranocen $U(C_8H_8)_2$



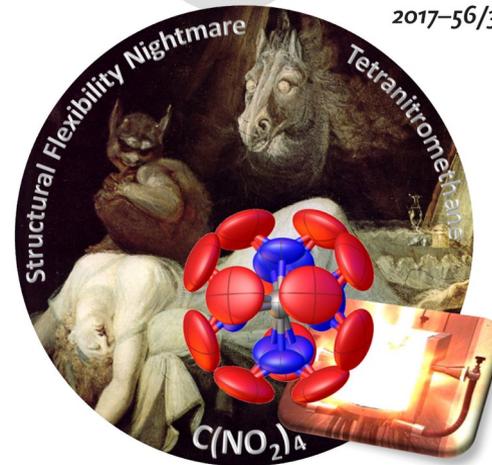
K. Yu. Chernichenko, V. V. Sumerin, R. V. Shpanchenko, E. S. Balenkova, V. G. Nenajdenko,
“Sulflower”: A New Form of Carbon Sulfide, *Angew. Chem. Int. Ed.*, 2006, 45, 7367–7370.

S₄

S₄: C(NO₂)₄



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Angewandte
International Edition **Chemie**
www.angewandte.org
2017-56/32



Cover Picture

N. W. Mitzel et al.
Tetranitromethane: A Nightmare of Molecular Flexibility
in the Gaseous and Solid States

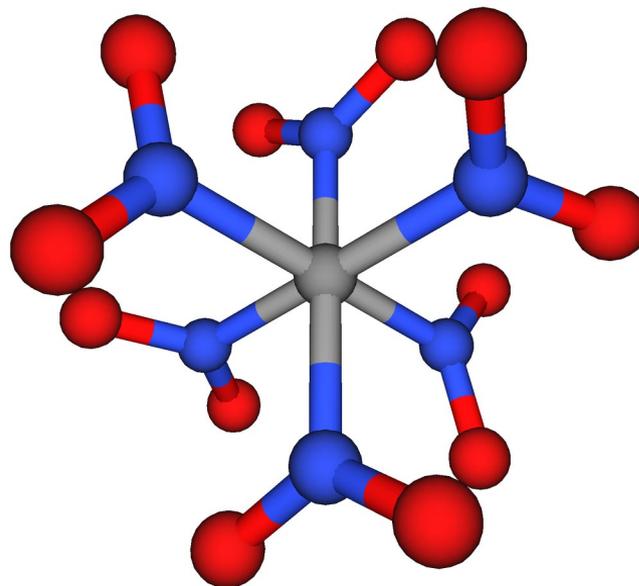
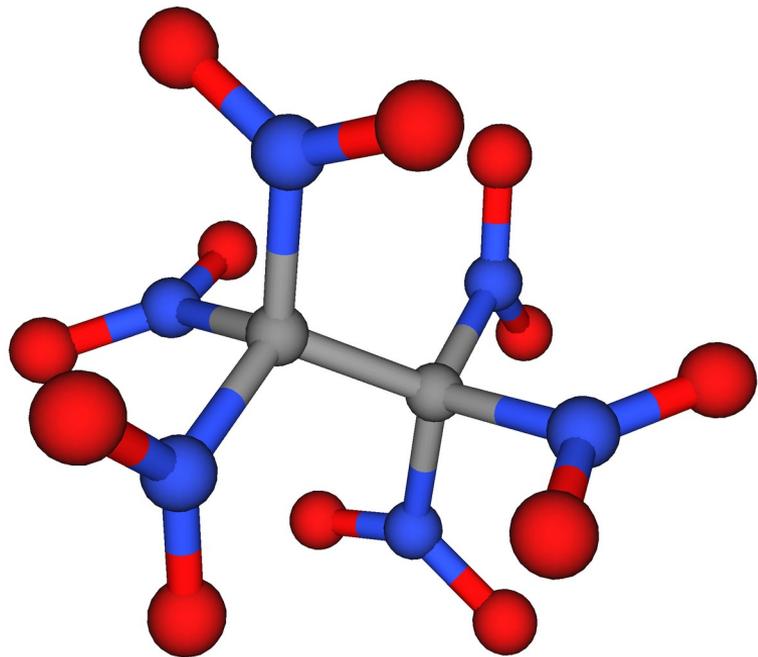
ADFS 56 (2) 9243–9626 (2017) · ISSN 1433-7851 · Vol. 56 · No. 32



WILEY-VCH

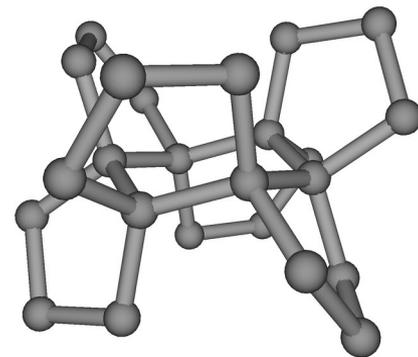
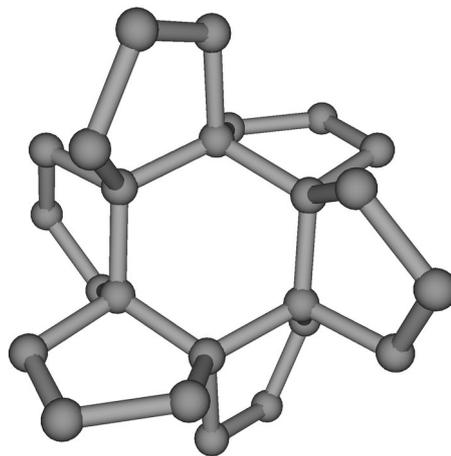
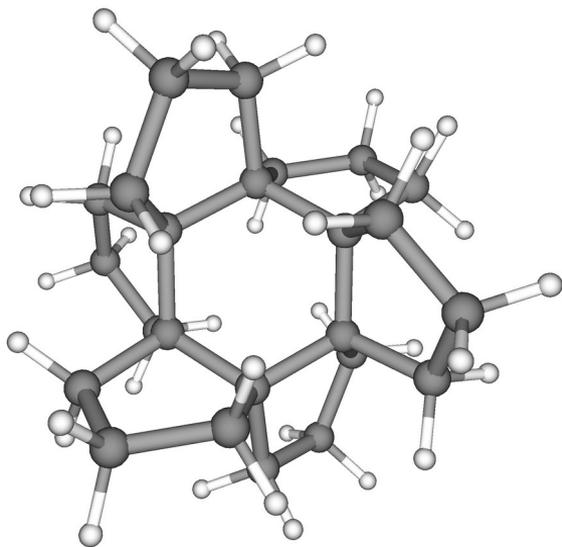
Yu. V. Vishnevskiy, D. S. Tikhonov, J. Schwabedissen, H.-G. Stammler, R. Moll, B. Krumm, T. M. Klapötke, N. W. Mitzel, Tetranitromethane: A Nightmare of Molecular Flexibility in the Gaseous and Solid States, *Angew. Chem. Int. Ed.* 2017, 56, 9619–9623.

S_6



S_6

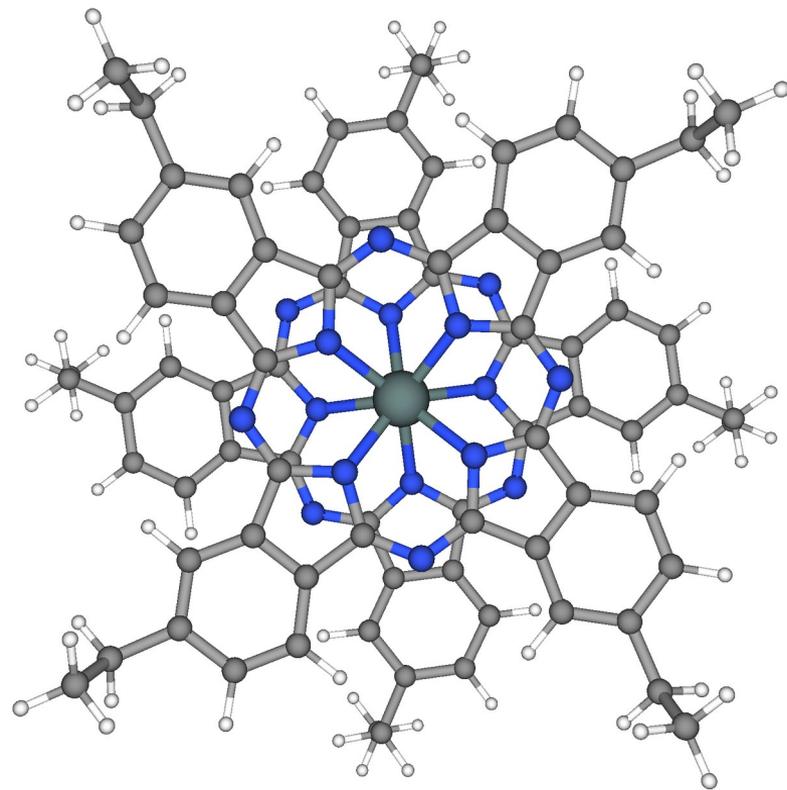
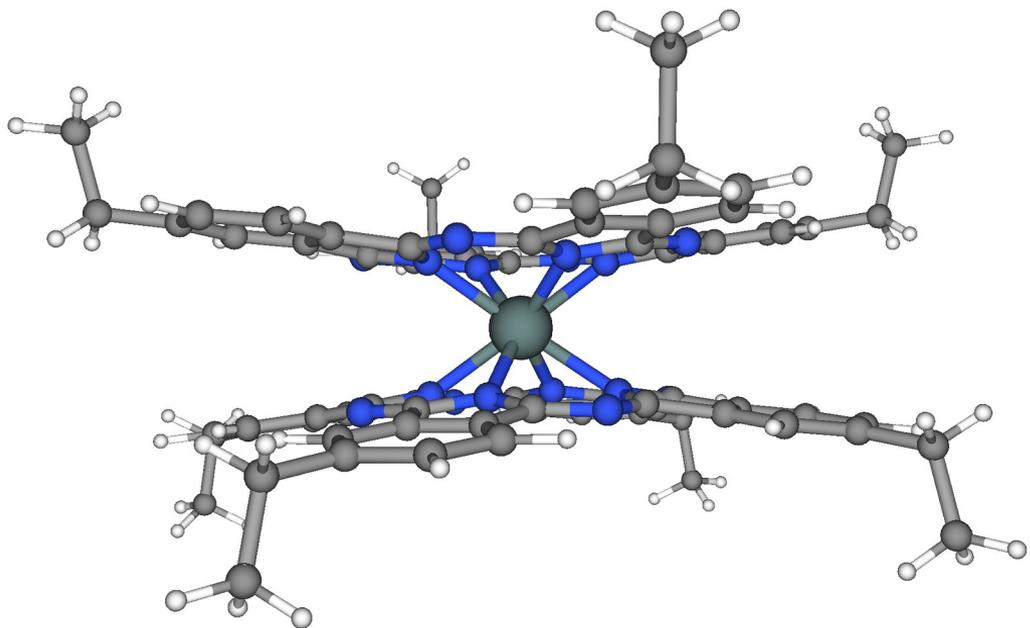
[6.5]Coronan $C_{24}H_{36}$



(Ohne H Atomen gezeigt)

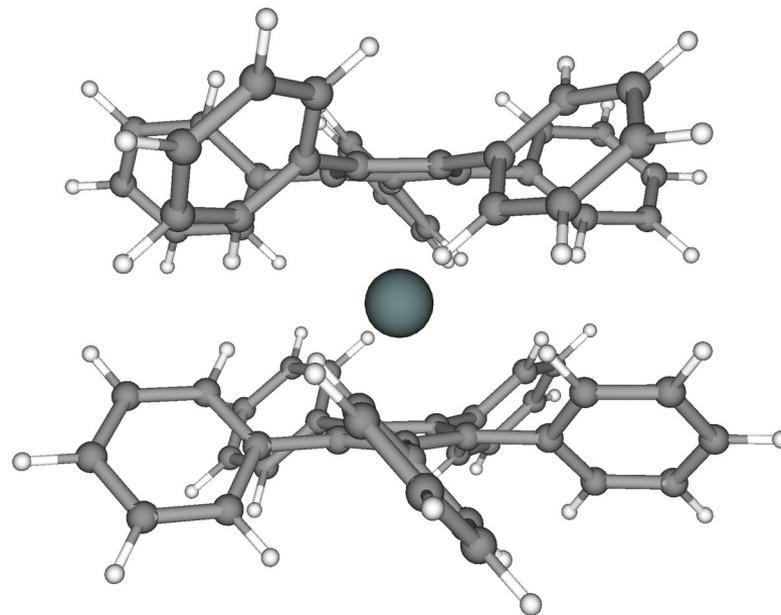
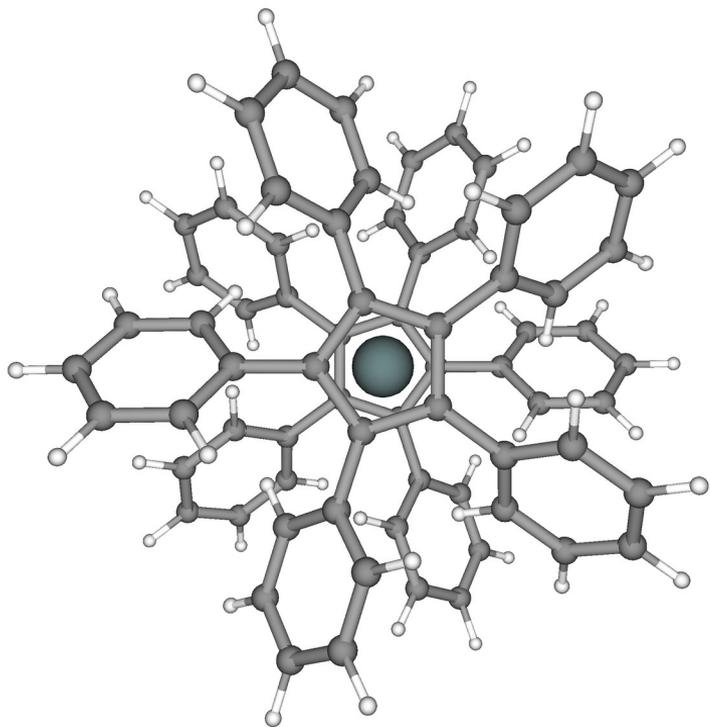
S_8

S_8 : Sn-bis(phthalocyanin)



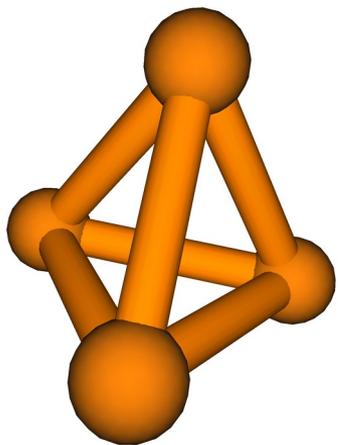
S_{10}

S_{10} : Sn-Metallocen $\text{Sn}(\text{C}_5\text{Ph}_5)_2$

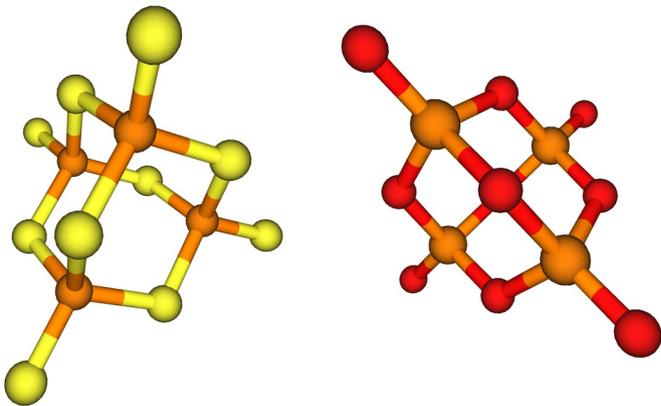


T_d

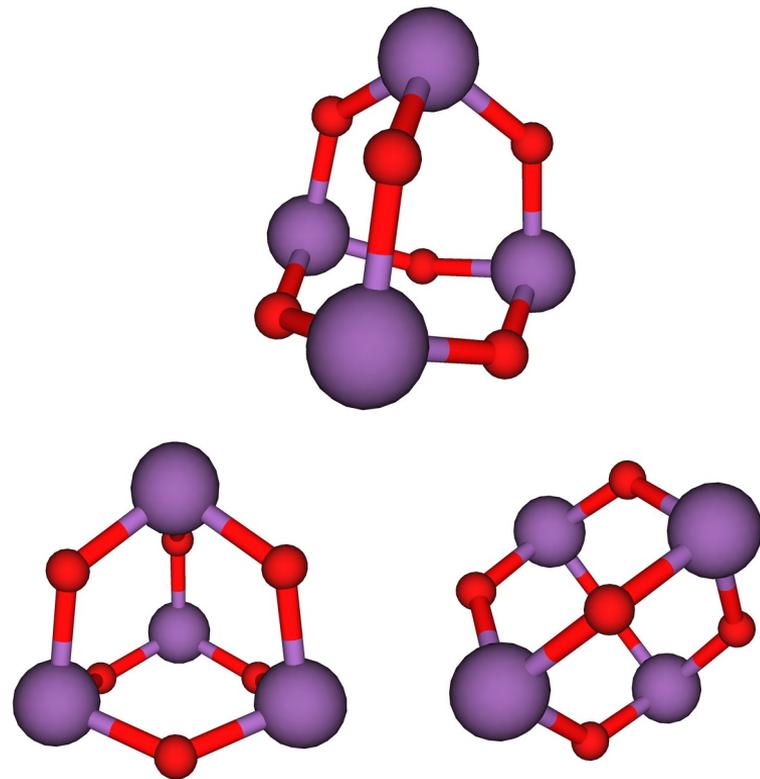
P_4



P_4S_{10} , P_4O_{10}



Sb_4O_6

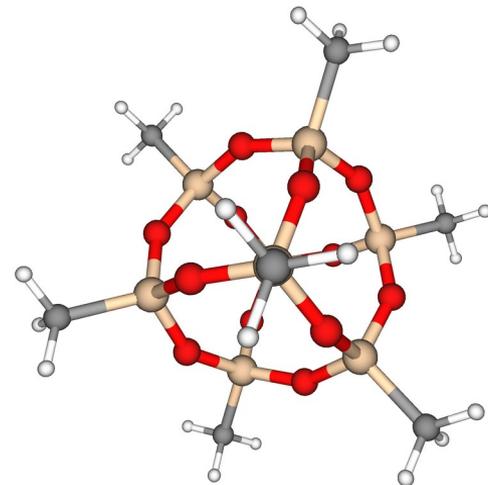
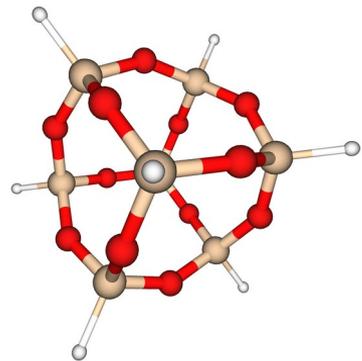
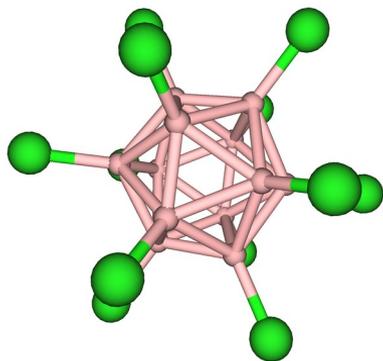
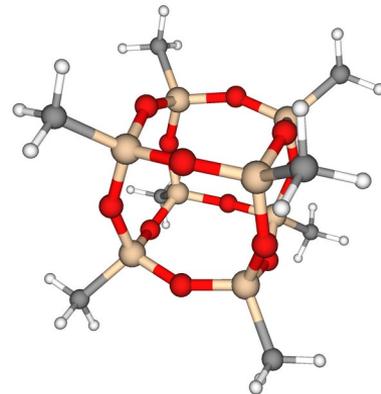
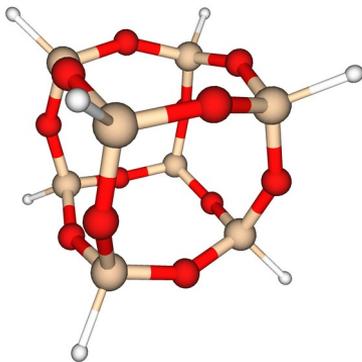
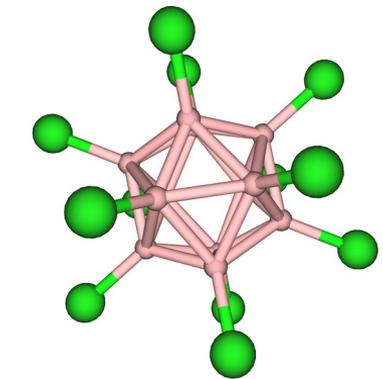


T_h

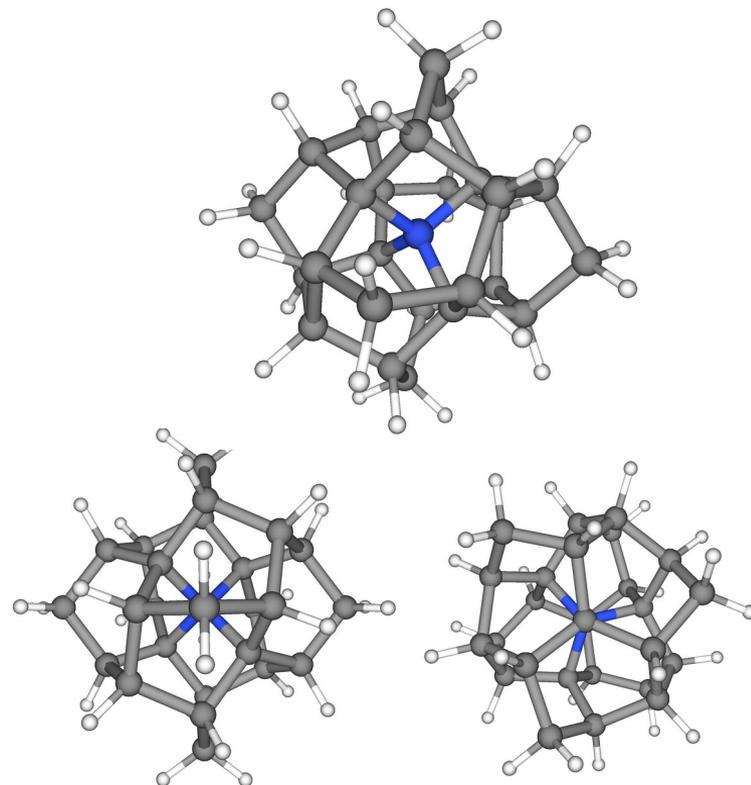
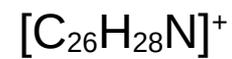
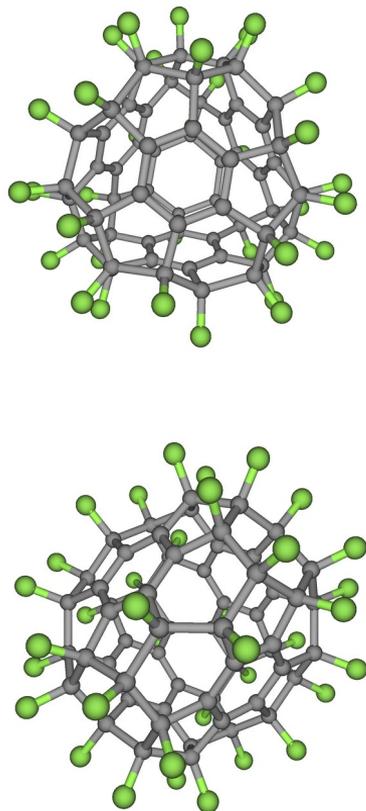
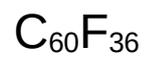
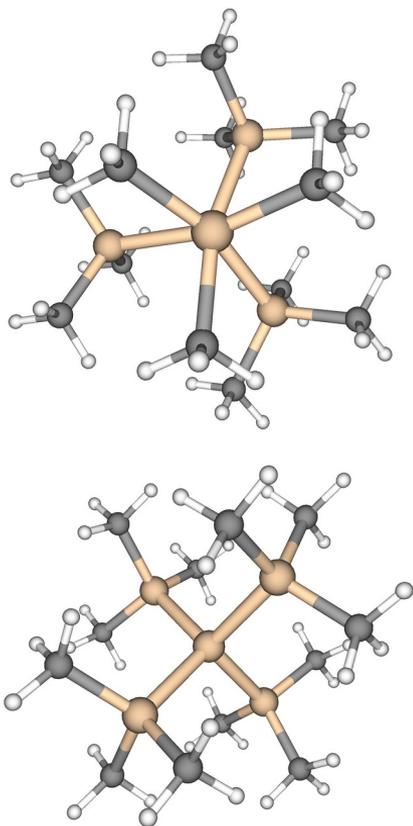
$B_{12}Cl_{12}$

Silsesquioxan
 $Si_8H_8O_{12}$

Octamethyl-Silsesquioxan

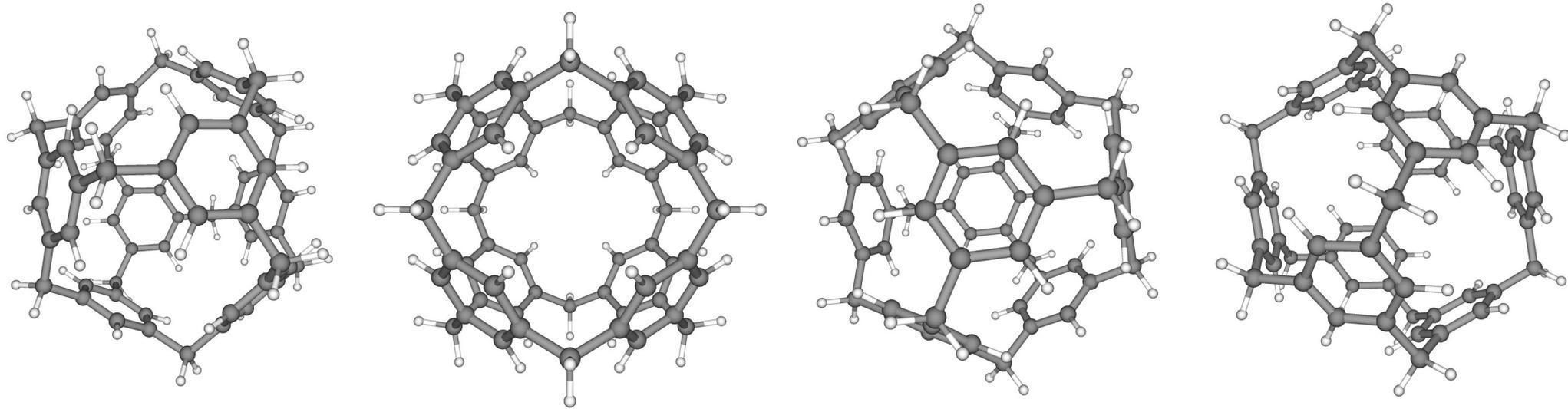


T



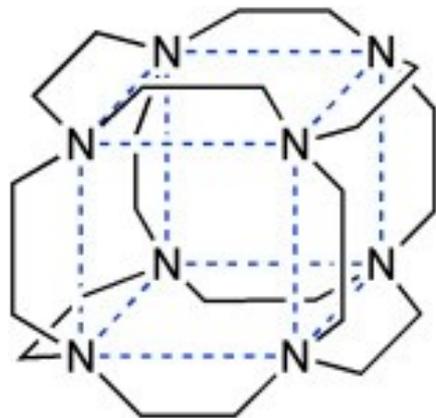
O_h

Spherophan

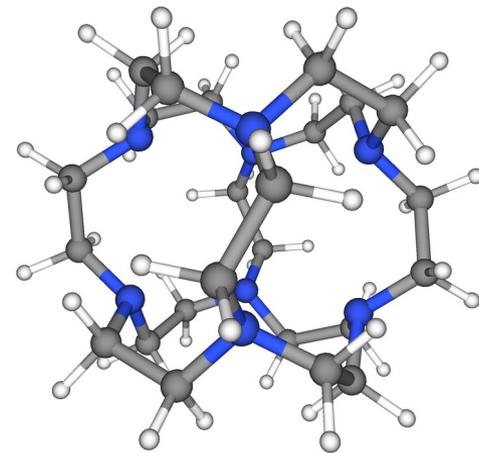
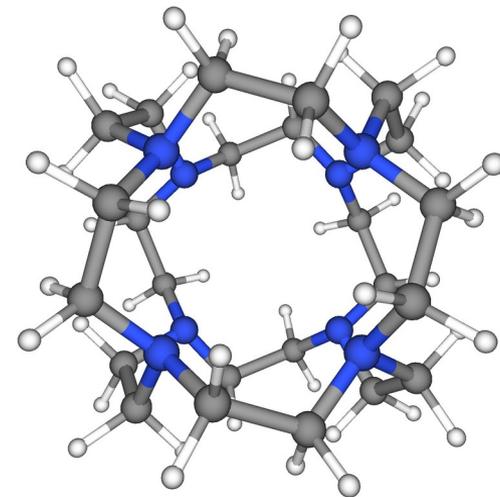
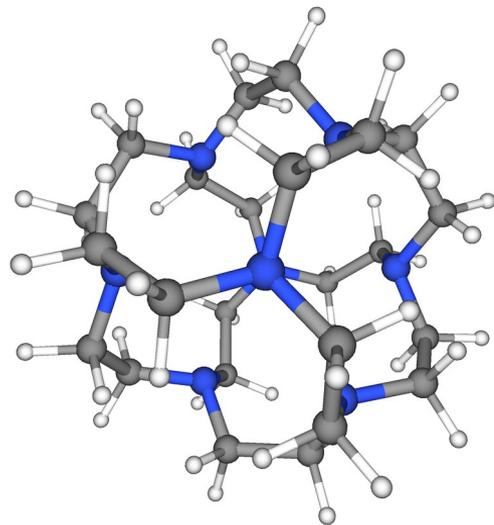


O

Extrem selten!

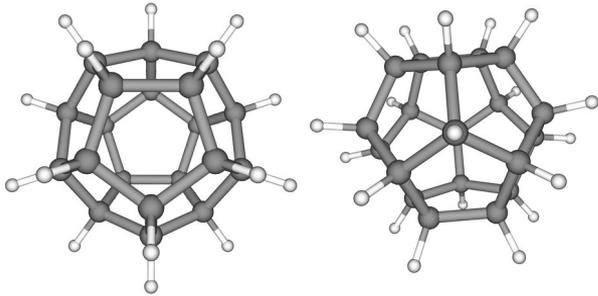
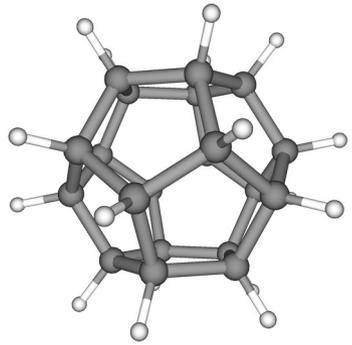


M. Bühl,
Dodeka(ethylene)octamine,
Chem. Eur. J. 2011, 17 (13),
3575–3578.

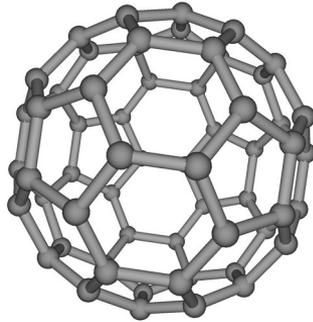
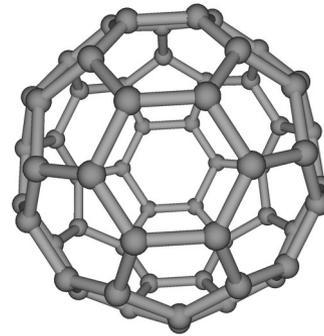
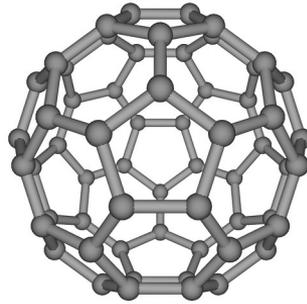


I_h

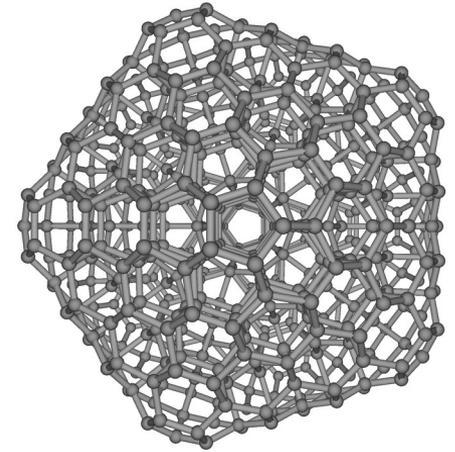
Dodecahedran
 $C_{20}H_{20}$



C_{60}



C_{600}



Die Punktgruppe /

Superselten!

Als Punktgruppe existiert!

Gibt es chemische Beispiele?

Vielleicht irgendwelche substituierte Dodecahedrane $C_{20}R_{20}$ ohne Spiegelebenen?

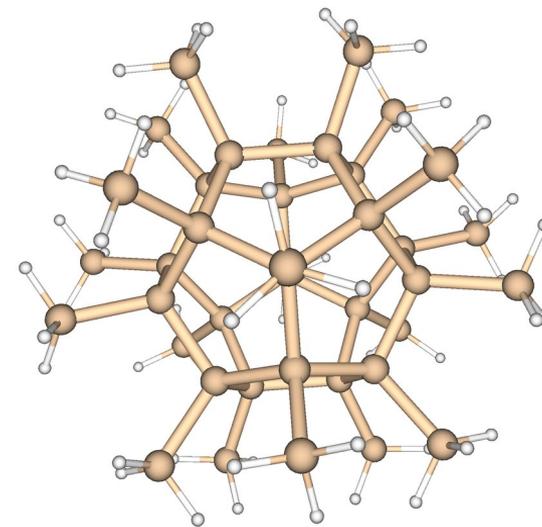
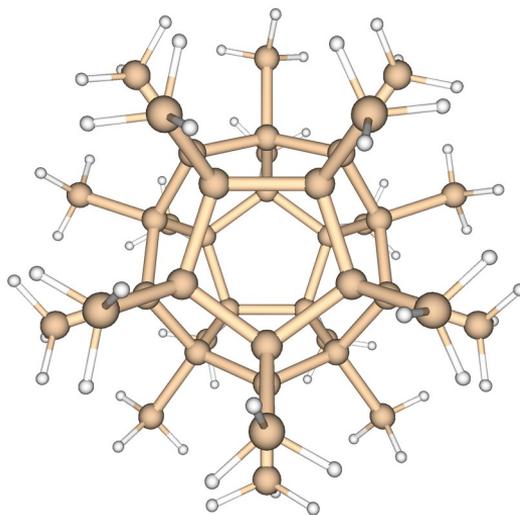
Aber dann müssen R die gesamte Rotationssymmetrie nicht brechen!

Eine Möglichkeit für /

$\text{Si}_{20}(\text{SiH}_3)_{20}$:

Keine imaginäre Frequenzen
in Symmetrie /

@ PBE0-D3BJ/def2-TZVPP



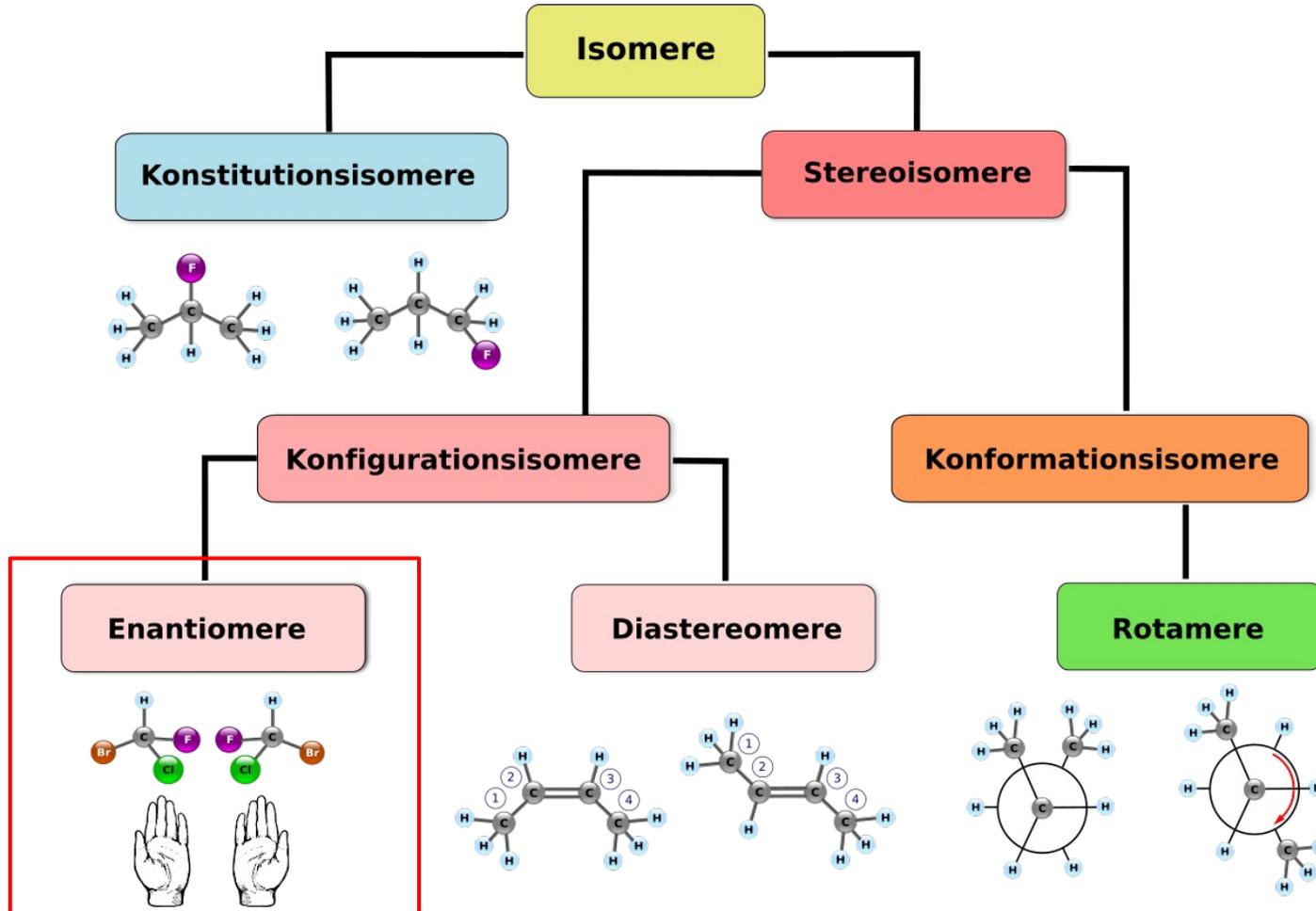
Erste Schritte in die Richtung?

M. Bamberg, M. Bursch, A. Hansen, M. Brandl, G. Sentis, L. Kunze, M. Bolte, H.-W. Lerner, S. Grimme, M. Wagner, $[\text{Cl}@\text{Si}_{20}\text{H}_{20}]^-$: Parent Siladodecahedrane with Endohedral Chloride Ion, *J. Am. Chem. Soc.* **2021**, 143, 10865–10871.

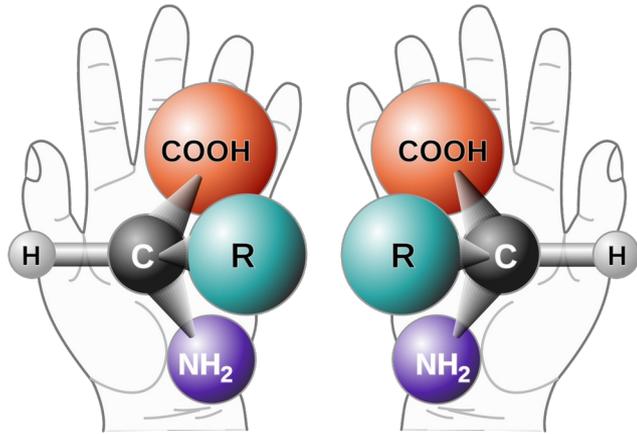
Anwendungen

- Polarität (Dipol-, Quadrupol- usw. Momente)
- Chiralität
- Schwingungsspektroskopien (Intensitäten, Schwingungsmoden klassifizieren, Rechnen)
- Quantenchemie (Orbitale aufbauen und klassifizieren, Rechnen!)
- Elektronische Zustände klassifizieren
- Chemische Reaktionen (Symmetriekontrolle)

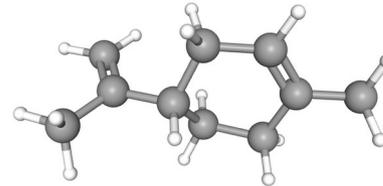
Isomerie



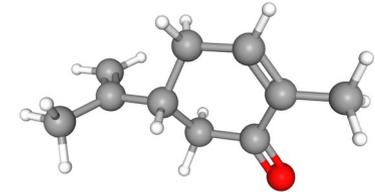
Chiralität, nur für C_1 ?



Limonen



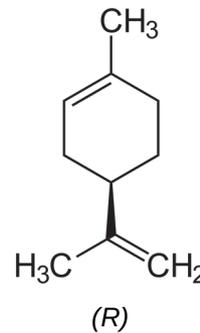
Carvon



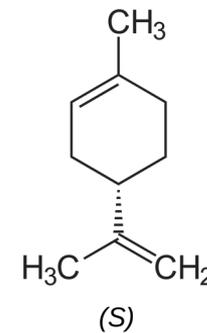
Nicht nur C_1 Moleküle!

Ein Molekül, das keine Drehspiegelachse (S_n , $n = 1, 2$, usw.) hat, muss chiral sein.

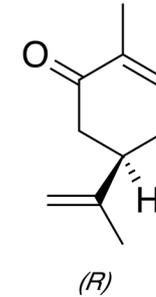
(Wieso?)



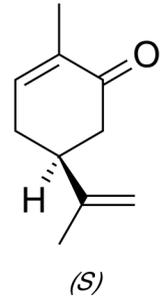
Zitronen-



Kiefer



Krauseminze-

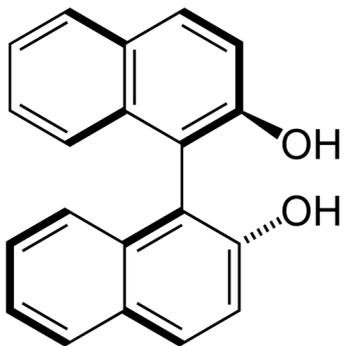


Kümmelgeruch

Chiralität

1,1'-Bi-2-naphthol:

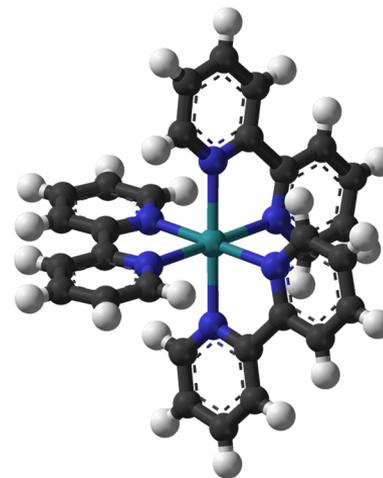
C_2 , chiral!



Tris(bipyridine)ruthenium(II) chlorid:

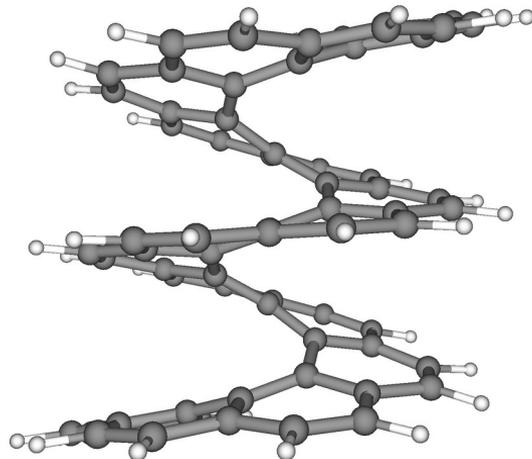
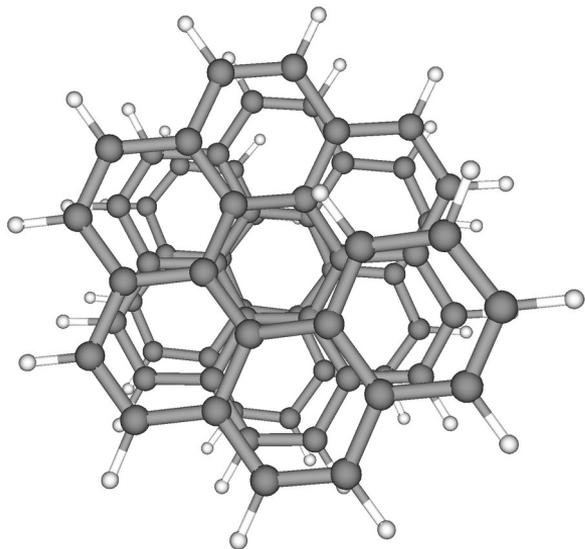
D_3 (Grundzustand), chiral!

Das erste Triplet ist C_2 .

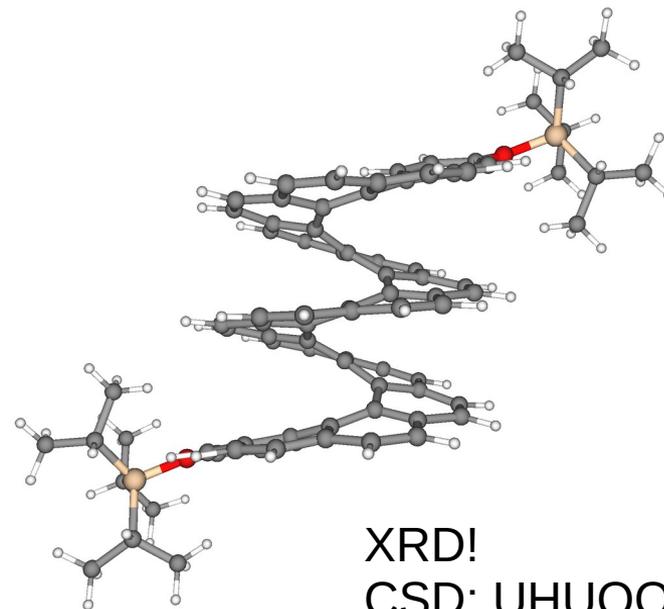


[16]Helicen

$C_{66}H_{36}$: C_2 , chiral!



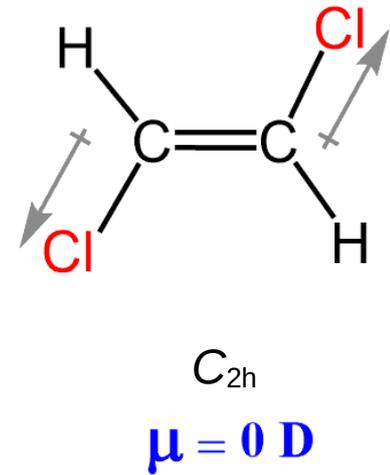
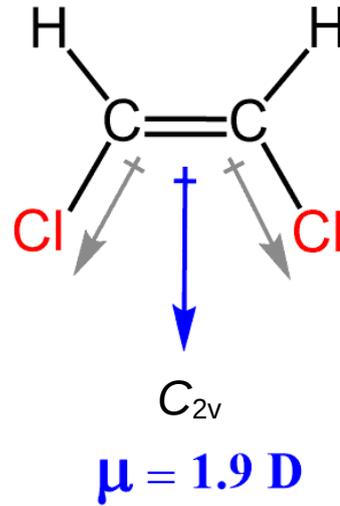
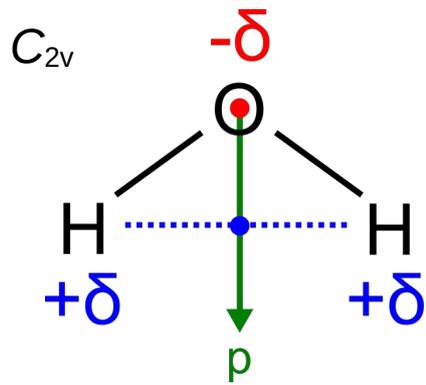
3,34-bis(triisopropylsilyloxy)-



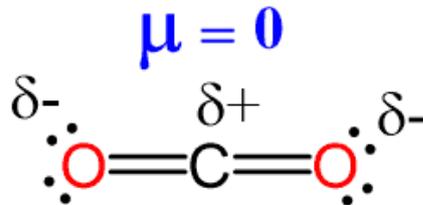
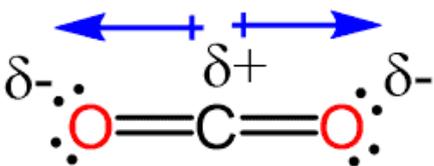
XRD!
CSD: UHUQOF

Dipolmoment

Nur Moleküle von C_n , C_{nv} , C_s haben permanentes elektrisches Dipolmoment.
Bei C_n , C_{nv} ($n > 1$) liegt es entlang der C_n -Achse.

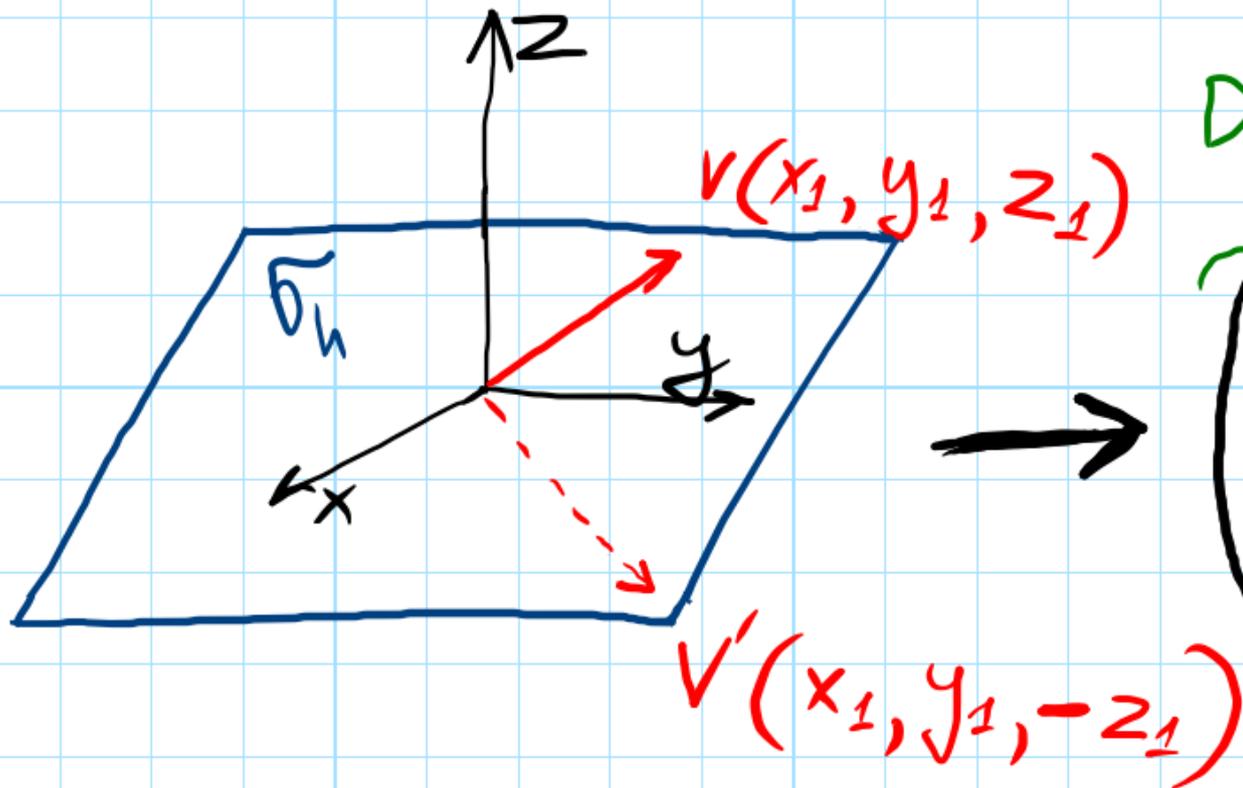


$D_{\infty h}$



Darstellungen

Spiegelung

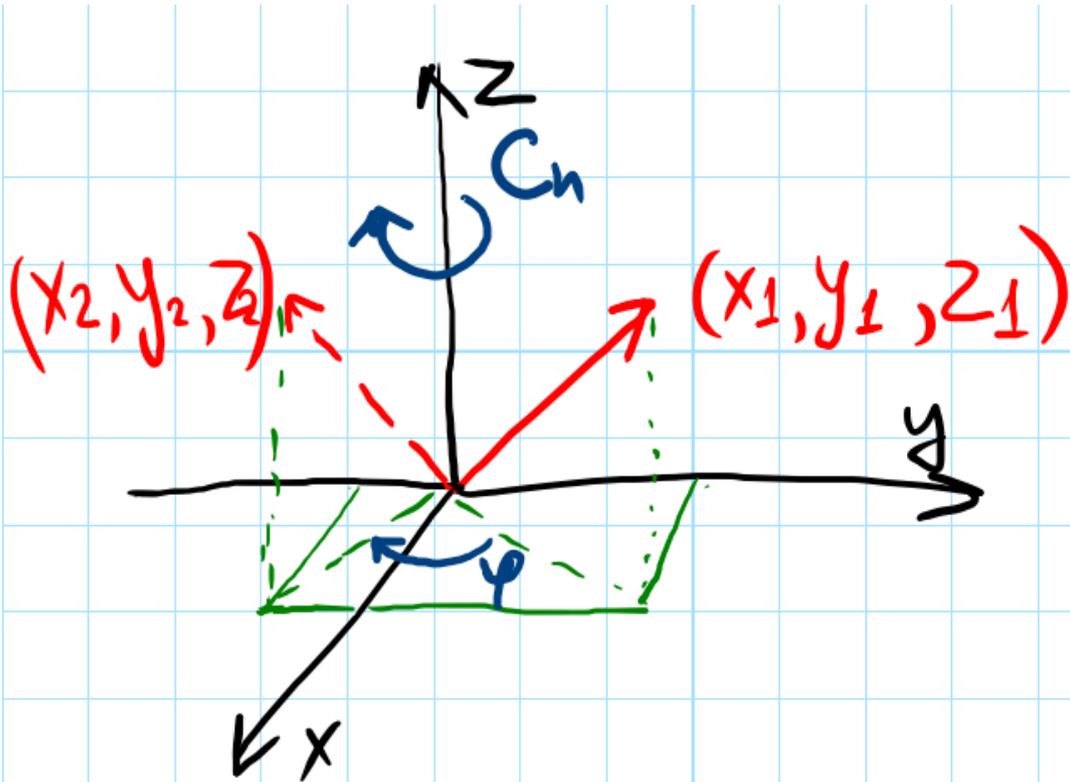


Darstellung des $\hat{\sigma}_h$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} x_1 \\ y_1 \\ -z_1 \end{pmatrix}$$

$$\hat{\sigma}_h \cdot v = v'$$

Drehung

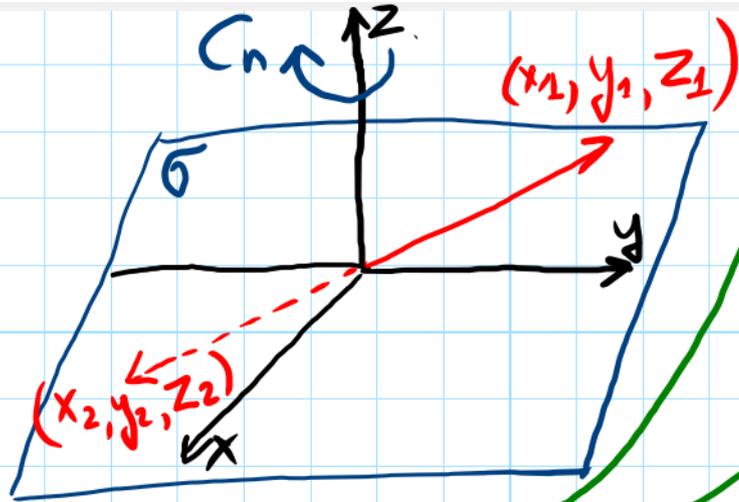


Darstellung der \hat{C}_n

$$\begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}$$

$$\det = 1!$$

Drehspiegelung



$$\begin{pmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \leftarrow \hat{C}_n$$
$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \leftarrow \hat{\sigma}$$

$$\hat{S}_n = \hat{C}_n \cdot \hat{\sigma} = \begin{pmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

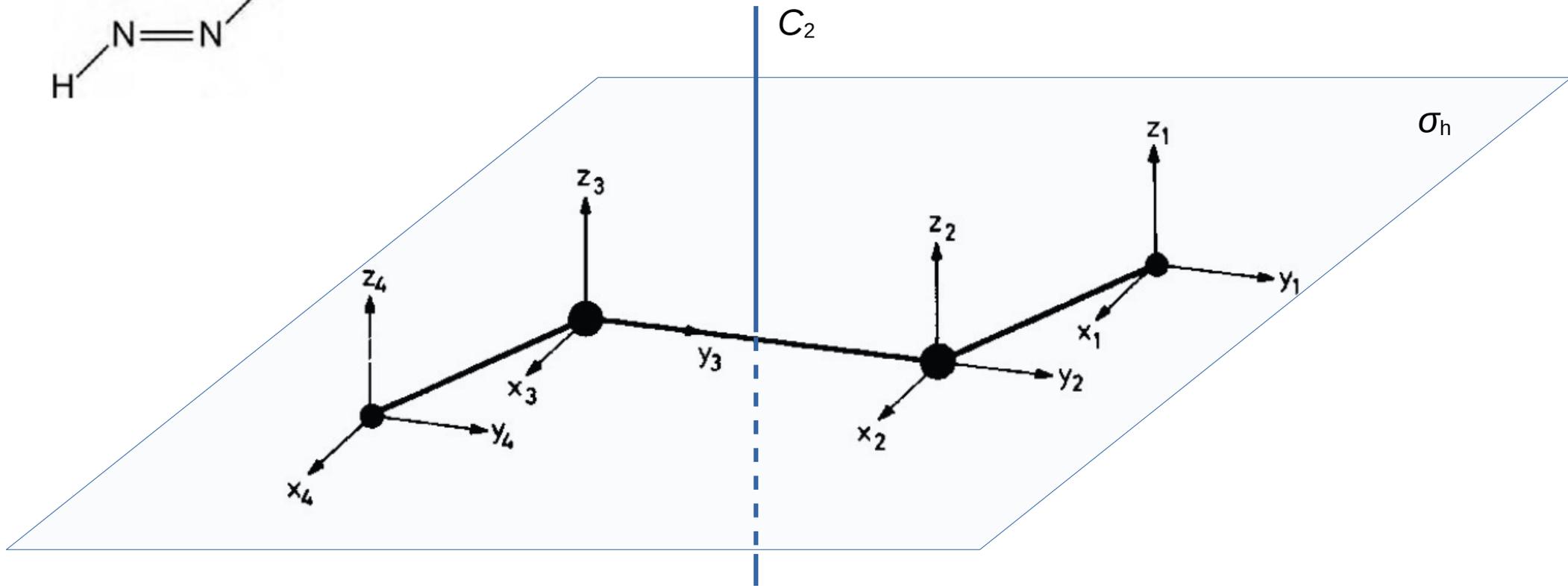
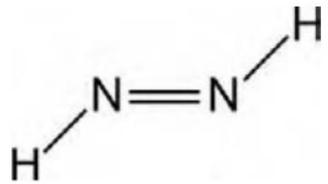
det = -1 : Orientierung umkehren!

E, i

$$\hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{i} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Basis: (x, y, z) ! Noch Basen?

Diimin, C_{2h}



Basis: $\{x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3, x_4, y_4, z_4\}$

Diimin, C_{2h}

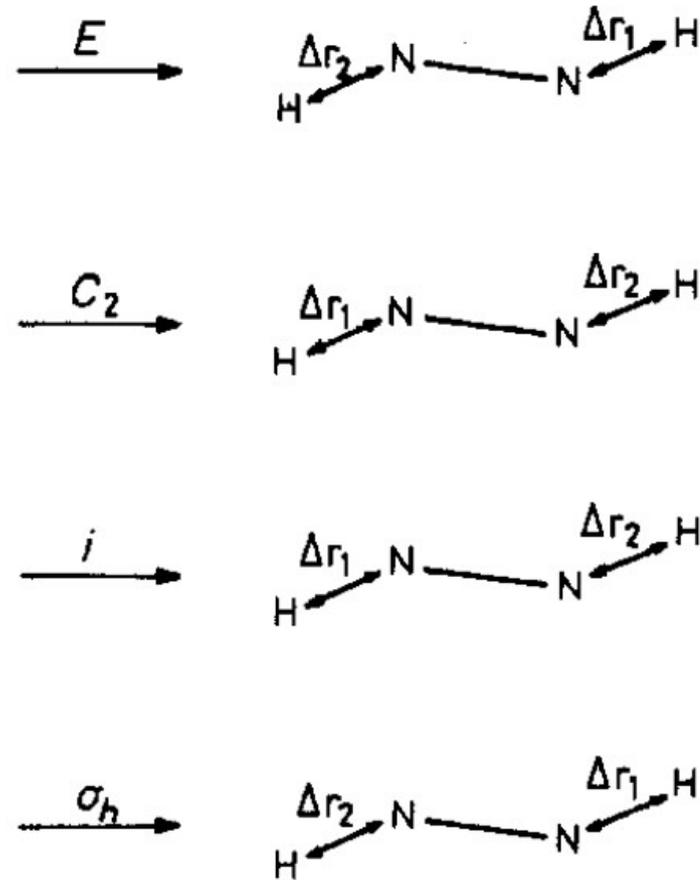
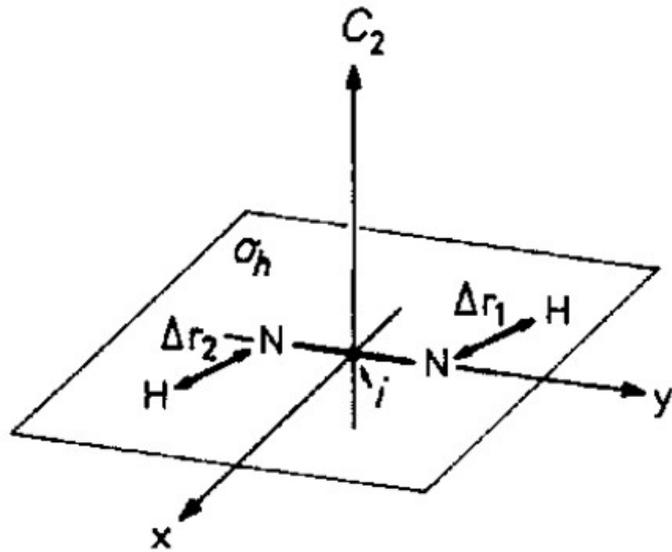
$$C_2 \cdot \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \\ x_4 \\ y_4 \\ z_4 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \\ x_4 \\ y_4 \\ z_4 \end{bmatrix} = \begin{bmatrix} -x_4 \\ -y_4 \\ z_4 \\ -x_3 \\ -y_3 \\ z_3 \\ -x_2 \\ -y_2 \\ z_2 \\ -x_1 \\ -y_1 \\ z_1 \end{bmatrix}$$

C_2 Darstellung in der Basis $\{x_1, y_1, z_1, \dots, x_4, y_4, z_4\}$

(In C_{2h} und für bestimmte Orientierung!)

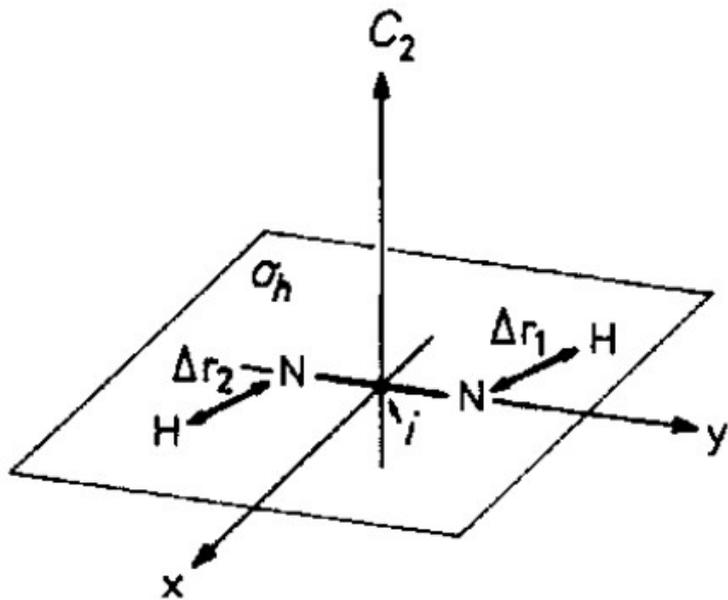
Diimin, noch eine Basis ...

Basis: $\{\Delta r_1, \Delta r_2\}$



... und noch eine Darstellung

Basis: $\{\Delta r_1, \Delta r_2\}$



$$E \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix}$$

$$C_2 \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} \Delta r_2 \\ \Delta r_1 \end{bmatrix}$$

$$i \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} \Delta r_2 \\ \Delta r_1 \end{bmatrix}$$

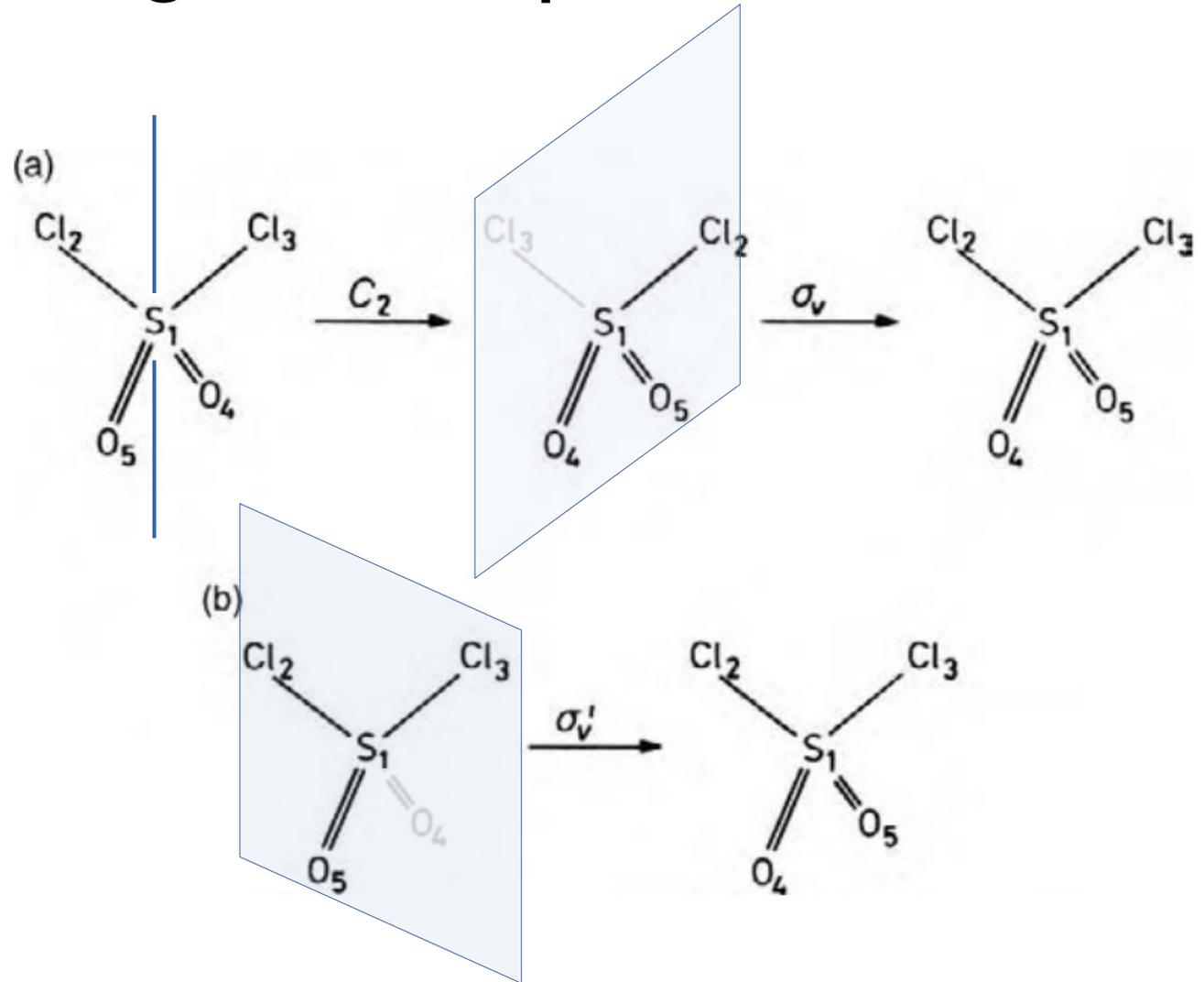
$$\sigma_h \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix} = \begin{bmatrix} \Delta r_1 \\ \Delta r_2 \end{bmatrix}$$

Darstellungen Multiplizieren

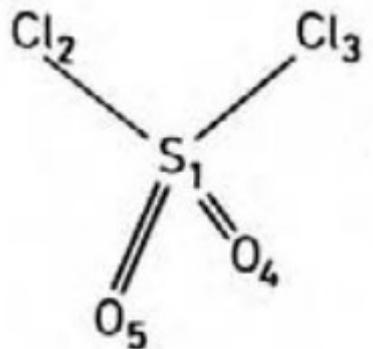
Sulfurylchlorid C_{2v}

Multiplikationstafel s. Oben!

$$\sigma_v \cdot C_2 = \sigma'_v$$



Sulfurylchlorid, Umstellungen



C_2

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} S_1 \\ Cl_2 \\ Cl_3 \\ O_4 \\ O_5 \end{bmatrix} = \begin{bmatrix} S_1 \\ Cl_3 \\ Cl_2 \\ O_5 \\ O_4 \end{bmatrix}$$

σ_v

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} S_1 \\ Cl_2 \\ Cl_3 \\ O_4 \\ O_5 \end{bmatrix} = \begin{bmatrix} S_1 \\ Cl_3 \\ Cl_2 \\ O_4 \\ O_5 \end{bmatrix}$$

σ'_v

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} S_1 \\ Cl_2 \\ Cl_3 \\ O_4 \\ O_5 \end{bmatrix} = \begin{bmatrix} S_1 \\ Cl_2 \\ Cl_3 \\ O_5 \\ O_4 \end{bmatrix}$$

Basis: Indices der Atomen

$$\sigma_v \cdot C_2 = \sigma'_v$$

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} =$$

σ_v C_2

$$\begin{bmatrix} 1 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 + 0 \cdot 0 + 0 \cdot 0 & 1 \cdot 0 + 0 \cdot 0 + 0 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 \dots \\ 0 \cdot 1 + 0 \cdot 0 + 1 \cdot 0 + 0 \cdot 0 + 0 \cdot 0 & 0 \cdot 0 + 0 \cdot 0 + 1 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 \dots \\ 0 \cdot 1 + 1 \cdot 0 + 0 \cdot 0 + 0 \cdot 0 + 0 \cdot 0 & 0 \cdot 0 + 1 \cdot 0 + 0 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 \dots \\ 0 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 + 1 \cdot 0 + 0 \cdot 0 & 0 \cdot 0 + 0 \cdot 0 + 0 \cdot 1 + 1 \cdot 0 + 0 \cdot 0 \dots \\ 0 \cdot 1 + 0 \cdot 0 + 0 \cdot 0 + 0 \cdot 0 + 1 \cdot 0 & 0 \cdot 0 + 0 \cdot 0 + 0 \cdot 1 + 0 \cdot 0 + 1 \cdot 0 \dots \end{bmatrix} =$$

5-Dimensional...

Geht es einfacher? Ja!

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \equiv \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix} \cdot \begin{bmatrix} S_1 \\ Cl_2 \\ Cl_3 \\ O_4 \\ O_5 \end{bmatrix} = \begin{bmatrix} S_1 \\ Cl_2 \\ Cl_3 \\ O_5 \\ O_4 \end{bmatrix}$$

σ'_v (s. oben!)

Reduzierung

$$\begin{bmatrix} A_1 & & \\ & A_2 & \\ & & A_3 \end{bmatrix} \cdot \begin{bmatrix} B_1 & & \\ & B_2 & \\ & & B_3 \end{bmatrix} = \begin{bmatrix} C_1 & & \\ & C_2 & \\ & & C_3 \end{bmatrix}$$

$$\begin{aligned} A_1 \cdot B_1 &= C_1 \\ A_2 \cdot B_2 &= C_2 \\ A_3 \cdot B_3 &= C_3 \end{aligned}$$

Irreduzible Darstellungen

Darstellungen für C_{2v}

Γ_1 : $E=+1$ $C_2=+1$ $\sigma_v=+1$ $\sigma'_v=+1$ ← Einfachste (irreduzible) 1-D Darstellung (kontrl. M-Tafel)

Sind noch irgendwelche andere irreduzible Darstellungen möglich?

Ja:

Γ_2 : $E=+1$ $C_2=+1$ $\sigma_v=-1$ $\sigma'_v=-1$

Γ_3 : $E=+1$ $C_2=-1$ $\sigma_v=+1$ $\sigma'_v=-1$

Γ_4 : $E=+1$ $C_2=-1$ $\sigma_v=-1$ $\sigma'_v=+1$

Gibt es noch welche?

Nein:

Lemma von Schur $\rightarrow \chi^\Gamma$ sind
orthonormal \rightarrow 4 Klassen von
Elementen \rightarrow
4 unterschiedliche irreps Γ .

C_{2v}	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

Charaktertafel

Für praktische Anwendungen brauchen wir nicht die gesamte Darstellungen.
Es reicht nur ihre Charaktere (Spuren) zu wissen!

$h = 4$ (Ordnung der Gruppe)

	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$\Gamma_1 \rightarrow$	A_1	1	1	1	1	z	x^2, y^2, z^2
$\Gamma_2 \rightarrow$	A_2	1	1	-1	-1	R_z	xy
$\Gamma_3 \rightarrow$	B_1	1	-1	1	-1	x, R_y	xz
$\Gamma_4 \rightarrow$	B_2	1	-1	-1	1	y, R_x	yz

↑
Mulliken-Symbole für Γ

Die Funktionen, die sich wie eine irreduzible Darstellung transformieren.

Mulliken-Symbole

Dimension of Representation	Character under					Symbol(s)
	E	C_n	i	σ_h	C_2^a or σ_v	
1	1	1				A
	1	-1				B
2	2					E
3	3					T
			1			A_g B_g E_g T_g
			-1			A_u B_u E_u T_u
				1		A' B'
				-1		A'' B''
					1	A_1 B_1
					-1	A_2 B_2

^a C_2 axis perpendicular to the principal axis

A , B , E , ... im Deutschen sind „Rassen“. Im Englischen: „symmetry species“.

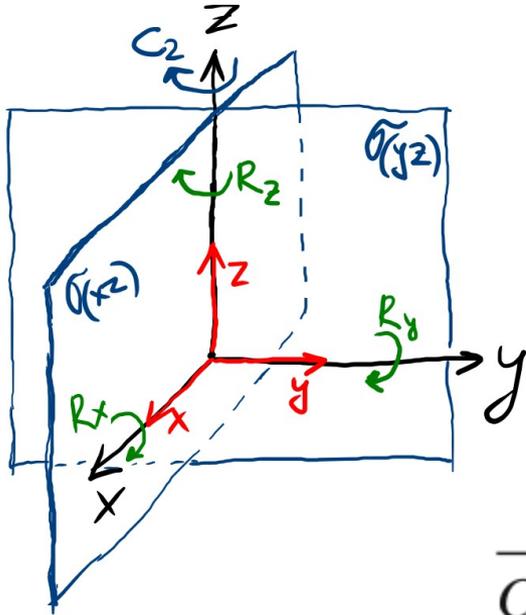
Mulliken-Symbole: Beispiele

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, x^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

...

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Transformationen



Die Translation in z-Richtung transformiert wie A_1 ,
 die Drehung um die x-Achse transformiert wie B_2 ,
 usw.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Abelsche Gruppen

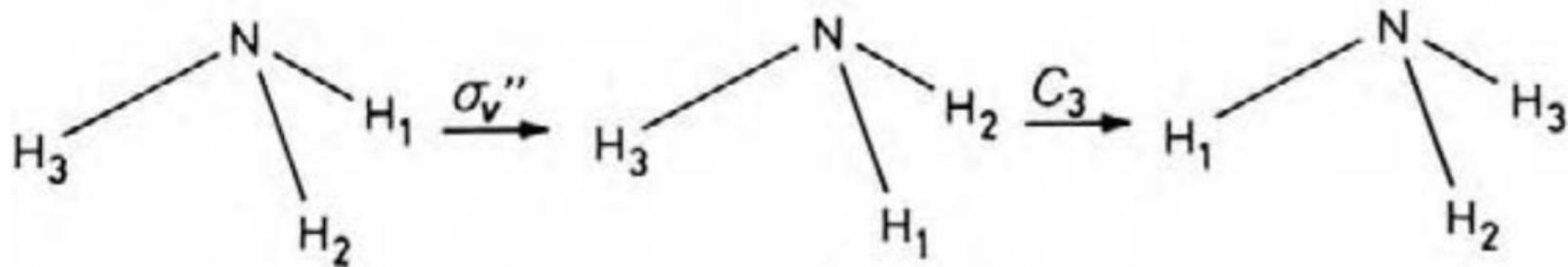
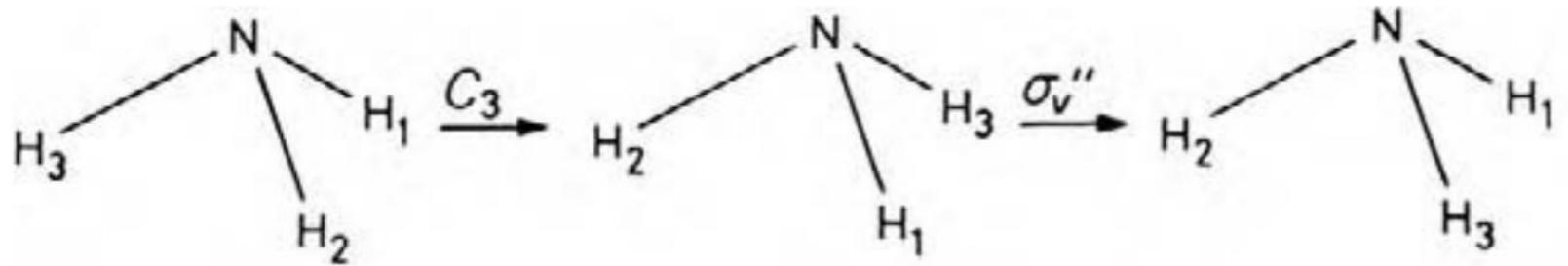
Eine Gruppe, in der die Multiplikationsreihenfolge keine Rolle spielt, heißt kommutative oder abelsche Gruppe.

Z. B.:

C_{2v}	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

Nichtabelsche Gruppen

z. B.: C_{3v}



Nichtabelsche Gruppen

z. B.: C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$

Satz von Lagrange: die Ordnung jeder Untergruppe teilt die Ordnung der Gruppe.

Auch:
$$h = \sum_{\text{irreps}} d_n^2$$

d_n – Dimension von Irrep n , z. B. hier: $h = 1^2 + 1^2 + 2^2 = 6$

Äquivalenzklassen

Mathematisch:

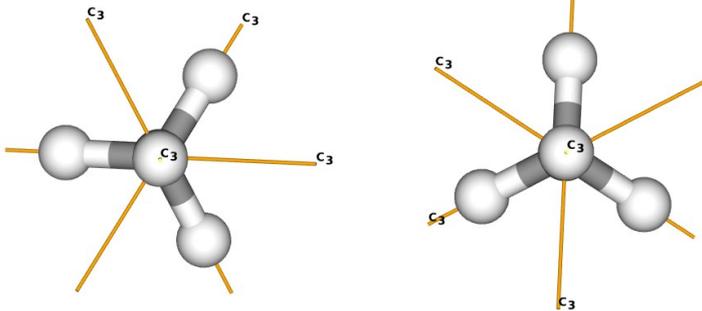
A und B gehören zu einer Klasse, wenn in der Gruppe ein Element Z existiert, sodass gilt

$$B = Z^{-1} \cdot A \cdot Z$$

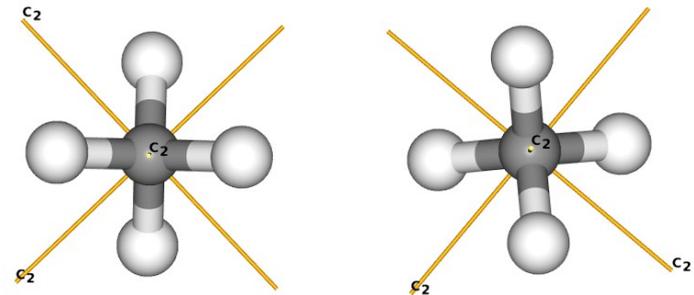
Für Chemiker:

A und B gehören zu einer Klasse, wenn ich für sie gleiche Perspektiven finde,

z. B. $8C_3$ in T_d :

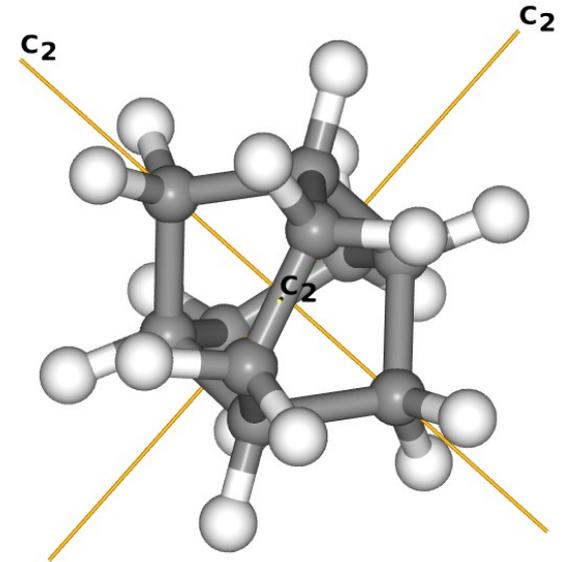
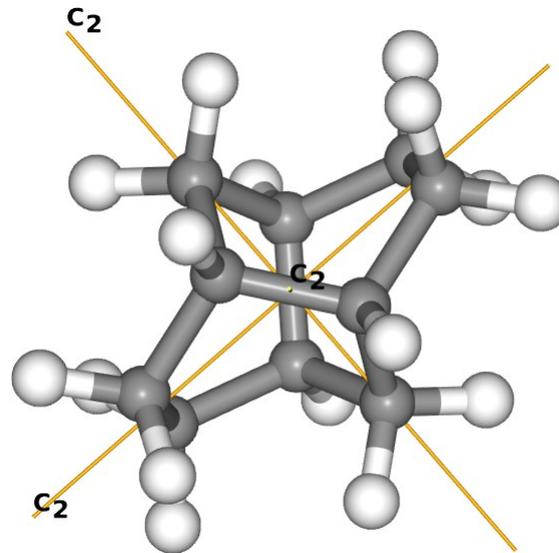
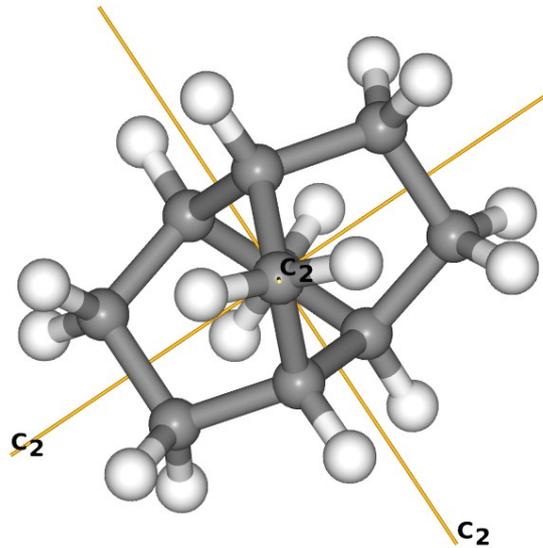


$3C_2$:

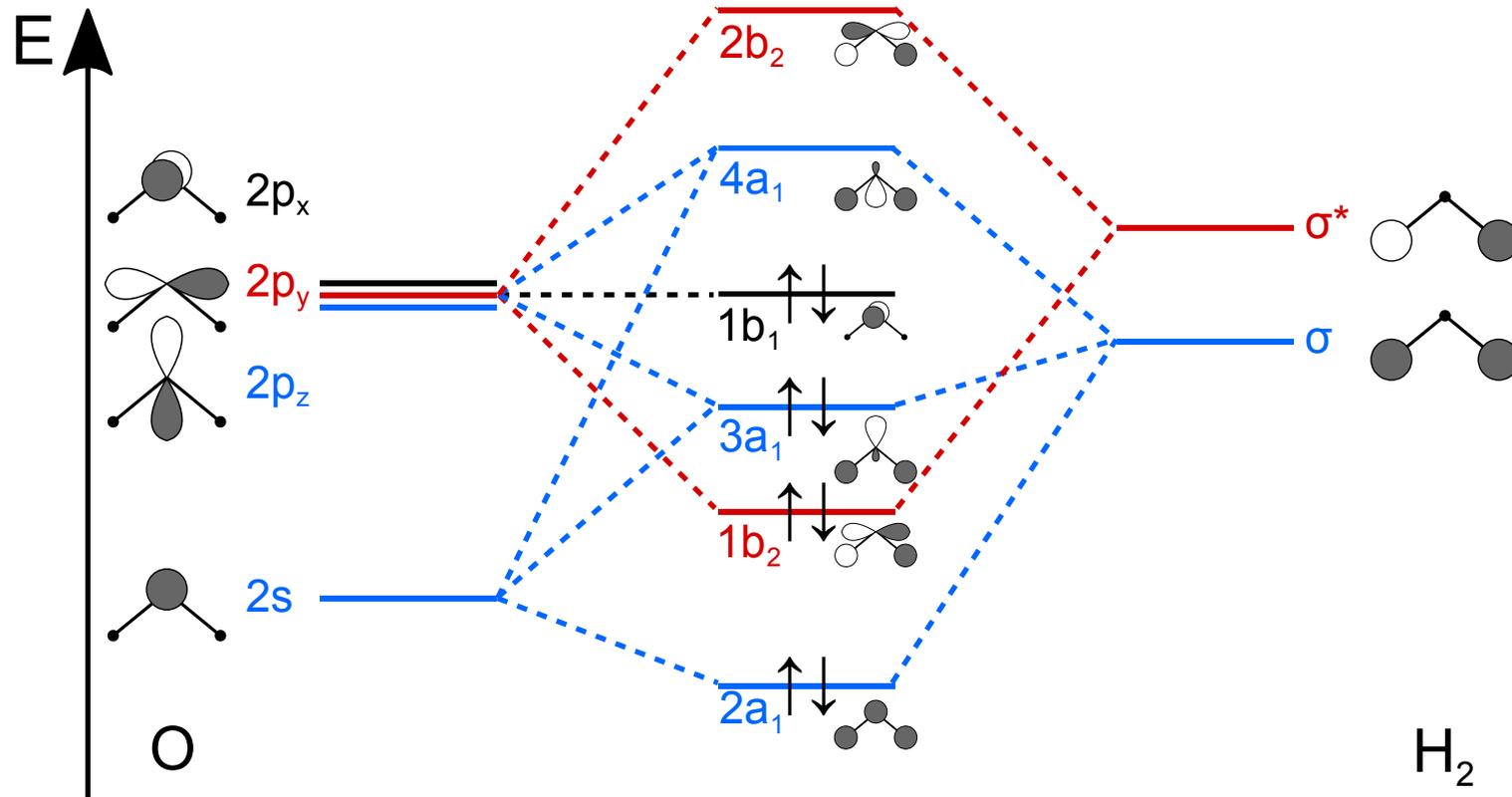


Abelsche Gruppe D_2

Twistan, C_2 Achsen bilden eigene Klassen

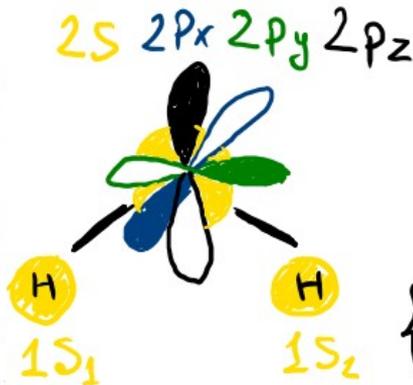
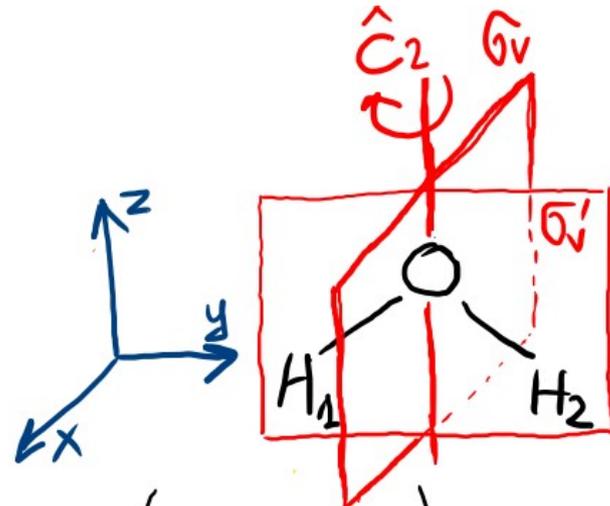


MO-LCAO: H₂O



Woher das kommt?

MO-LCAO: H₂O



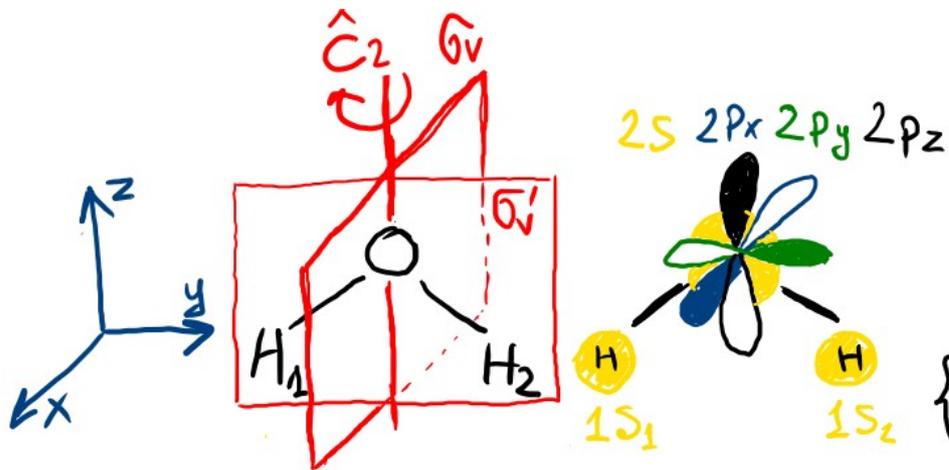
Basis:
 $\{1s_1, 1s_2, 2s, 2p_z, 2p_y, 2p_x\}$

$$\hat{E} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\text{tr}(\hat{E}) = \sum_i (\hat{E})_{ii} = 6$$

$$\hat{E} \cdot \begin{pmatrix} 1s_1 \\ 1s_2 \\ 2s \\ 2p_z \\ 2p_y \\ 2p_x \end{pmatrix} = \begin{pmatrix} 1s_1 \\ 1s_2 \\ 2s \\ 2p_z \\ 2p_y \\ 2p_x \end{pmatrix}$$

MO-LCAO: H₂O



Basis:
 $\{1s_1, 1s_2, 2s, 2p_z, 2p_y, 2p_x\}$

$$\text{tr}(\hat{C}_2) = 0 + 0 + 1 + 1 - 1 - 1 = 0$$

$$\text{tr}(\hat{\sigma}_v) = 0 + 0 + 1 + 1 - 1 + 1 = 2$$

$$\text{tr}(\hat{\sigma}_v') = 1 + 1 + 1 + 1 + 1 - 1 = 4$$

Charaktere der reduzierbaren Darstellungen →

$$\Gamma_{\text{red}} = (6 \ 0 \ 2 \ 4)$$

$$?A_1 + ?A_2 + ?B_1 + ?B_2$$

MO-LCAO: H₂O

$$\Gamma = (6 \ 0 \ 2 \ 4) = k_1 \underline{A_1} + k_2 \underline{A_2} + k_3 \underline{B_1} + k_4 \underline{B_2}$$

$$k_1 = \frac{1}{4}(6 \cdot 1 + 0 \cdot 1 + 2 \cdot 1 + 4 \cdot 1) = 12/4 = 3$$

$$k_2 = \frac{1}{4}(6 \cdot 1 + 0 \cdot 1 - 2 \cdot 1 - 4 \cdot 1) = 0/4 = 0$$

$$k_3 = \frac{1}{4}(6 \cdot 1 - 0 \cdot 1 + 2 \cdot 1 - 4 \cdot 1) = 4/4 = 1$$

$$k_4 = \frac{1}{4}(6 \cdot 1 - 0 \cdot 1 - 2 \cdot 1 + 4 \cdot 1) = 8/4 = 2$$

$$\Gamma = 3A_1 + B_1 + 2B_2$$

$$k_i = \frac{1}{h} \sum_{\hat{R}} n \cdot \chi^R \cdot \chi_i^R$$

Reduktionsformel ↗

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

MO-LCAO: H₂O

$$\hat{P}_i = \frac{d_i}{h} \sum_{\hat{R}} \chi_i^R \cdot \hat{R} \quad \leftarrow \text{Projektionsoperator}$$

$$\hat{P}_{A_1}(1s_1) = \frac{1}{4} (1 \cdot 1s_1 + 1 \cdot 1s_2 + 1 \cdot 1s_2 + 1 \cdot 1s_1) = \frac{1}{2} (1s_1 + 1s_2) \quad \leftarrow \psi_1 \text{ Symm.}$$

$$\hat{P}_{B_2}(1s_1) = \frac{1}{4} (1 \cdot 1s_1 - 1 \cdot 1s_2 - 1 \cdot 1s_2 + 1 \cdot 1s_1) = \frac{1}{2} (1s_1 - 1s_2) \quad \leftarrow \psi_2 \text{ Antisymm.}$$

$$\hat{P}_{A_1}(2s) = \frac{1}{4} (1 \cdot 2s + 1 \cdot 2s + 1 \cdot 2s + 1 \cdot 2s) = 2s \quad \psi_3$$

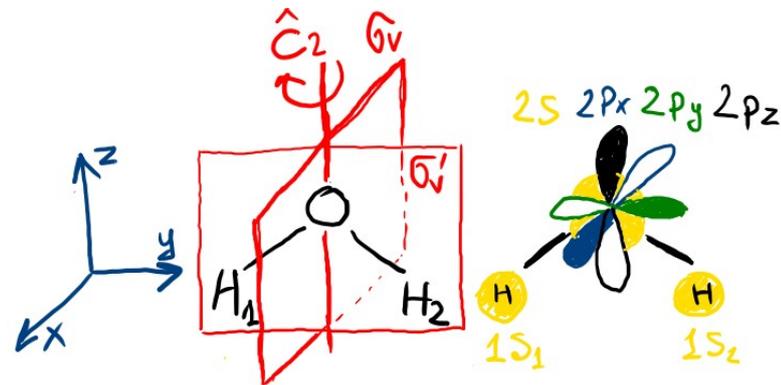
$$\hat{P}_{A_2}(2s) = \frac{1}{4} (1 \cdot 2s + 1 \cdot 2s - 1 \cdot 2s - 1 \cdot 2s) = 0!$$

genauso: $2p_x \rightarrow B_1 \quad \psi_4$

$2p_y \rightarrow B_2 \quad \psi_5$

$2p_z \rightarrow A_1 \quad \psi_6$

$$\Gamma = 3A_1 + B_1 + 2B_2$$



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

MO-LCAO: H₂O

$$\hat{P}_i = \frac{d_i}{h} \sum_{\hat{R}} \chi_i^R \cdot \hat{R} \leftarrow \text{Projektoroperator}$$

$$\hat{P}_{A_1}(1s_1) = \frac{1}{4} (1 \cdot 1s_1 + 1 \cdot 1s_2 + 1 \cdot 1s_2 + 1 \cdot 1s_1) = \frac{1}{2} (1s_1 + 1s_2) \quad \psi_1 \leftarrow \text{Symm.}$$

$$\hat{P}_{B_2}(1s_1) = \frac{1}{4} (1 \cdot 1s_1 - 1 \cdot 1s_2 - 1 \cdot 1s_2 + 1 \cdot 1s_1) = \frac{1}{2} (1s_1 - 1s_2) \quad \psi_2 \leftarrow \text{Antisymm.}$$

$$\hat{P}_{A_1}(2s) = \frac{1}{4} (1 \cdot 2s + 1 \cdot 2s + 1 \cdot 2s + 1 \cdot 2s) = 2s \quad \psi_3$$

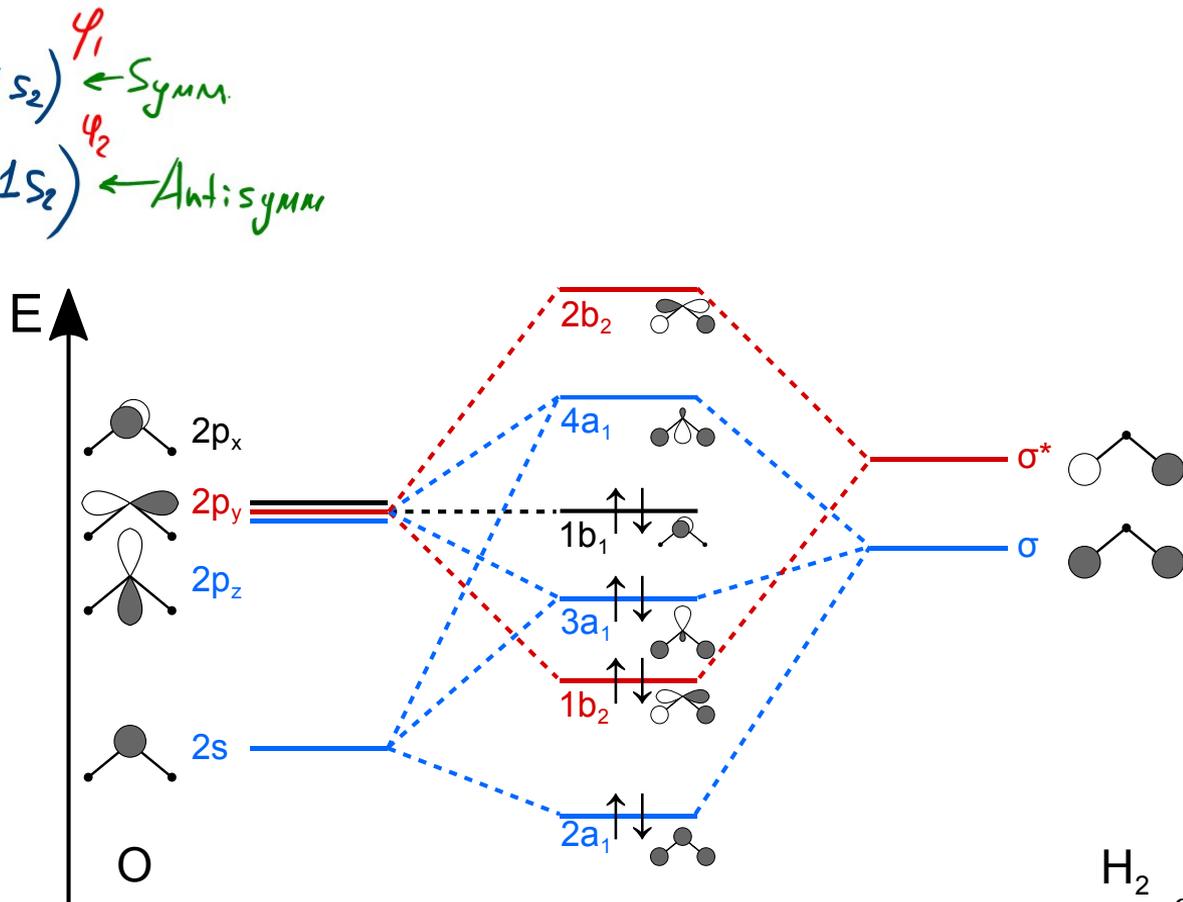
$$\hat{P}_{A_2}(2s) = \frac{1}{4} (1 \cdot 2s + 1 \cdot 2s - 1 \cdot 2s - 1 \cdot 2s) = 0!$$

genauso: $2p_x \rightarrow B_1 \quad \psi_4$

$2p_y \rightarrow B_2 \quad \psi_5$

$2p_z \rightarrow A_1 \quad \psi_6$

$$\Gamma = 3A_1 + B_1 + 2B_2$$



Molekül(e) des Tages

A Short History of Cyclocarbons[#]

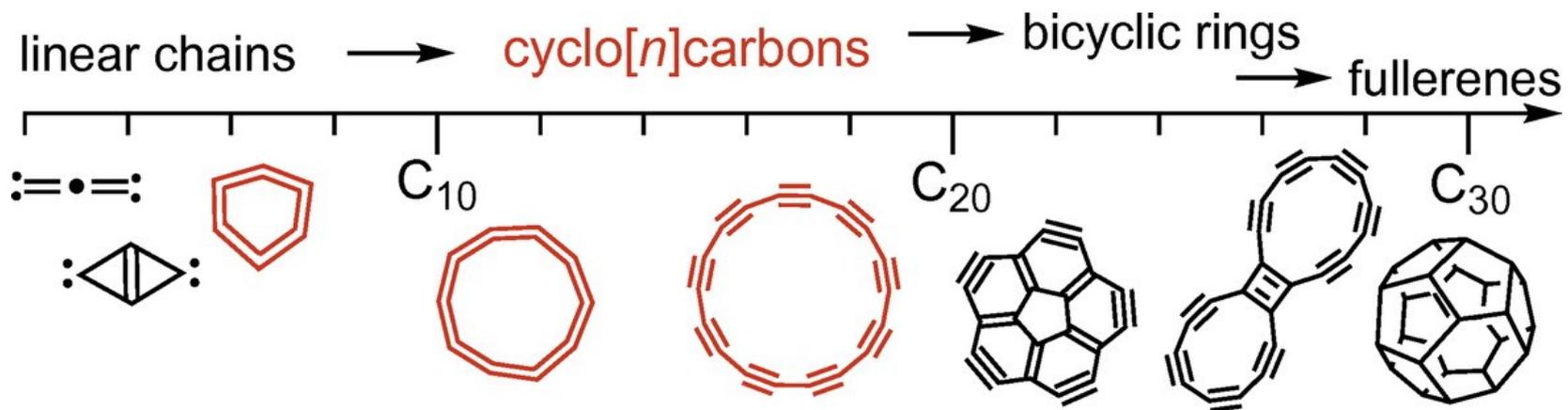
Harry L. Anderson,* Connor W. Patrick, Lorel M. Scriven, and Steffen L. Woltering

Department of Chemistry, Oxford University, Chemistry Research Laboratory, Oxford, OX1 3TA, UK

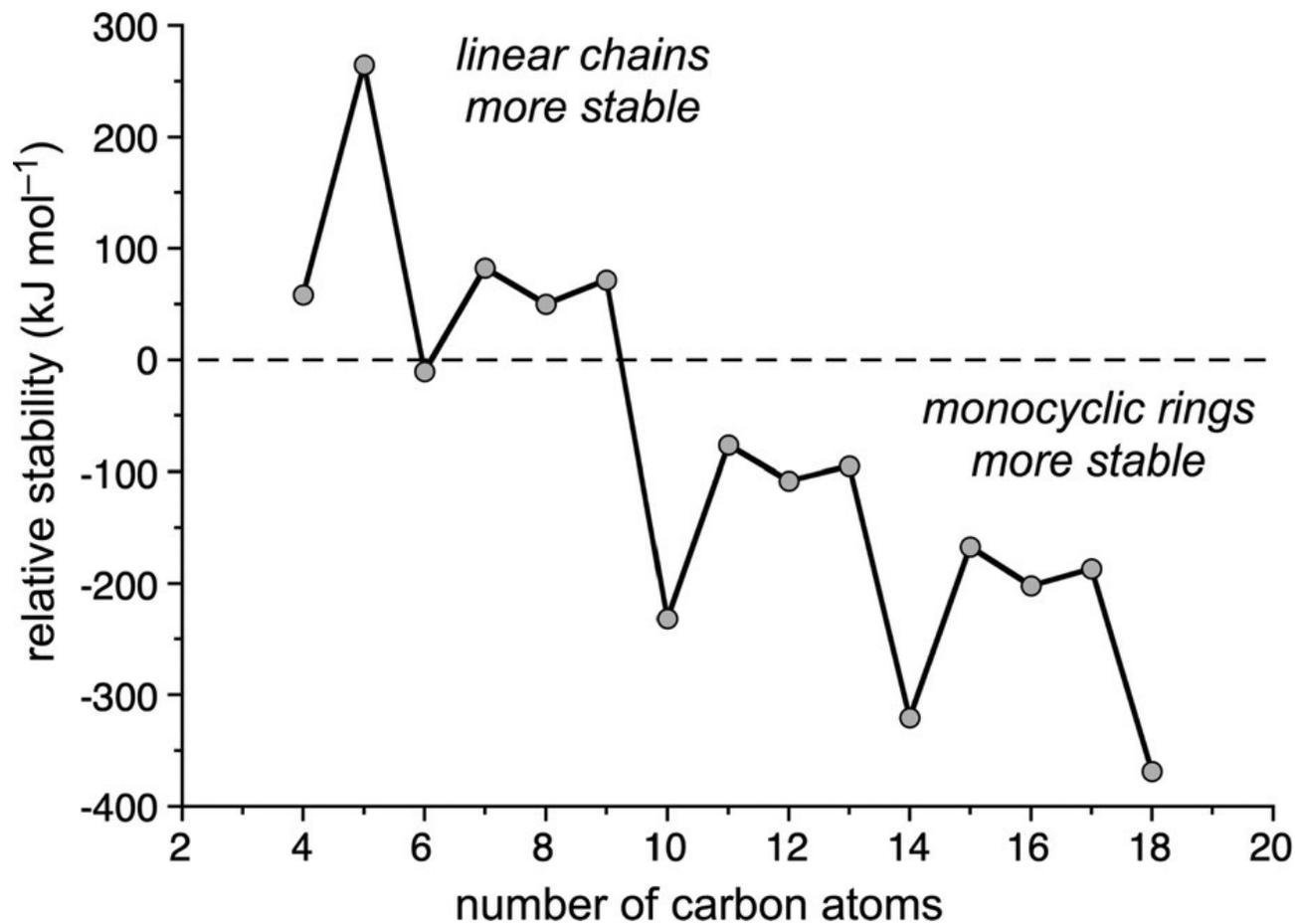
E-mail: harry.anderson@chem.ox.ac.uk

Received: October 30, 2020; Accepted: December 1, 2020; Web Released: December 9, 2020

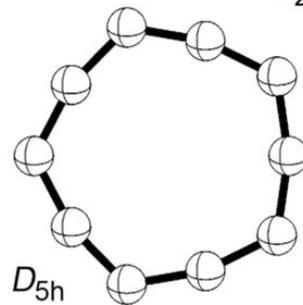
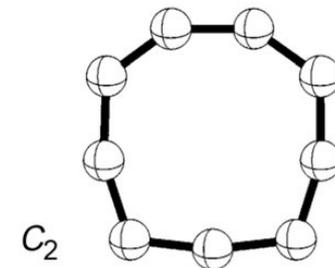
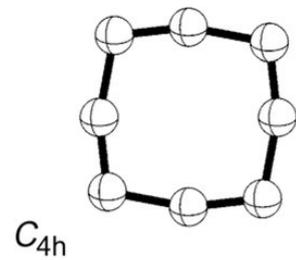
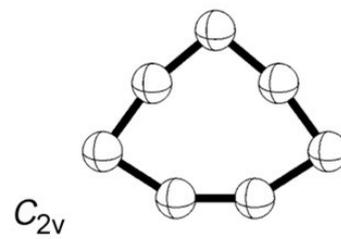
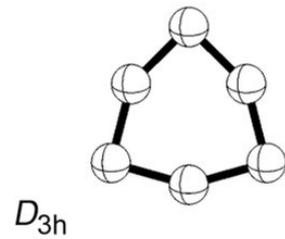
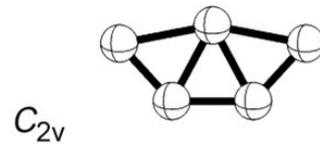
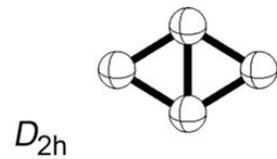
Cyclocarbons



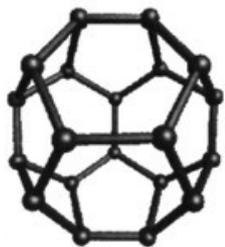
Linear oder Ringförmig?



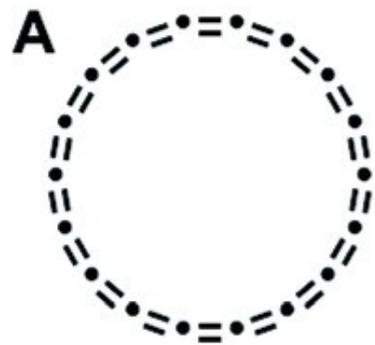
$C_4 - C_{10}$



C₂₀ Isomere



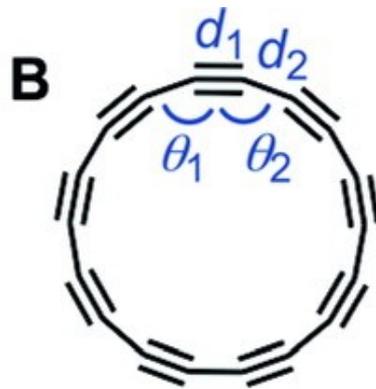
C₁₈: Cumulen oder Polyyn?



$$d_1 = d_2$$

$$\theta_1 = \theta_2$$

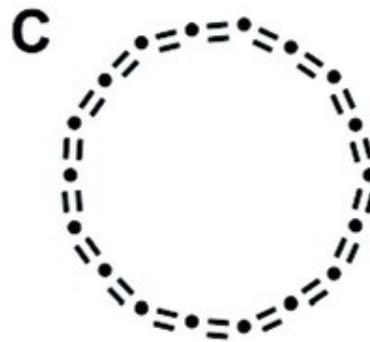
D_{18h} cumulene



$$d_1 \neq d_2$$

$$\theta_1 = \theta_2$$

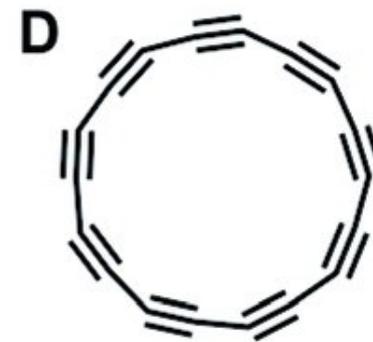
D_{9h} polyyne



$$d_1 = d_2$$

$$\theta_1 \neq \theta_2$$

D_{9h} cumulene



$$d_1 \neq d_2$$

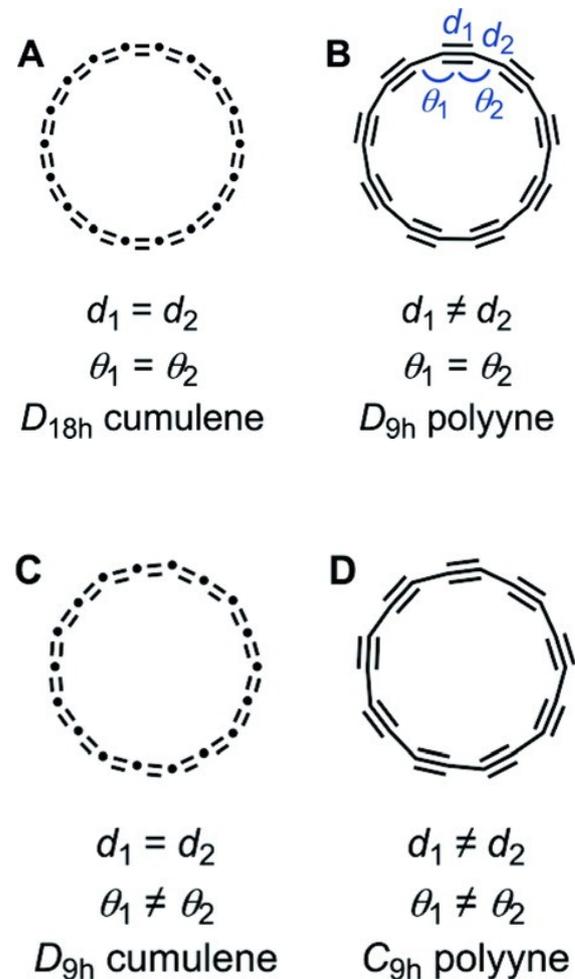
$$\theta_1 \neq \theta_2$$

C_{9h} polyyne

C₆ – C₂₄: Rechnungen

Table 1. Survey of the predicted ground state geometries of even cyclo[n]carbons C₆–C₂₄.^a

year [ref.]	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C ₂₀	C ₂₂	C ₂₄	level of theory
1986 [46]	C										HF
1989 [19]							B				HF
1990 [47]			C								CISD/DZP
1991 [48]							B A				SCF MP2
1992 [49]			C								SCF and CCSD/cc-pVDZ
1992 [38]							B A	B B	A	B B	SCF MP2
1994 [30]	C		C	D	A	D*	A*				DFT (* not energy minima)
1995 [50]			C C		C D		C D				DFT/6-31G*/B-LYP RHF/6-31G*
1995 [51]	C	D	C	D	C	D	C				DFT/cc-pVDZ/B3LYP
1999 [42]	C		C		C		C		D		DFT/cc-pVDZ/B3LYP
2000 [43]	C	D	C	D	C	D	C	B	C		LDA/84Ry
2000 [52]	C		C		B		B				QMC
2005 [53]							C		C		DFT/6-31G*/B3LYP
2007 [45]	C	D	C								CCSD(T) cc-pVTZ
2008 [54]	C		C		D		D		D		CCSD cc-pVTZ
2009 [28]	C	D	C	D	C	D	C	D	C	D	DFT/6-31G(d)/B3LYP
2010 [55]			C		B		B		B		DFT/cc-pVDZ/rCAM-B3LYP
2016 [33]	C	D	C	D	C	D	C	D	C	D	DFT/6-311++g(d,p)/meta-GGA
2019 [56]							B				DFT/def2-TZVP/RSX-PBE
2019 [57]							B				CASSCF
2020 [58]	C	D	C	D	D	D	D	D	D	D	DFT/6-311++G(d,p)/ωB97XD



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