2. Aliphatische Verbindungen

2.2 Alicyclen (Cycloalkane)

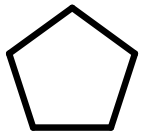
Übersicht und Nomenklatur
Konstitutionsisomerie
Konformation

Übersicht (1)

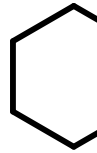
Homologe Reihe: C_nH_{2n}

Cyclopropan
C_3H_6

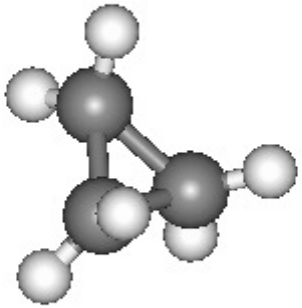
Cyclobutan
C_4H_8

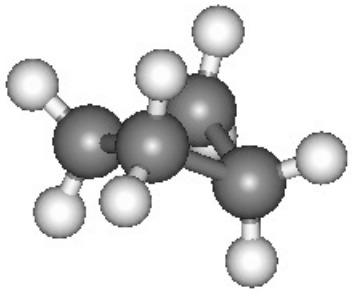


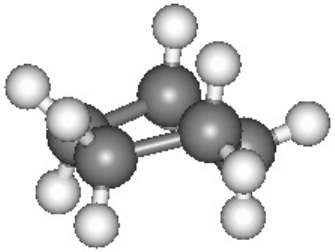
Cyclopentan
C_5H_{10}

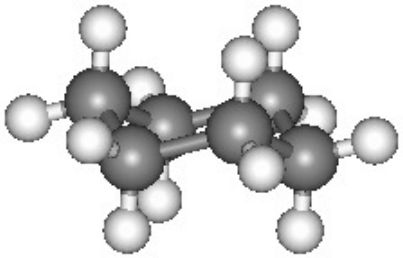


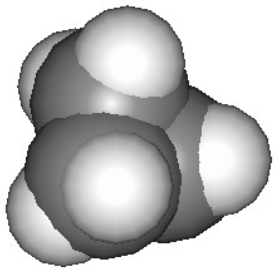
Cyclohexan
C_6H_{12}

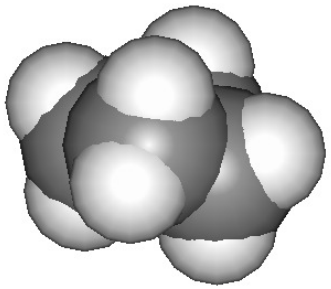


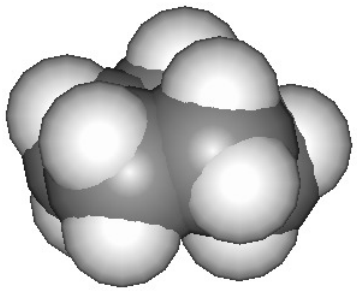


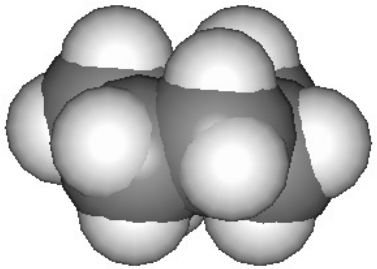




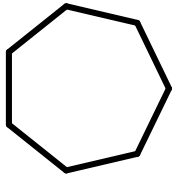




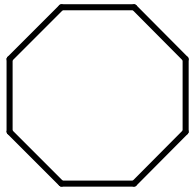




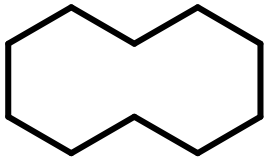
Übersicht (2)



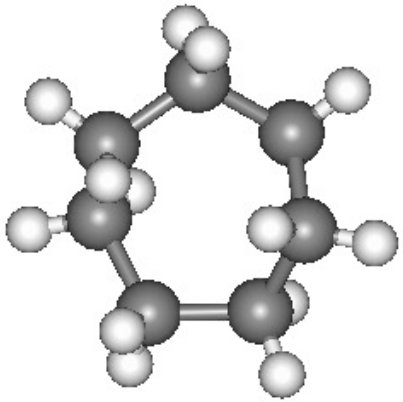
Cycloheptan
C_7H_{14}

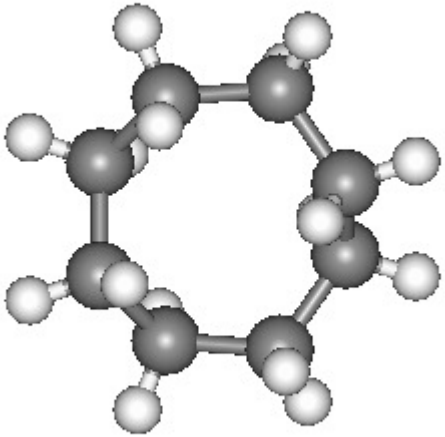


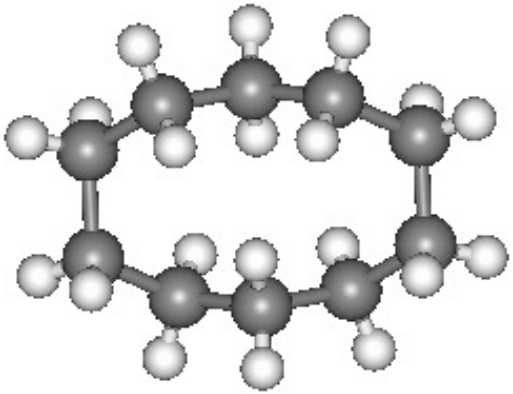
Cyclooctan
C_8H_{16}



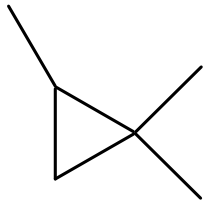
Cyclodecan
$C_{10}H_{20}$



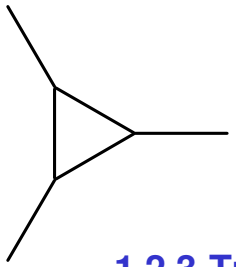




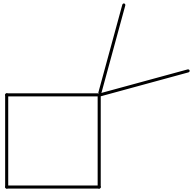
Konstitutionsisomere C_6H_{12}



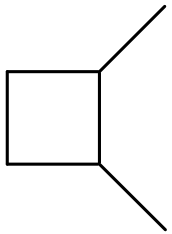
1,1,2-Trimethyl-



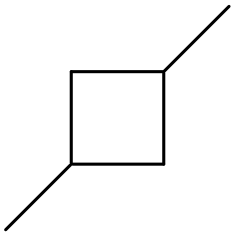
1,2,3-Trimethylcyclopropan



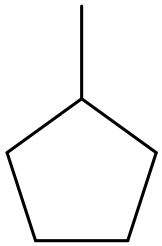
1,1-Dimethyl-



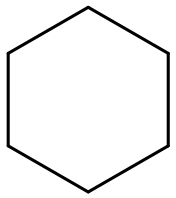
1,2-Dimethyl-



1,3-Dimethylcyclobutan

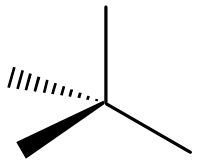


Methylcyclopentan

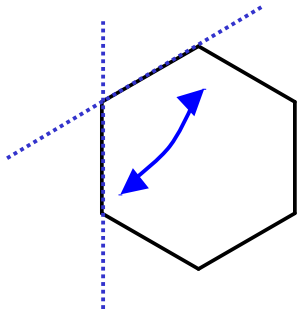


Cyclohexan

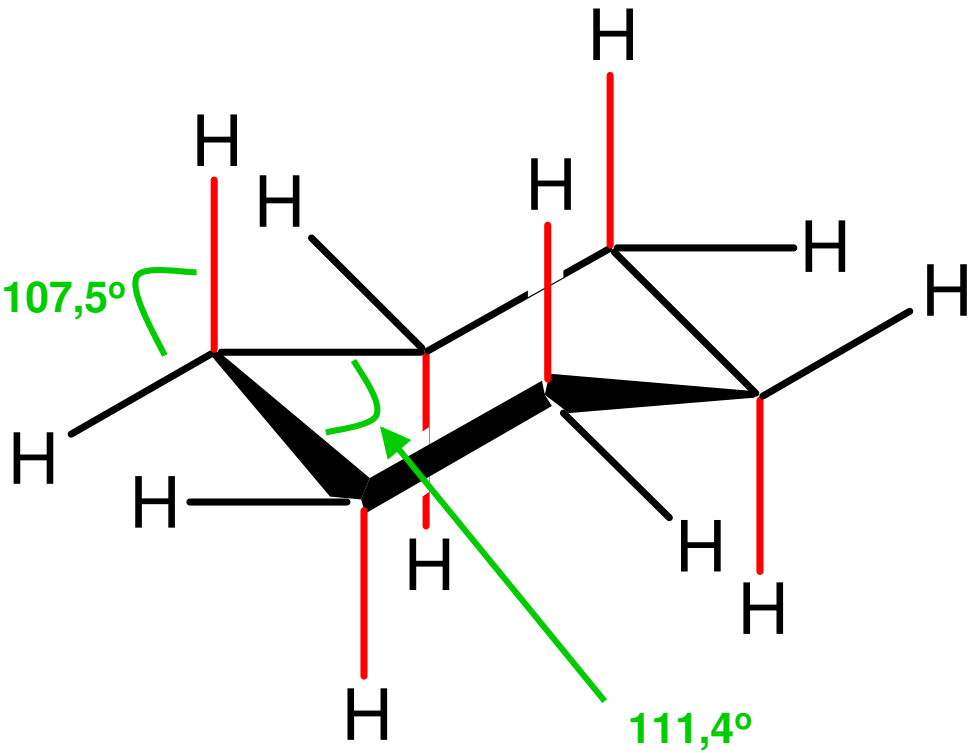
Struktur von Cyclohexan



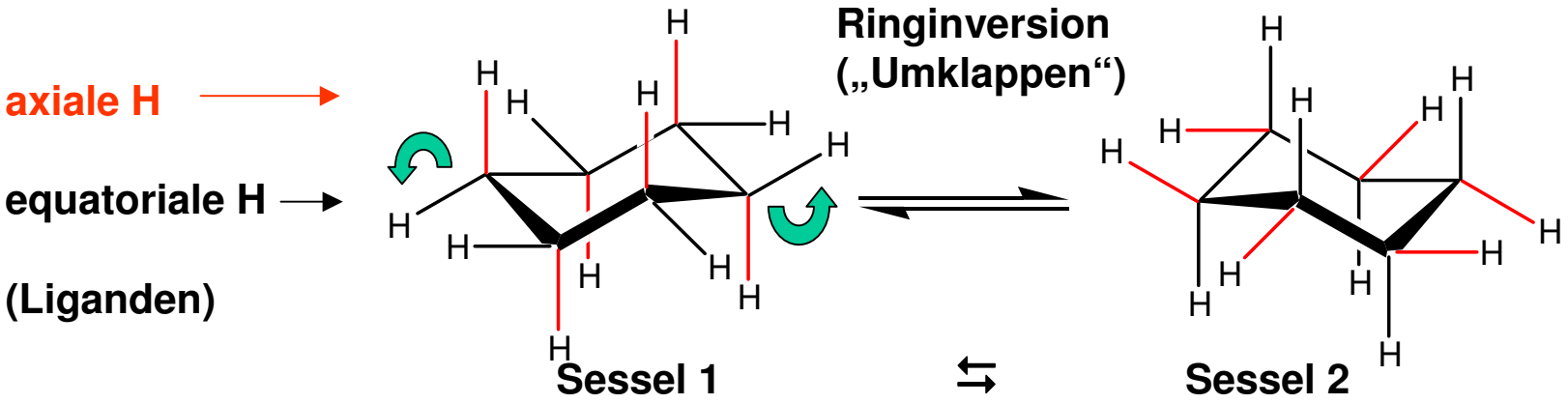
sp^3 Kohlenstoff
Tetraeder
Bindungswinkel 109,5°

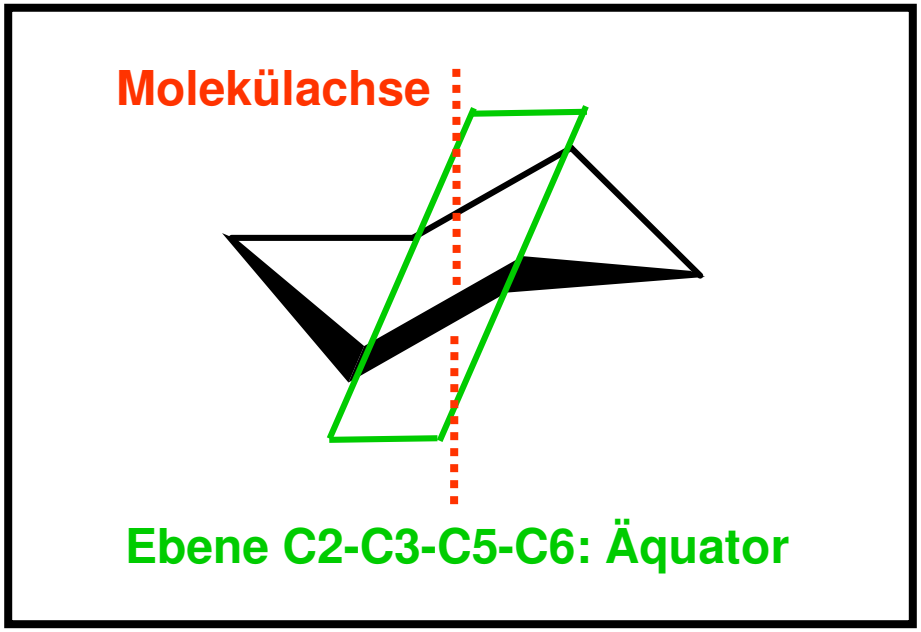


Cyclohexan
Bindungswinkel 120° ?
Bei sp^3 nicht möglich !



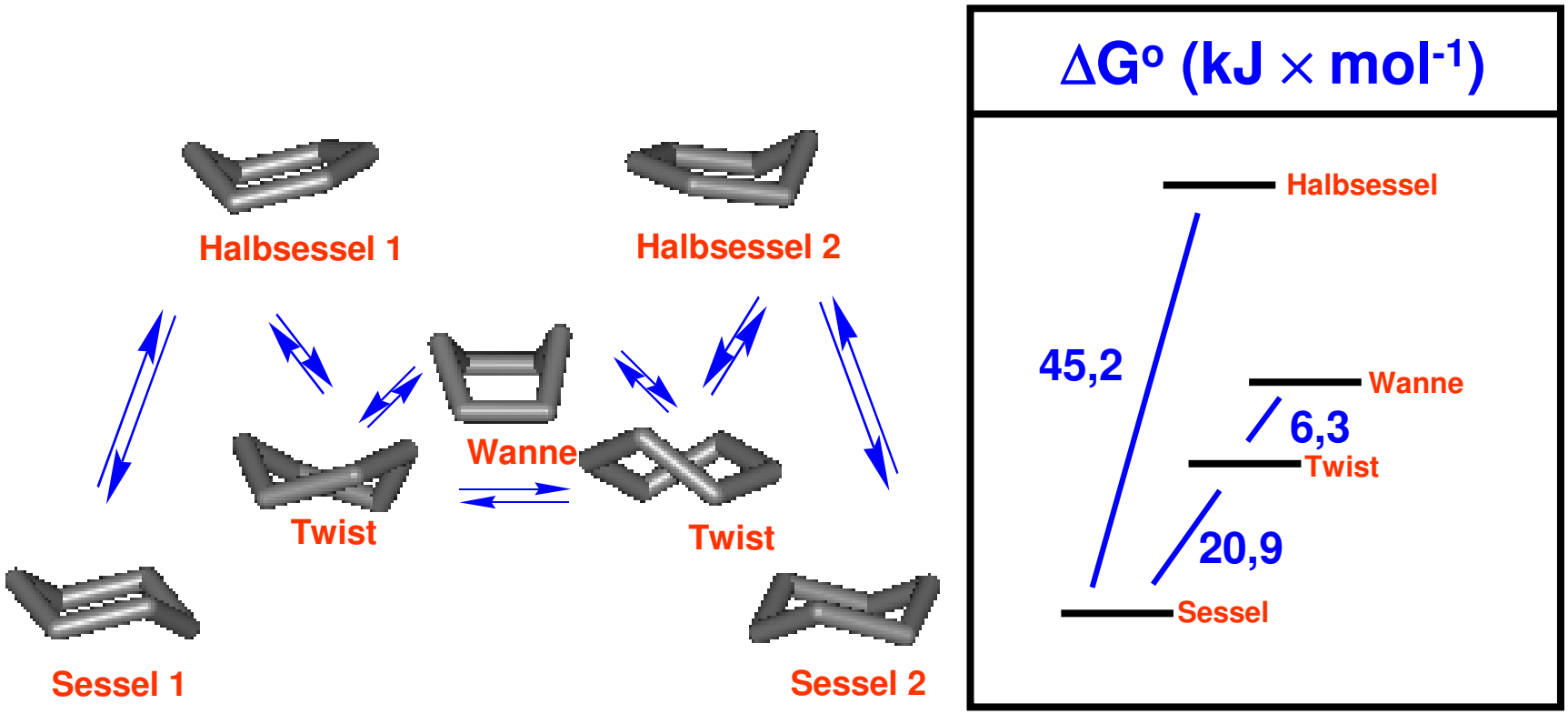
Cyclohexan: Ringinversion



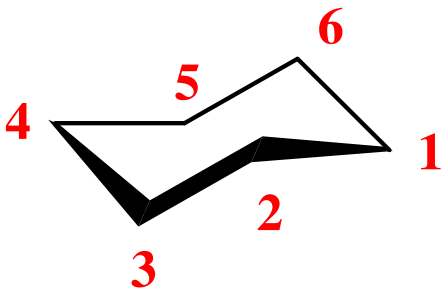


Bei der Ringinversion werden aus axialen equatoriale und aus equatorialen axiale Liganden

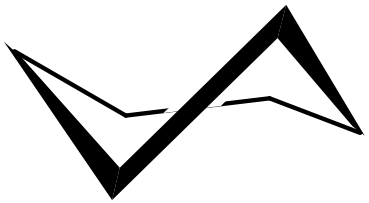
Cyclohexan: Konformationen



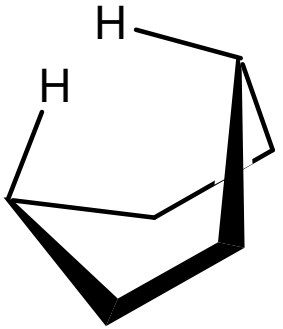
Newman Projektion von Cyclohexan



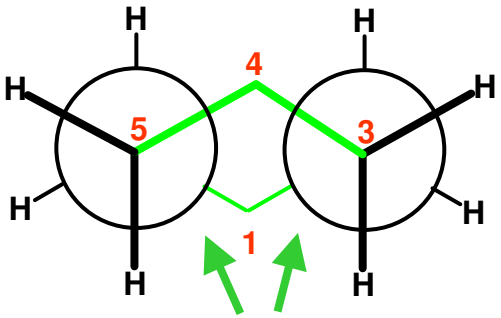
Sessel (chair)



Twist

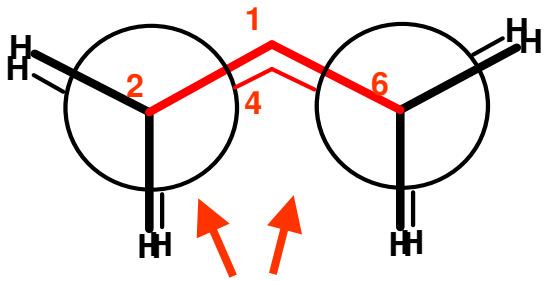


Wanne (boat)



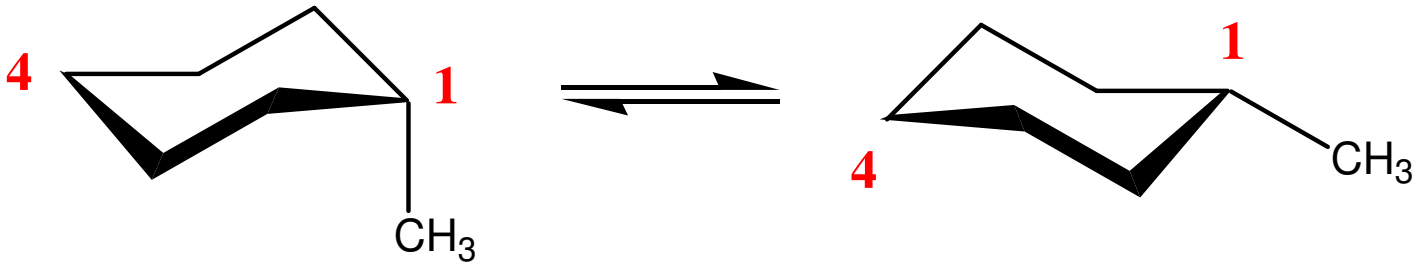
gauche
(gestaffelt)

Die ekliptische WW wird auch als Pitzer-Spannung bezeichnet

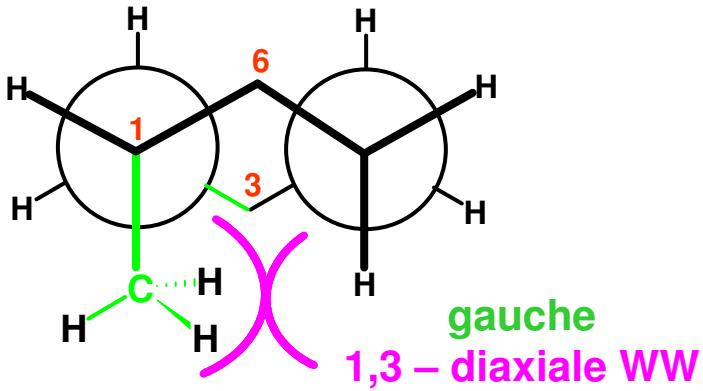


syn
(ekliptisch)

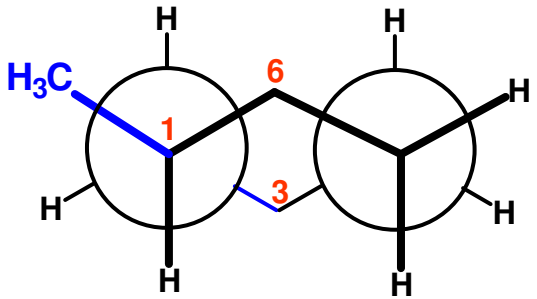
Konformere von Methylcyclohexan



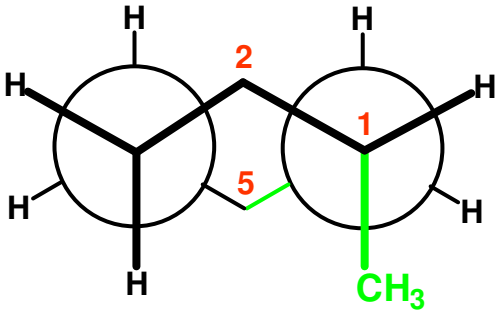
$^4C_1$-Konformation | **"C" steht für "Chair"** | **$^1C_4$-Konformation**



gauche
1,3 – diaxiale WW



anti



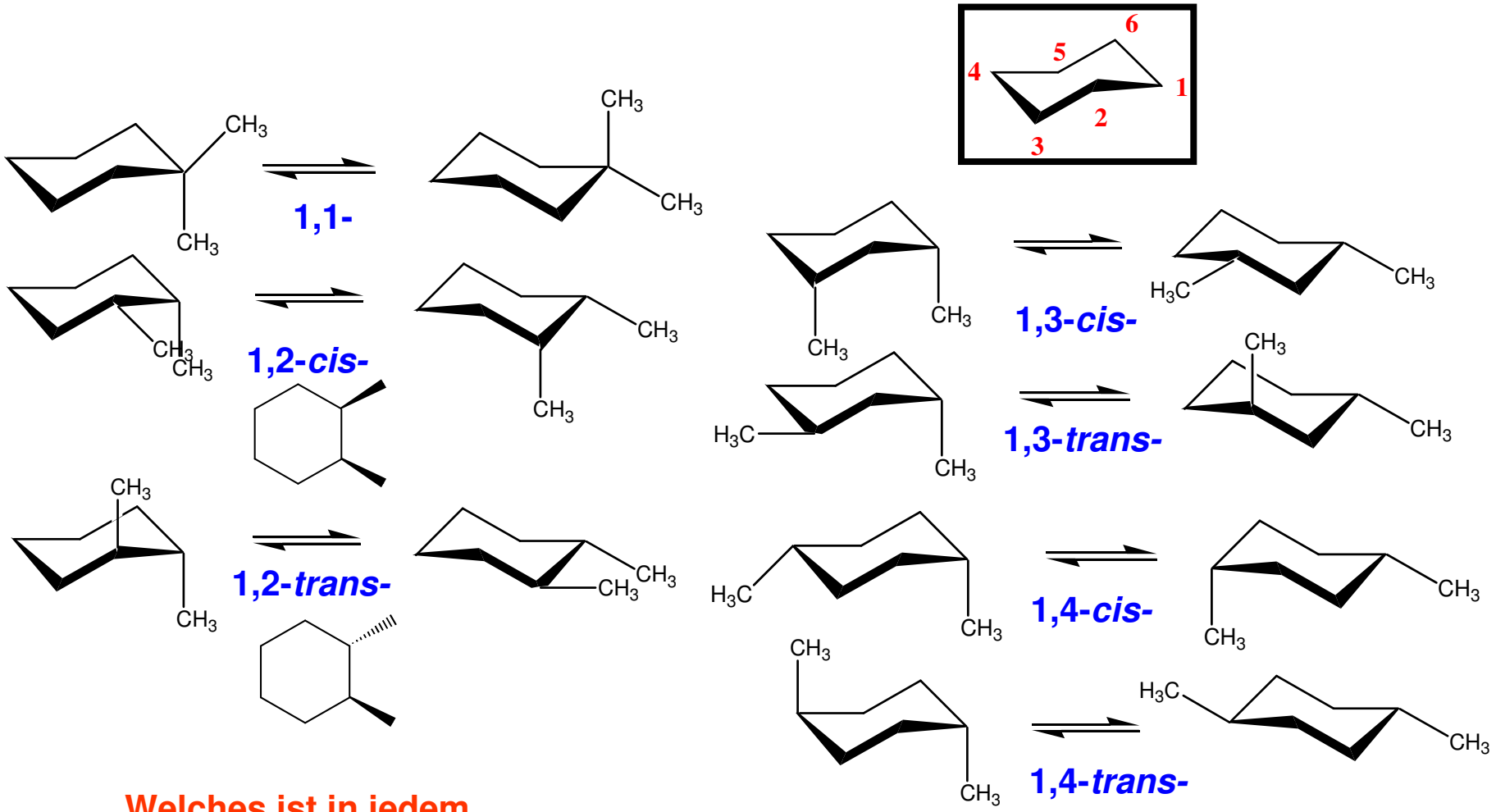
Das Konformer mit axialer Methylgruppe ist im Vergleich zum Konformer mit equatorialer Methylgruppe destabilisiert ($\Delta G^o_{ax\text{-}eq} \approx 7{,}8\ kJ \times mol^{-1}$)
Konformerengleichgewicht: ca. 95% eq : 5% ax

Gleichgewichtskonstante, Gleichgewichtslage und Freie Energie

$$\Delta G^o = \Delta H^o - T\Delta S^o = - RT \times \ln K$$

K (298 K)	% in energieärmerer Form	$-\Delta G$ (kJ × mol^{-1})
2	67	1,71
3	75	2,72
4	80	3,43
5	83	3,97
10	91	5,85
20	95	7,52
100	99	11,29
1000	99,9	17,14
10000	99,99	22,99

Dimethylcyclohexan: Konstitution und Konformation

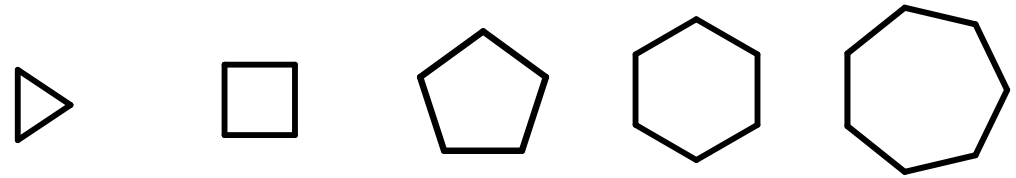


Welches ist in jedem Gleichgewicht das stabilere Konformer ?

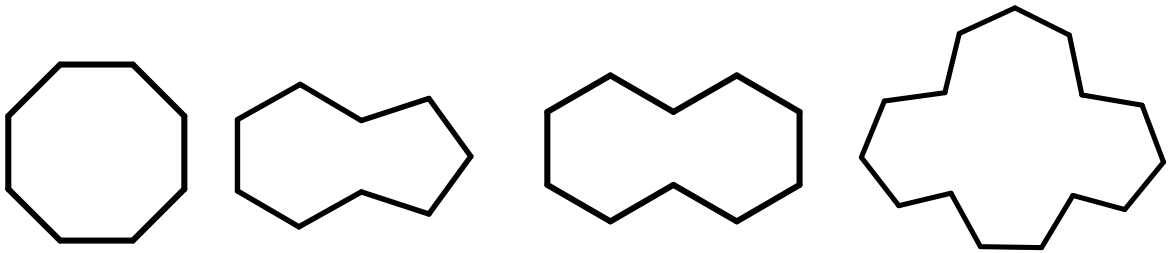
Zur *cis*- / *trans*-Stereoisomerie: siehe Kapitel 4

Ringspannung (Baeyer-Spannung)

Kleine (3 und 4), normale (5, 6 und 7), mittlere (8-12) und grosse (>12) Ringe

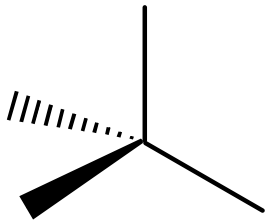


Verbrennungswärme (kcal × mol^{-1})	**500**	**656**	**793**	**944**	**1108**
Ringspannung	**28**	**26,7**	**6,3**	**0**	**6,7**
Spannung pro CH_2	**9,3**	**6,7**	**1,3**	**0**	**1,0**

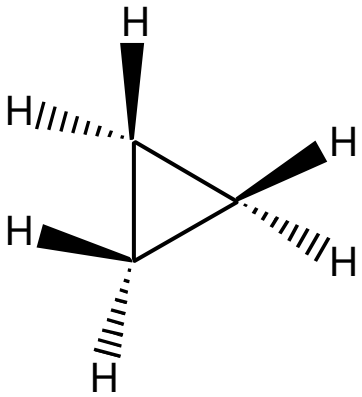


Verbrennungswärme (kcal × mol^{-1})	**1269**	**1429**	**1586**	**2363**
Ringspannung	**10,3**	**13,0**	**12,7**	**1,5**
Spannung pro CH_2	**1,3**	**1,4**	**1,3**	**0,1**

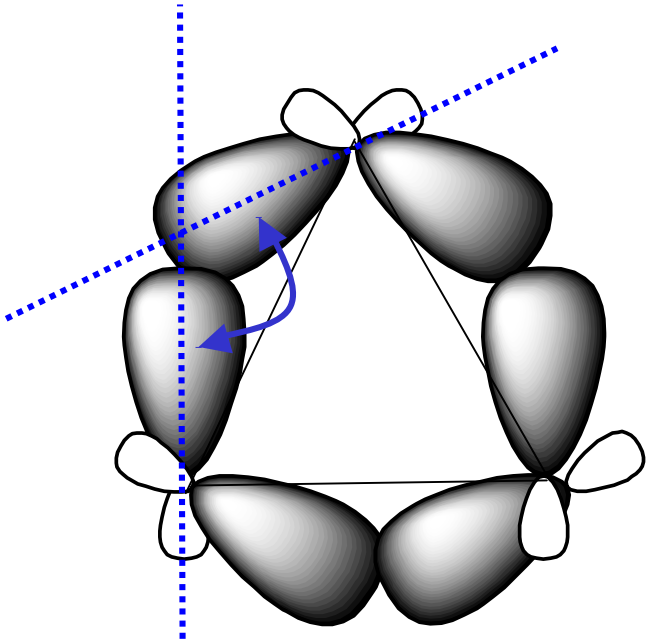
Struktur von Cyclopropan



sp^3 Kohlenstoff
Tetraeder
Bindungswinkel 109,5°

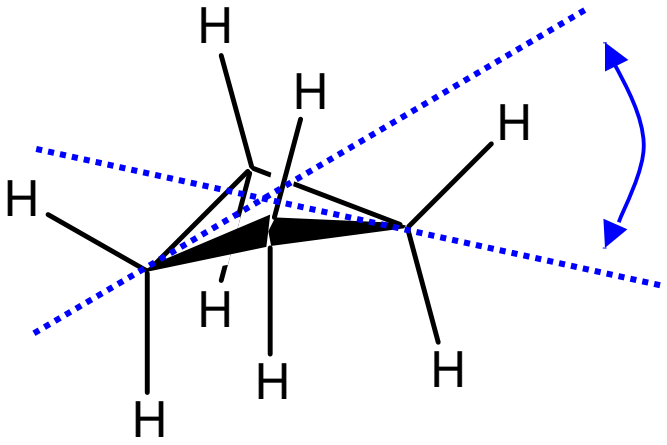


Cyclopropan:
3 tetravalente C-Atome
Bindungswinkel 60° ?
UNMÖGLICH !



Cyclopropan:
Drei tetravalente C-Atome
Interorbitalwinkel 104°
Banana Bond

Struktur von Cyclobutan

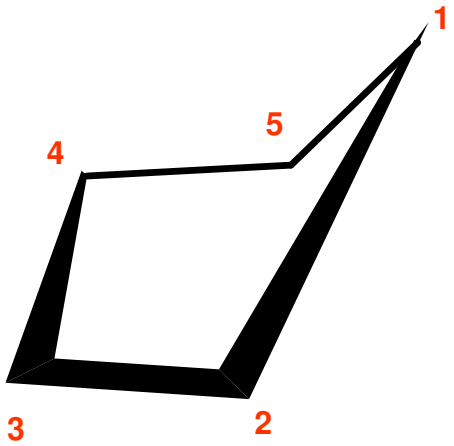


Cyclobutan ist gefaltet
Winkel zwischen den Ebenen: 26°

Minimieren von ekliptischen WW

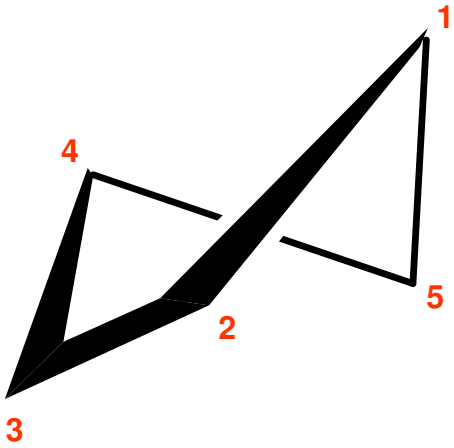
rasches Umklappen

Konformere von Cyclopentan



Briefumschlag
(envelope)
10 Konformere

C2, C3, C4 und C5 in einer Ebene
C1 darüber oder darunter



Twist
10 Konformere

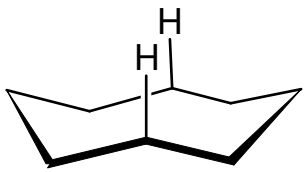
C1, C2 und C3 in einer Ebene
C4 darüber, C5 darunter
oder umgekehrt

PSEUDOROTATION

Alle C-Atome schwingen rasch durch die mittlere Ringebene

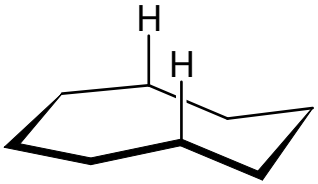
Mittlere Ringe

Cyclooctan

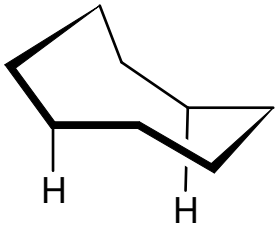


Krone

CCC 113,2°

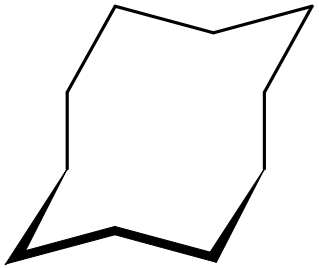


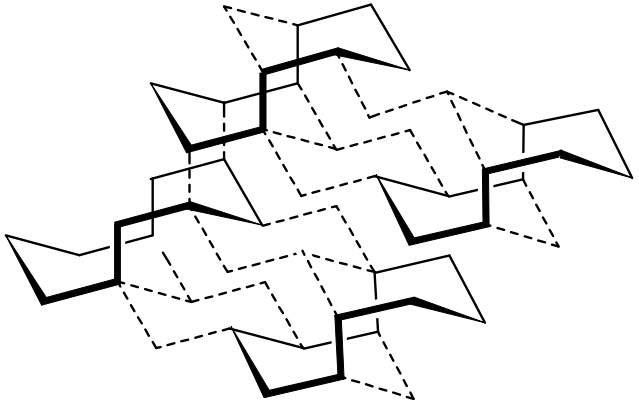
CCC 112°



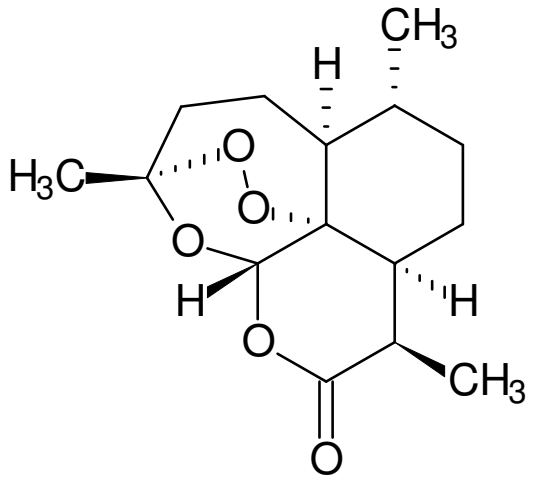
CCC 114°

Cyclodecan

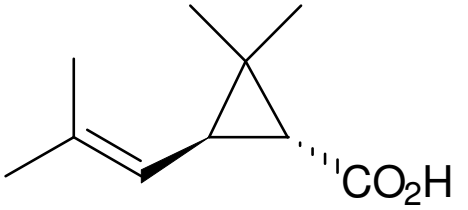




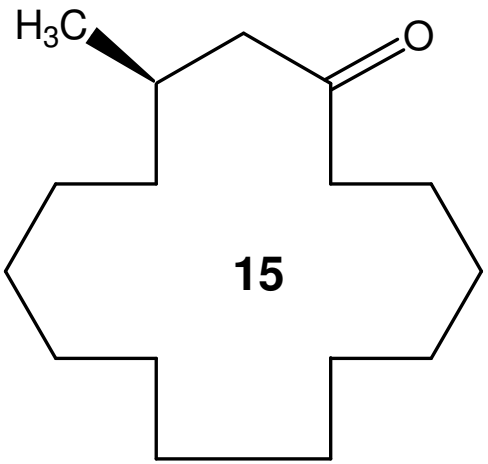
Alicyclen in Naturstoffen



Qinghaosu (artemisinin)
endoperoxide from *Artemisia annua*
active against multi-drug resistant strains of *Plasmodium falciparum*
generation of $^1O_2$ and/or O_2^- → oxidative stress, lethal to *P. falciparum*

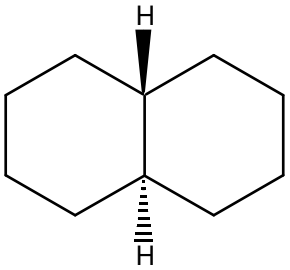


Chrysanthemic acid

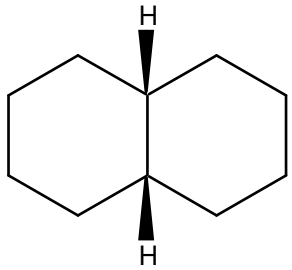


Muscon

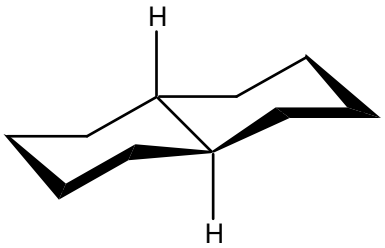
Polycyclische Aliphaten: Decalin



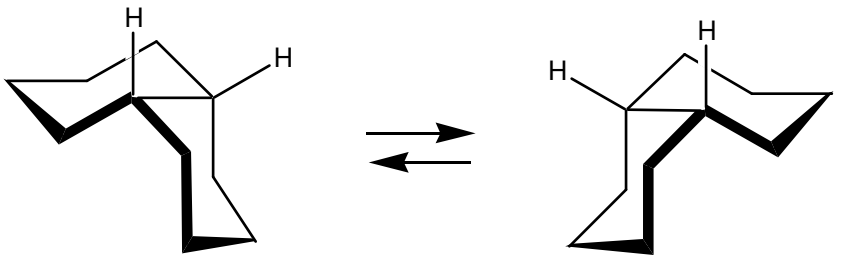
***trans*-Decalin**



***cis*-Decalin**

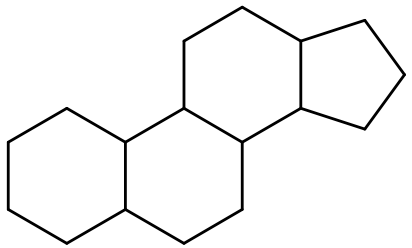


Konformation starr

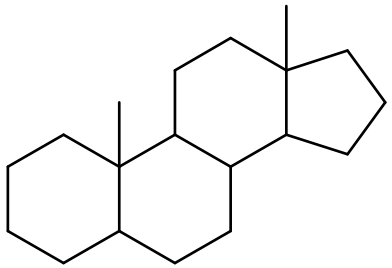


Konformation flexibel

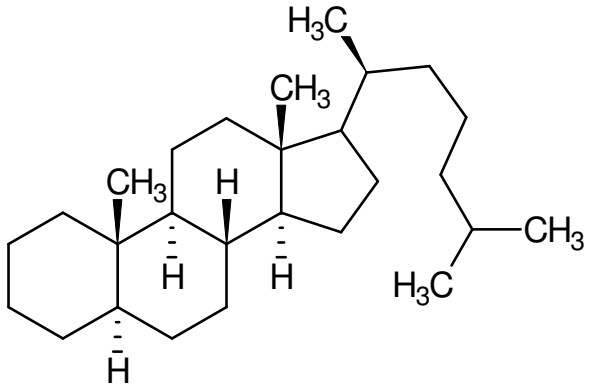
Polycyclische Naturstoffe: Steroide



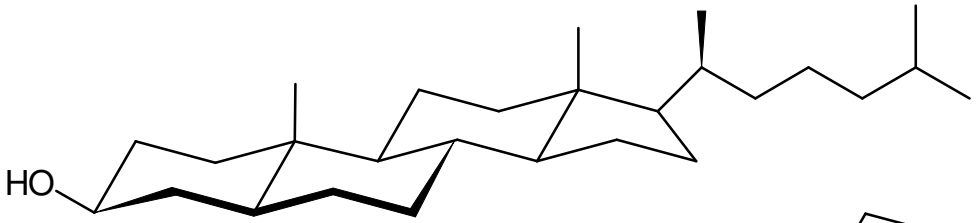
Cyclopentanoperhydro-phenanthren (Steran; Gonan)



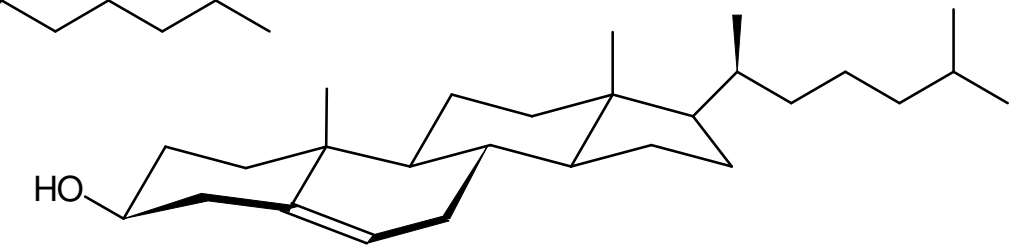
Androstan



Cholestan

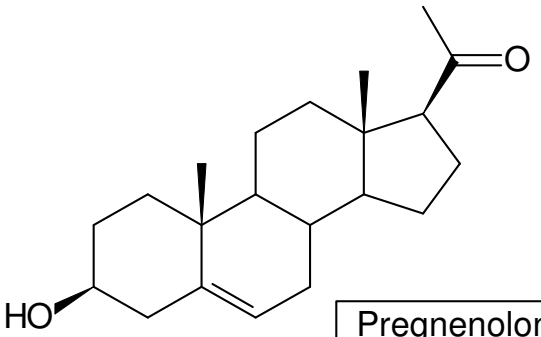


Cholestanol

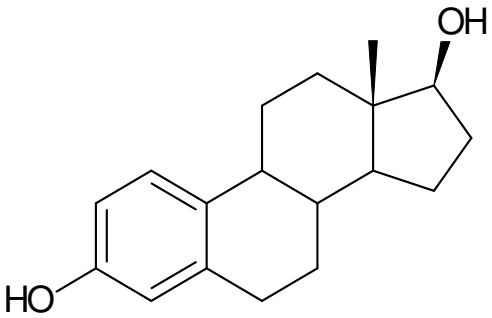


Cholesterin

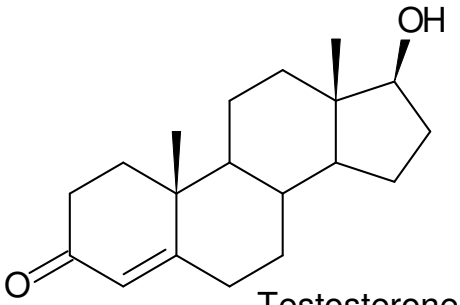
Steroidhormone



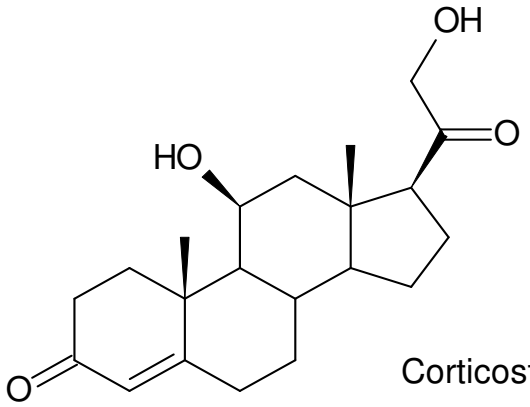
Pregnenolone



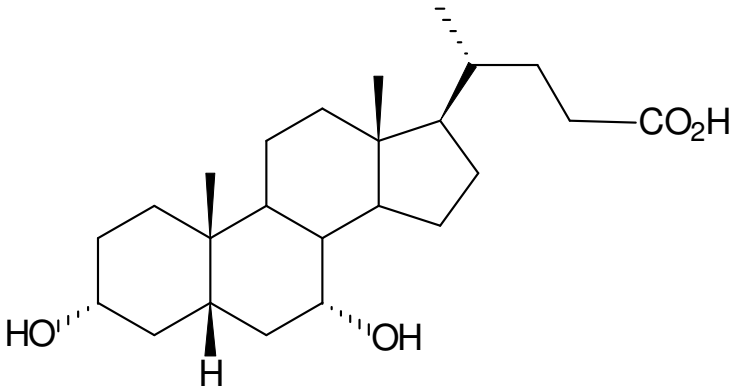
Estradiol



Testosterone



Corticosterone



Chenodesoxycholic acid