

STEREOCHEMIA ORGANICZNA- I

Sławomir Jarosz

Podręczniki podstawowe

- Organic stereochemistry, Henri Kagan (1979)
- Stereochemistry of organic compounds**, Ernest L. Eliel (1994)
- Stereochemia w syntezie organicznej, Jacek Gawroński (1988)
- Stereochemia: podstawy i zastosowania, Mihály Nógrádi (1988)
- Classics in Stereoselective Synthesis, E.M. Carreira, L. Kvaerno (Wiley, 2009)

Milowe (historycznie) kroki w stereochemii

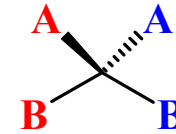
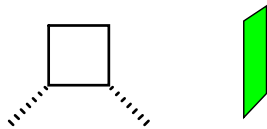
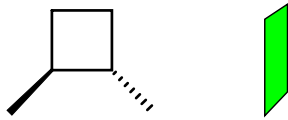
1. Pasteur 1860; van't Hoff 1874; Le Bel 1874
2. Analiza konformacyjna: Hughes i Ingold (1935, 1953), **Barton** (1950)
3. Reguła Cahna, Ingolda, **Preloga**: 1966
4. Opis stereochemii językiem topologii: **Prelog** 1969
5. Reaktywność a stereochemia (**NOBEL**: Fischer 1902; Haworth, Karrer 1937; Robinson 1947; Todd 1957; Pauling 1954; Woodward 1965; Barton, Hassel 1969; Cornforth, Prelog 1975; Fukui, Hoffmann 1981; Sharpless, Noyori, Knowles 2001)

Izomery – związki o takim samym wzorze sumarycznym różniące się budową

Izomery konstytucyjne (*strukturalne*) C₅H₈

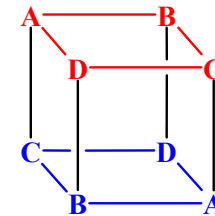
Izomery steryczne (*stereoizomery*) C₅H₈

Czy przedmiot i odbicie są na siebie nakładalne ???

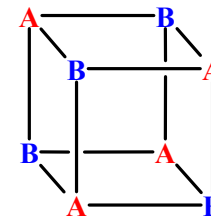


Elementy symetrii

1. Oś symetrii właściwa C_n
2. Płaszczyzna symetrii σ
3. Środek symetrii i



Osie przemienne wyższych rzędów

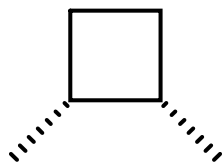
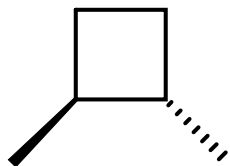


Poszukajmy elementów symetrii w cząsteczce

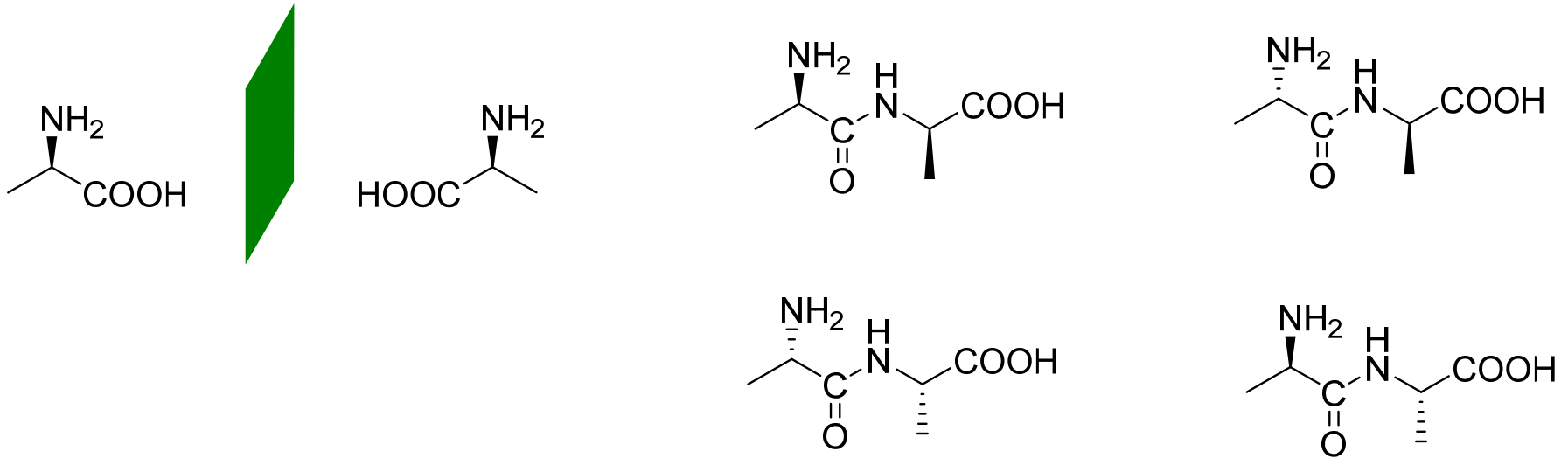
oś

płaszczyzna

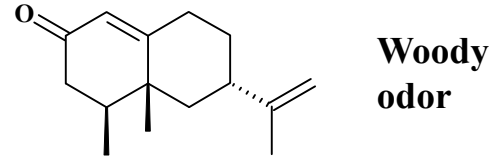
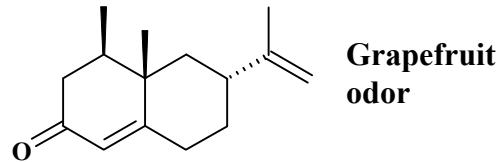
środek



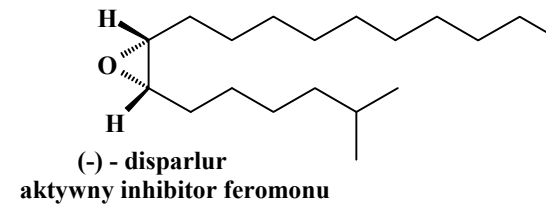
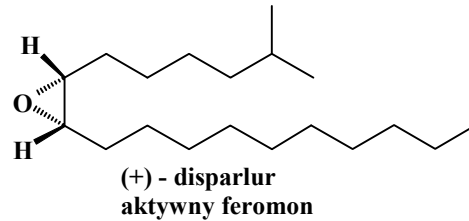
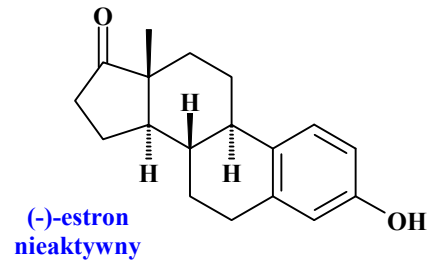
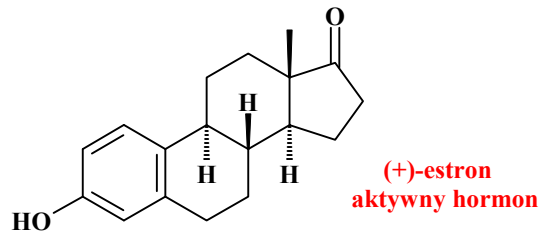
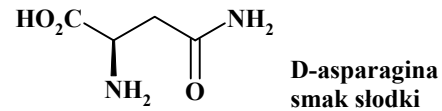
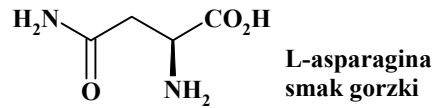
Enancjomery - diastereoizomery



Enancjomery MOGĄ być różnie postrzegane przez organizm żywy

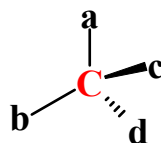


The Nose as a Stereochemist. Enantiomers and Odor, R. Bentley, *Chem. Rev.* **2006**, *106*, 4099-4112

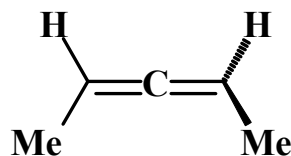


CHIRALNOŚĆ MOLEKULARNA

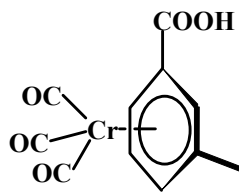
Centrum Stereogeniczne
punkt



chiralność aksjalna

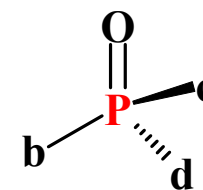
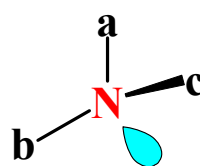
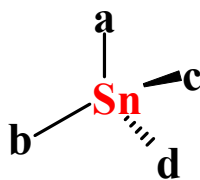
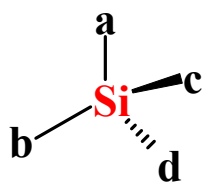
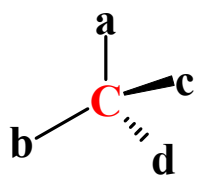


chiralność planarna
(pł. *chiralności*)

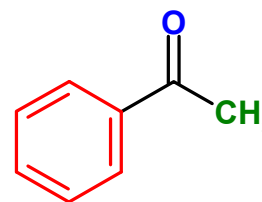
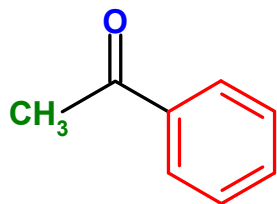


Binaftol i pochodne: *Chem. Rev.* **2005**, *105*, 857–89. *Chem. Rev.* **2013**, *113*, 6234–6458

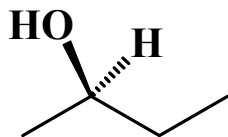
CENTRUM STEREOGENICZNE



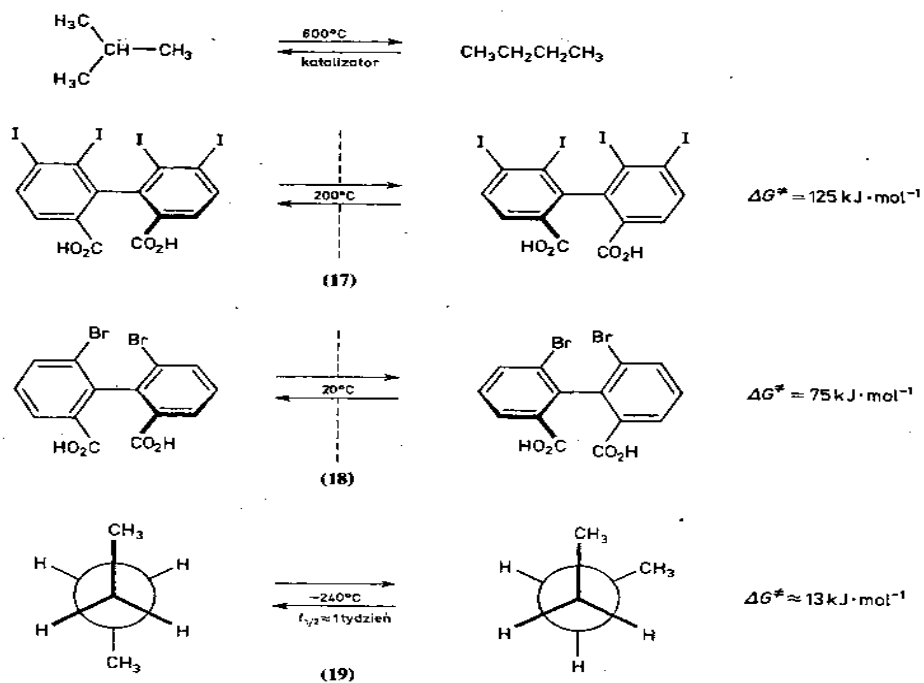
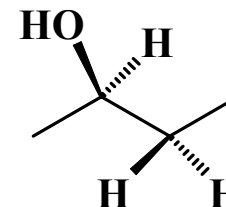
Strony re i si cząsteczki

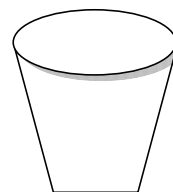
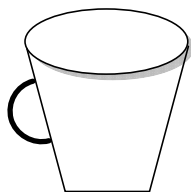


KONFIGURACJA Przestrzenne (trwale)
 ułożenie atomów (grup) w cząsteczce



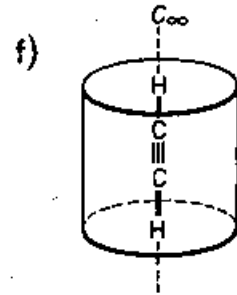
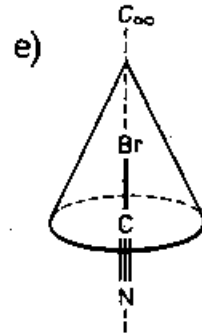
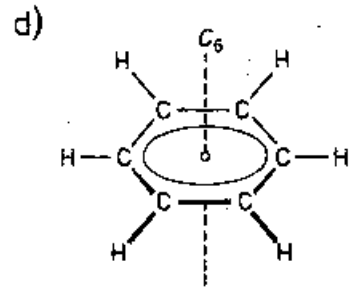
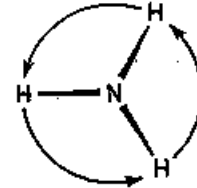
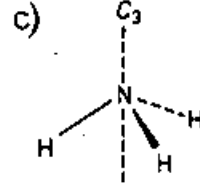
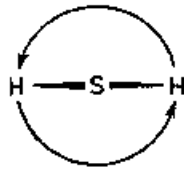
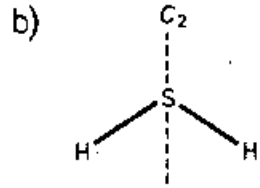
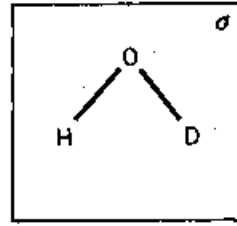
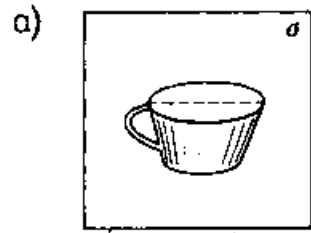
KONFORMACJA Przestrzenne ułożenie atomów
 (grup) w cząsteczce (poszczególne konformery łatwo
 przechodzą jeden w drugi)

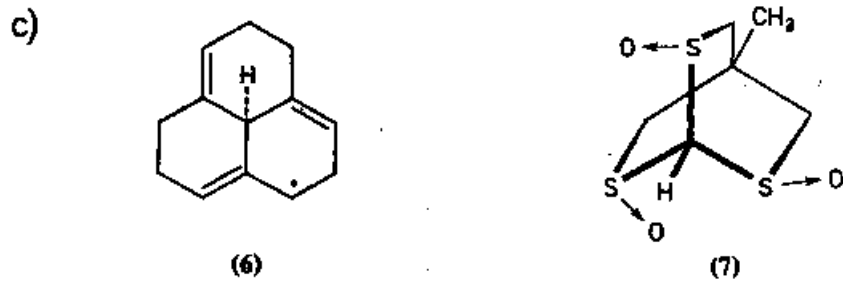
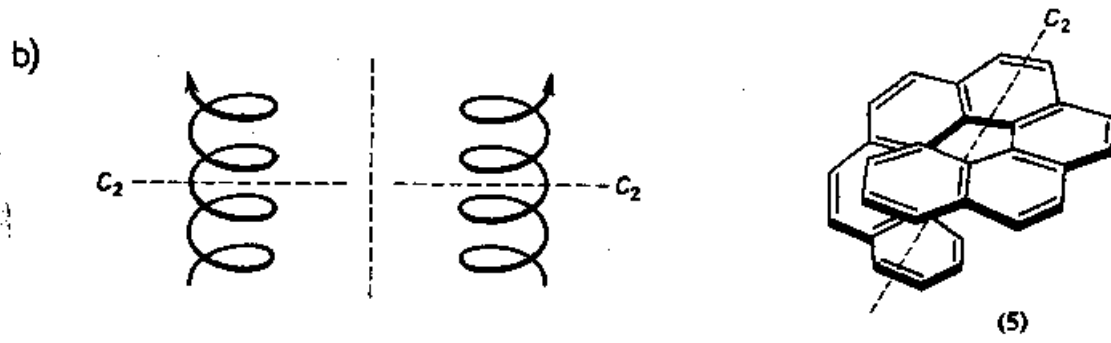
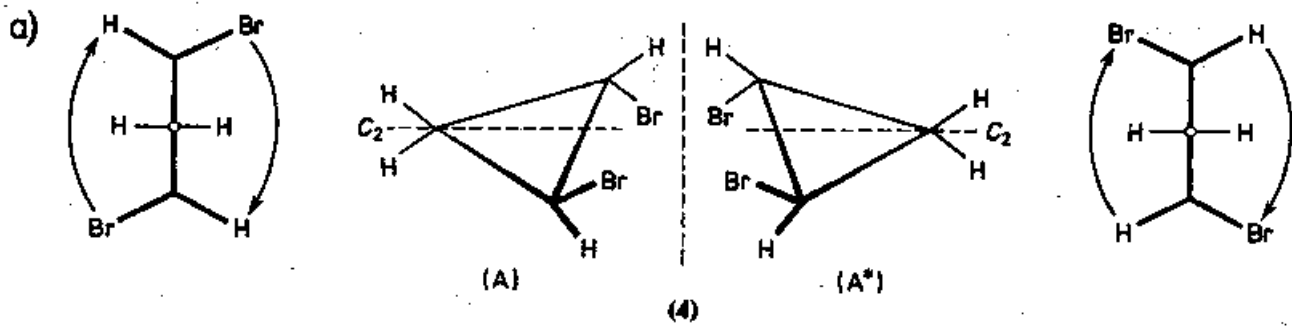




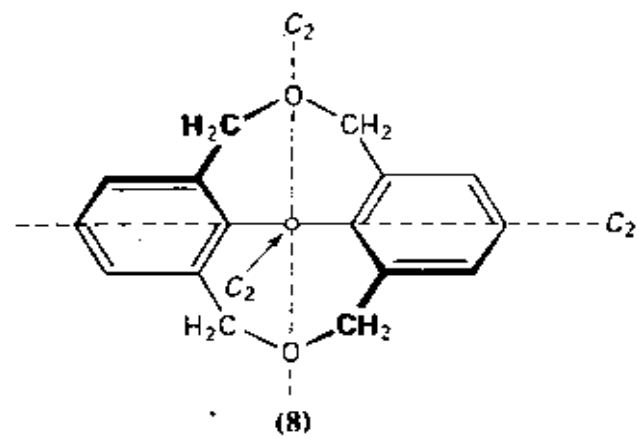
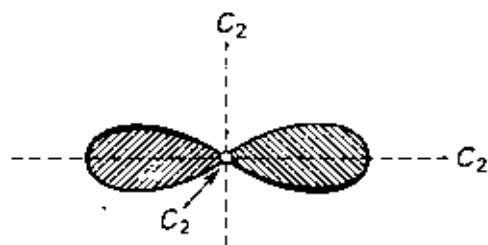
Klasyfikacja grup według symetrii. Notacja grup punktowych Schoenfliesa

Grupy chiralne	grupy achiralne
C_n (tylko jedna oś C_n) D_n ($C_n + n \perp C_2$) T ($4C_3 + 3C_2$, <i>brak</i> σ)	C_s (tylko jedna σ) S_n (brak σ n parzyste) C_{nv} ($C_n + n \sigma_v$ brak σ_h) C_{nh} ($C_n + \sigma_h$ brak σ_v) D_{nd} ($C_n + n \perp C_2 + n \sigma_v$ brak σ_h) D_{nh} ($C_n + n \perp C_2 + n \sigma_v + \sigma_h$) T_d ($4C_3 + 3C_2$, 6 σ)

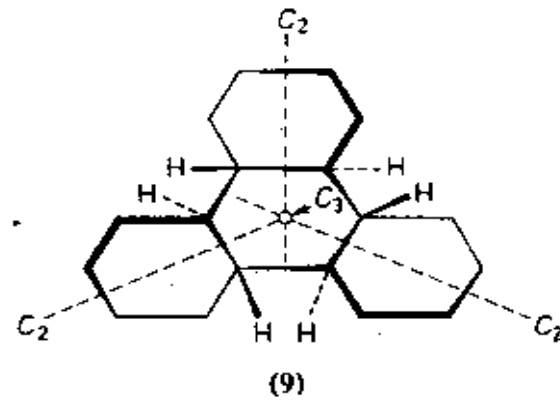
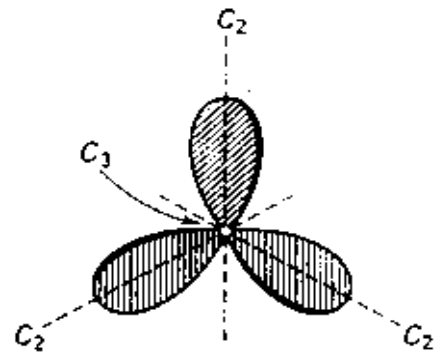




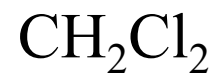
a)



b)



Elementy symetrii



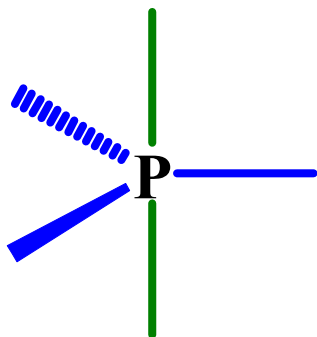
Klasyfikacja grup według symetrii

Notacja grup punktowych Schoenfliesa

1. Grupa punktowa C_1 : cząsteczki z tej grupy nie posiadają elementu symetrii z wyjątkiem trywialnej osi C_1
2. Grupa punktowa C_2 : cząsteczki z tej grupy posiadają jeden element symetrii oś C_2
3. Grupa punktowa C_3 : cząsteczki z tej grupy posiadają jeden element symetrii oś C_3

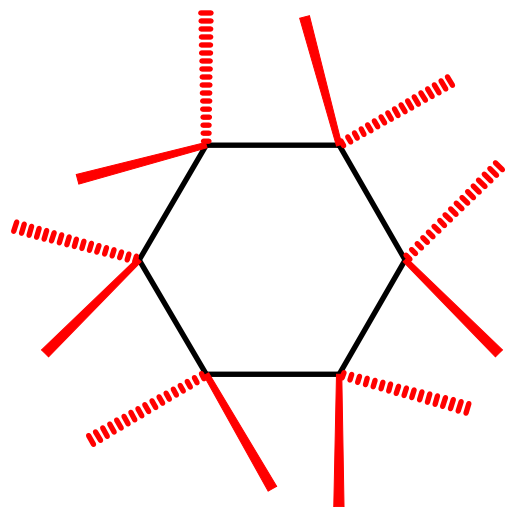
Stereoizomeria związków pięcio-koordynacyjnych

Stereochemia jest znacznie bardziej skomplikowana



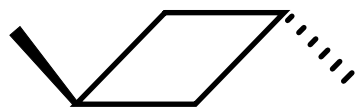
Ćwiczenie: elementy symetrii, grupa punktowa

CYKLOHEKSAN

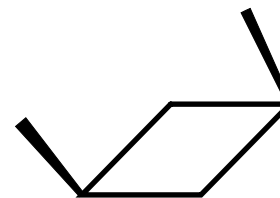


Temat do ćwiczeń: znaleźć **wszystkie** elementy symetrii tego układu jeśli pierścień sześcioczłonowy jest płaski (a wszystkie podstawniki są takie same np. H)

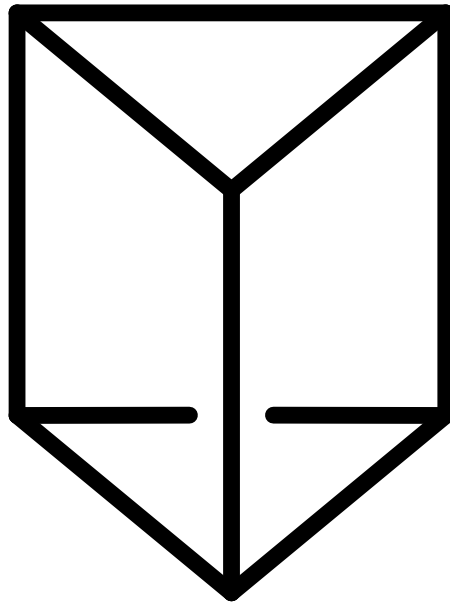
elementy symetrii



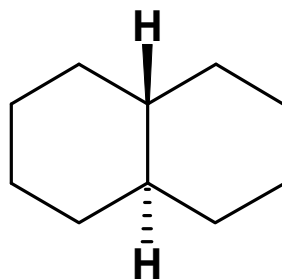
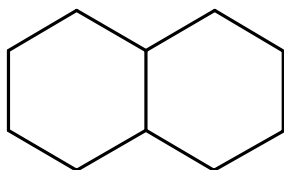
ćwiczenie



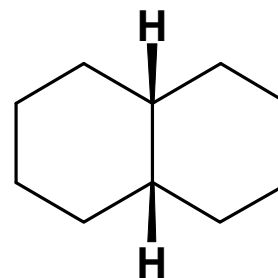
Znaleźć elementy symetrii



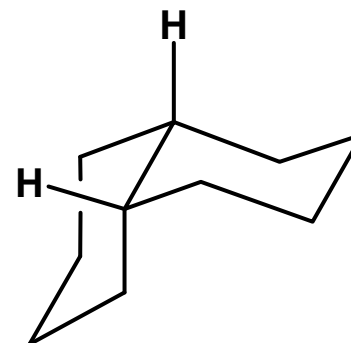
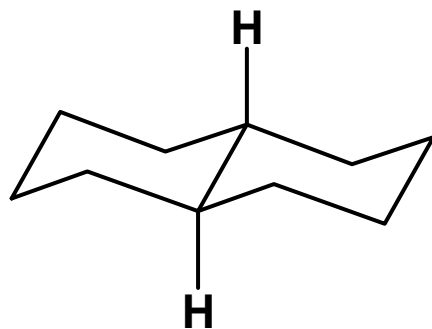
dekalina



trans

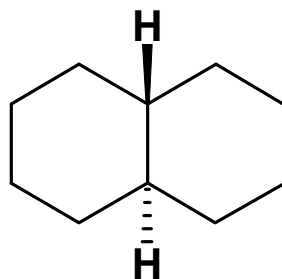
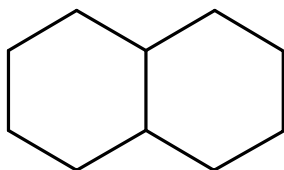


cis

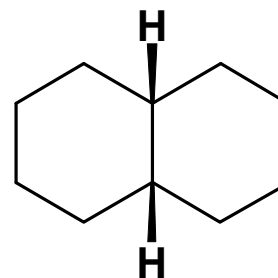


Proszę znaleźć elementy symetrii

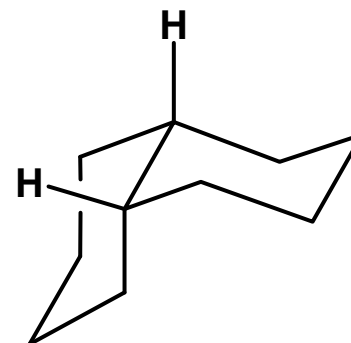
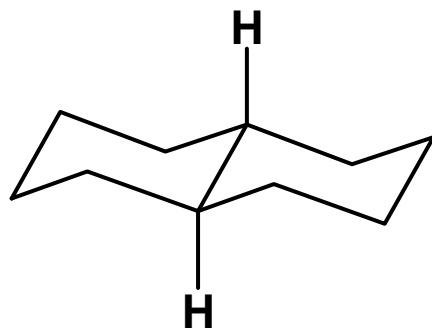
dekalina



trans



cis



Proszę znaleźć elementy symetrii