

10.


seminář LC

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HETEROCYKLIČKÉ

SLOUČENINY

- organické sloučeniny


- kruh  uhlíkové atomy
jiné atomy ("heteros") O, S, N
aj. =

obvykle: 3, 4, 5, 6 a 7 členné kruhy

Vzestup stability :

- s méně deformovanými vazebnými úhly (menší pnutí) 5 a 6 členné kruhy
- s maximem konjugovaných dvojných vazeb (aromatický charakter, delokalizované π -elektrony).

Malá stabilita :

- 
- jednoduché laktony
 - laktamy
 - anhydridy dikarboxylových kyselin
 - hemiacetaly (= cyklické formy mono-sacharidů)
- chybí konjugované vazby !

O -ox-

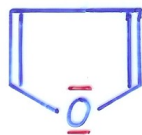
S -thi-

N -az-

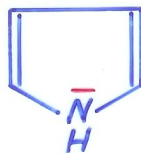
5 členný -ol

6 členný -in

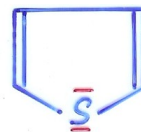
7 členný -epin



furan



pyrrol/e



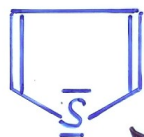
thiofen
thiophene

elektronegativita / electronegativity: C 2,5

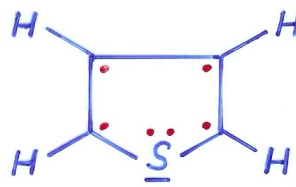
O 3,5

N 3,0

S 2,5

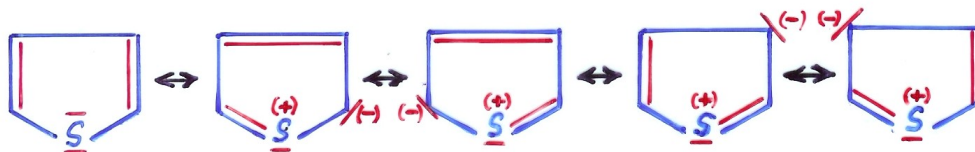


thiofen
thiophene
schematický
vzorec
common formula



sextet
 $\pi-e^-$

elektronový
vzorec
electron formula



mezomerie thiofenu
resonance in thiophene

aromatický charakter
→ "heteroarény"

aromatic character

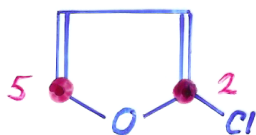
~~adiční reakce~~
~~zásadité vlastnosti~~
~~addition reaction~~
~~basic properties~~

Elektronová hustota

(vyšší v polohách 2 a 5
u 5členných heterocyklů)

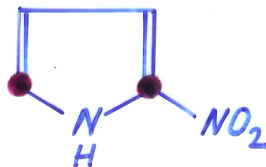
Electron density

(higher in the positions 2 and 5
in 5-membered heterocycles)



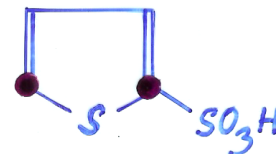
halogenace
halogenation

(2-chlor(o)furan)



nitrace
nitration

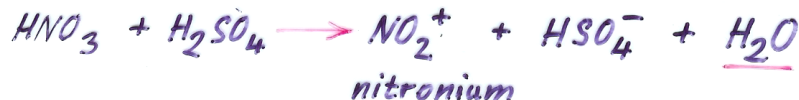
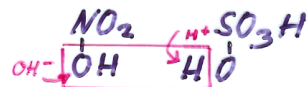
(2-nitro-pyrrol(e))



sulfonace
sulfonation

(2-thiopen-
sulfonová kys.
2-thiophene-
sulfonic acid)

elektrofilní substituce
electrophilic substitution





Elektronová hustota

(vyšší v polohách 3 a 5
u 6 členných heterocyklů)

Electron density

(higher in the positions
3 and 5 in 6-membered
heterocycles)

Hückelovo pravidlo aromaticity :

monocyklické planární uhlovodíky,
které obsahují $(4n + 2) \pi$ elektrony ($n = 0, 1, 2, 3, \dots$)
mají velkou stabilizační (konjugační) energii
a nepodléhají reakcím typickým
pro sloučeniny s dvojnými vazbami
→ aromatický charakter → elektrofilní substituční reakce

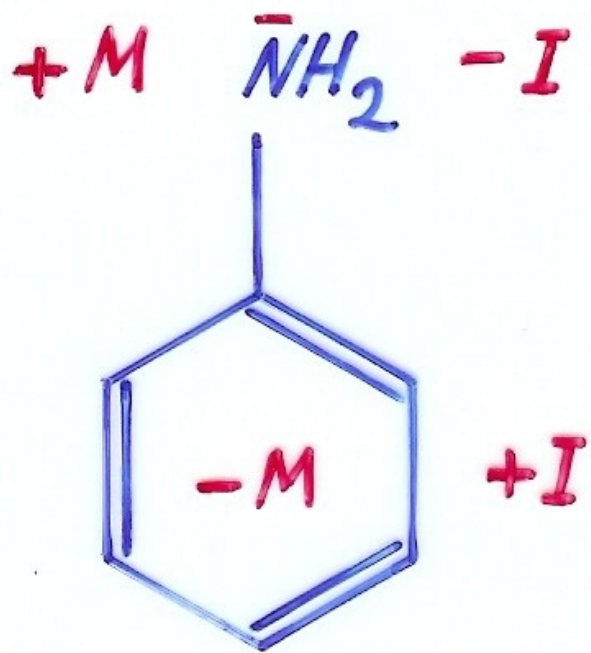
Aromatický charakter :

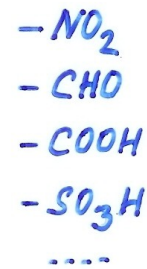
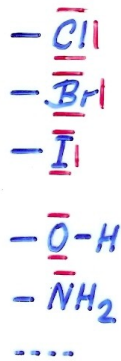
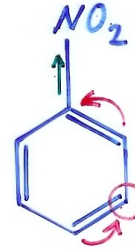
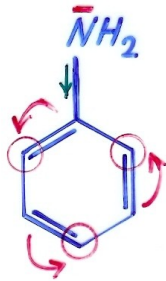
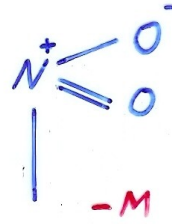
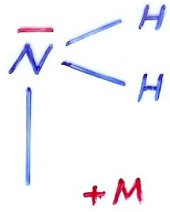
- 1/ nesnadnost adice
- 2/ odolnost vůči oxidačnímu štěpení
- 3/ substituce
- 4/ elektronegativní vliv na substituenty
- 5/ polarizace kruhu vlivem mesomerního efektu substituentů



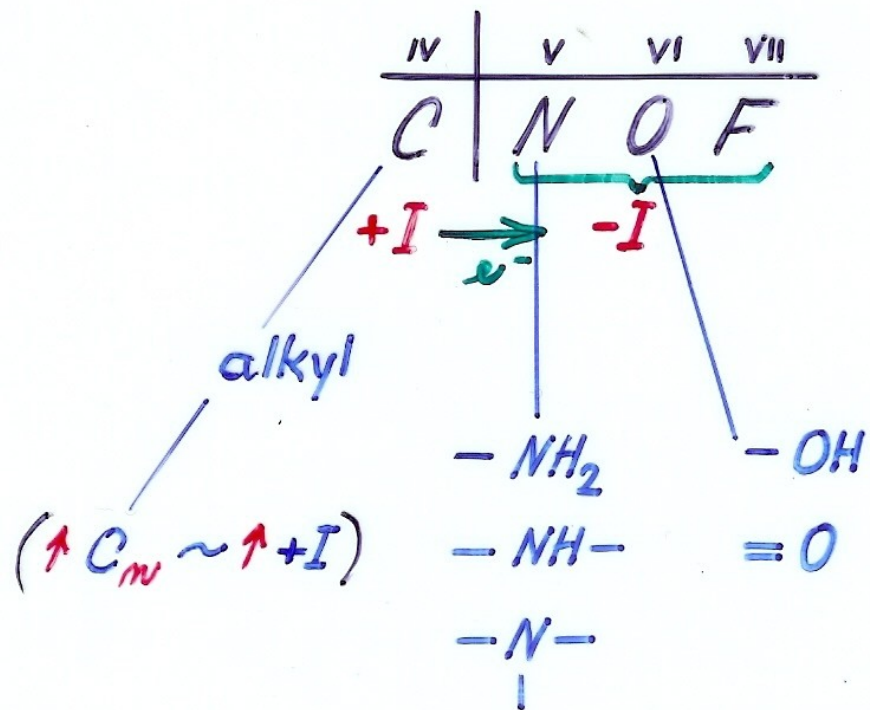
elektrofilní substituce

(nitrace, halogenace
sulfonace ...)

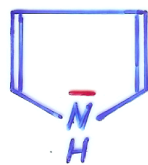




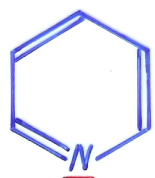
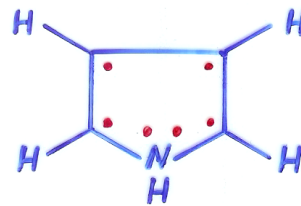
O ?
elektro-
neg.



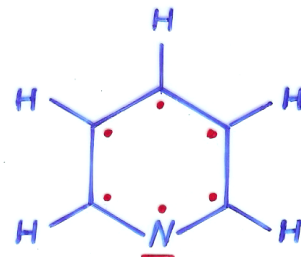
- název: výsledný stav
- "součet" I



pyrrol/e



pyridin/e



V 5-členných heterocyklech heteroatom poskytuje 2 elektrony pro aromatický sextet π elektronů.

V 6- _____ " _____
 1 elektron _____ " _____

In the 5-membered heterocycles, the heteroatom contributes 2 electrons to the aromatic 6π system, whereas in 6- _____ " _____

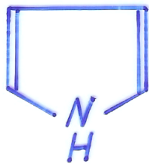
_____ " only 1 electron _____ " _____

pyrrol/e

- kyselý (bezvodé prostředí)
- acidic (waterfree medium)

pyridin/e

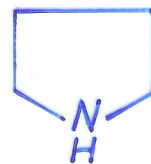
- zásaditý
- basic



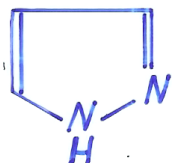
pyrrol/e
(azol/e)



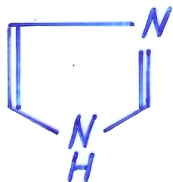
pyrrolin/e



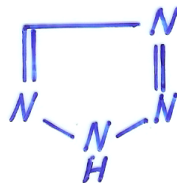
pyrrolidin/e



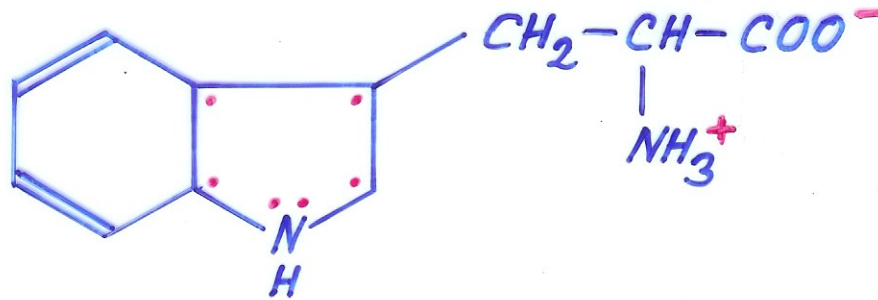
pyrazol/e
(1,2-diazol/e)



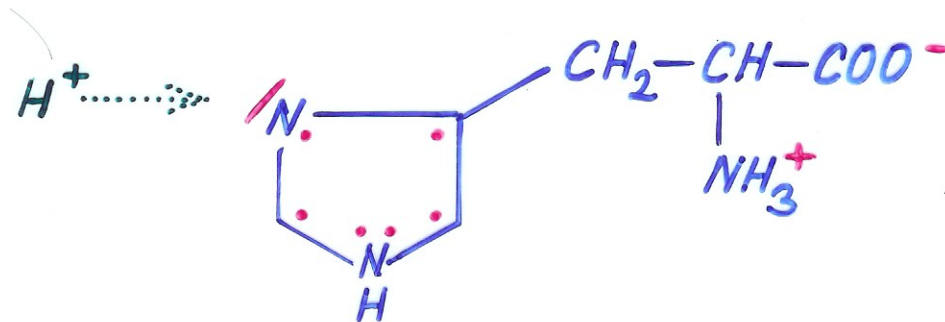
imidazol/e
(1,3-diazol/e)



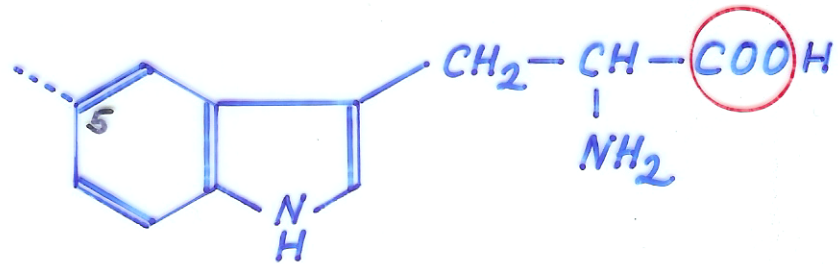
1,2,3,4-
tetrazol/e



Trp

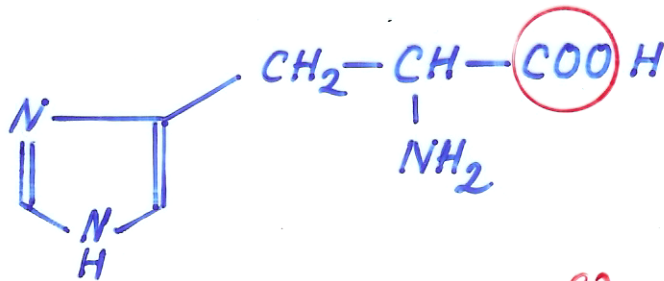


His

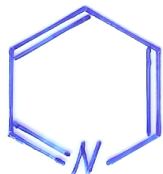


Trp $\xrightarrow{-\text{CO}_2}$ tryptamin/e

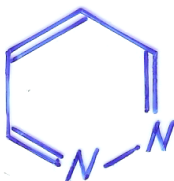
serotonin = 5-hydroxy-tryptamin/e



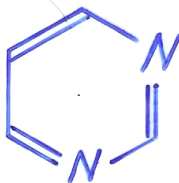
His $\xrightarrow{-\text{CO}_2}$ histamin/e



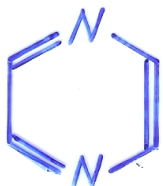
pyridin/e
(azin/e)



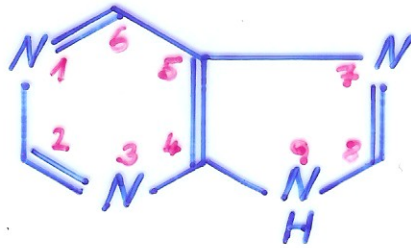
pyridazin/e
(1,2-diazin/e)



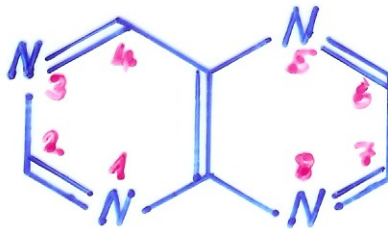
pyrimidin/e
(1,3-diazin/e)



pyrazin/e
(1,4-diazin/e)



purin/e

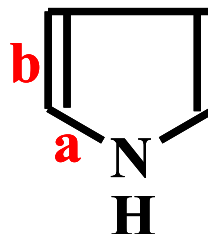
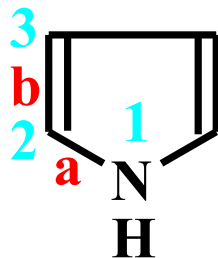
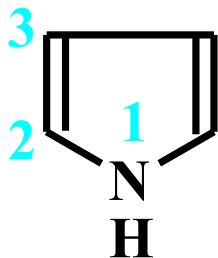


pteridin/e

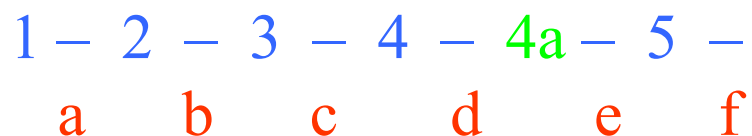
Označování vazeb pro připojení dalšího kruhu (1) :

1 – 2 – 3 – 4 – 5 – 6 – 7 – 8
a b c d e f g

Další kruh se napojuje na cyklus, který měl své *původní* číslování (a tedy i *původní* označení vazeb písmeny). Uvažované místo kondenzace (zde „b“) má nejnižší možná čísla atomů.



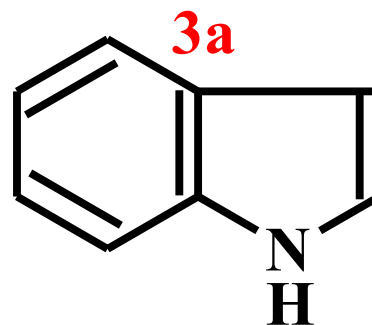
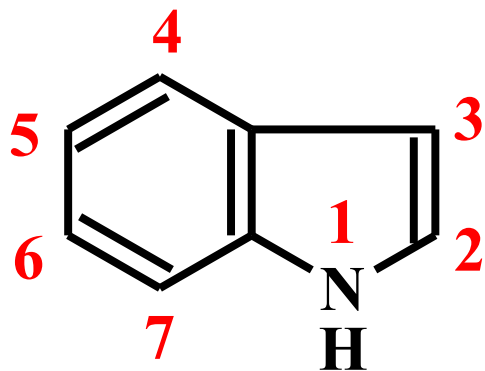
Označování vazeb pro připojení dalšího kruhu (2) :



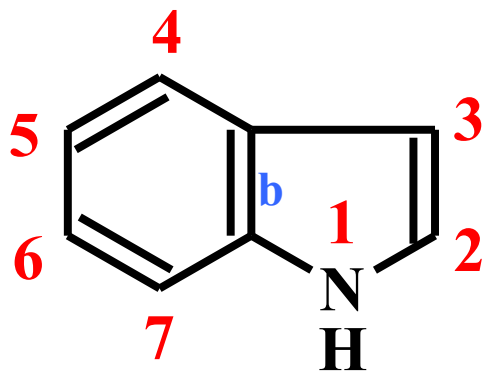
Pokud se vyskytne samostatným číslem neoznačený atom (zde 4a), označují se i jeho vazby písmeny plynule dál.

Samostatnými čísly se neoznačují atomy, které jsou všemi vazbami zapojeny do skeletu - jsou to místa, kde nemůže dojít k substituci (neexistujících H atomů).

Označování vazeb pro připojení dalšího kruhu (3) :

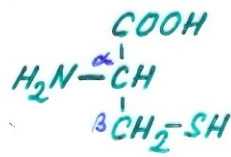
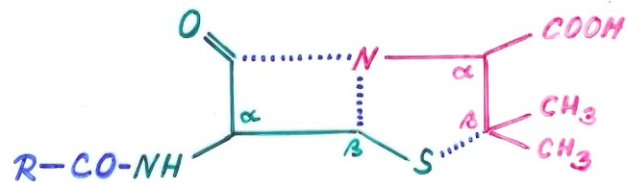
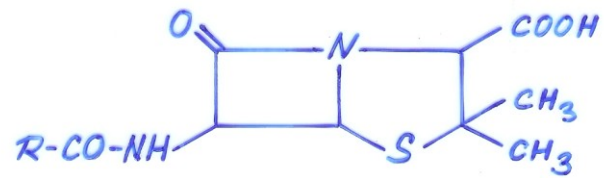


Kondenzovaná sloučenina (zde indol)
má odlišné od číslování (od původního pyrrolu) !!

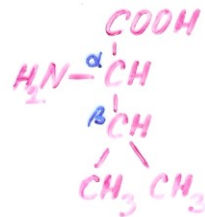


**benzo[b]pyrrol
(indol)**

penicilín
penicillin



Cys



Val



Diazepam
Valium

