

## 10. Előadás

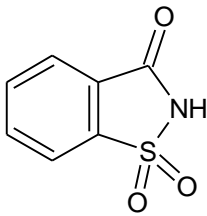
Szerves vegyületek kénatommal.  
Heterociklusos (porfinvázás) vegyületek.

# SZERVES VEGYÜLETEK KÉNATOMMAL

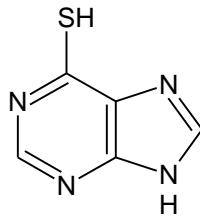
Példák:



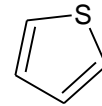
diallil-diszulfid (fokhagyma olaj)



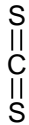
szacharin



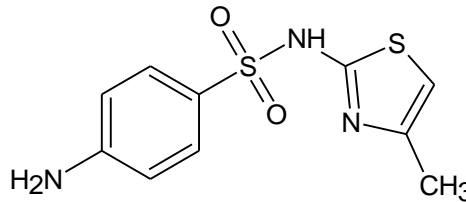
merkaptó-purin



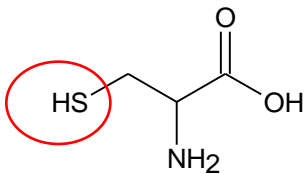
tiofén



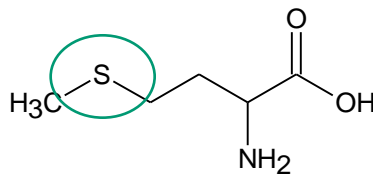
szén-diszulfid



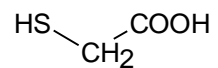
szulfonamid  
(Ultraseptyl)



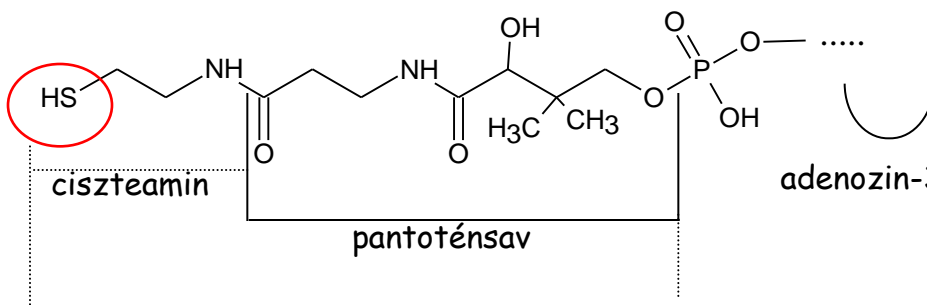
cisztein (Cys)



metionin (Met)



tio-glikolsav  
(merkaptocetsav,  
szulfhidril-ecetsav)



pantotein

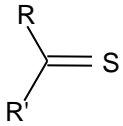
adenozin-3',5'-difoszfát

KOENZIM A

# Áttekintés

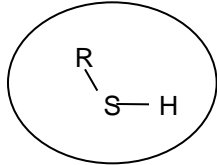
A kénatomhoz kapcsolódó ligandumok száma

[1]



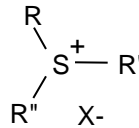
tioegyület  
(pl. tioketon)

[2]



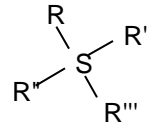
tiol

[3]

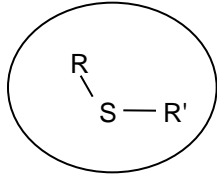


szulfóniumsó

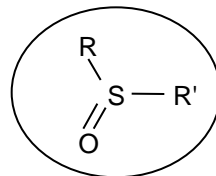
[4]



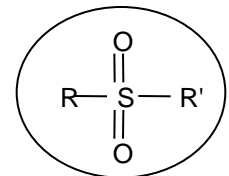
szulfurán



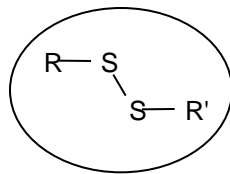
szulfid



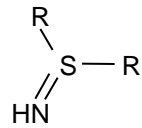
szulfoxid



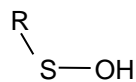
szulfon



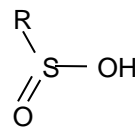
diszulfid



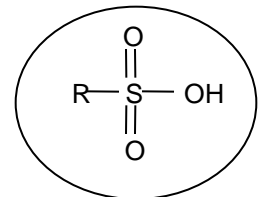
szulfilimin



szulfénsav

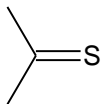


szulfinsav



szulfonsav

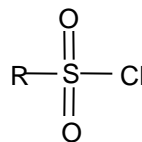
Csoportok:



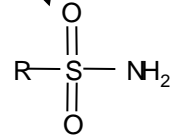
tio karbonil

-SH

merkaptó-  
(szulfhidril)

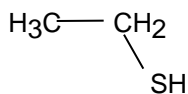


szulfonil-klorid

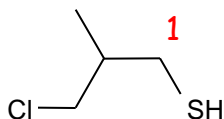


szulfon(sav)amid

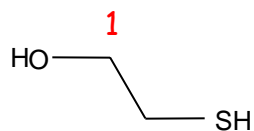
## Nomenklatúra, példákkal



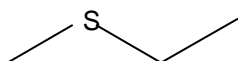
etán-tiol  
(etil-hidrogénszulfid,  
etil-merkaptán)



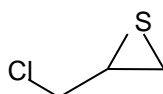
3-klór-2-metil-1-  
propántiol



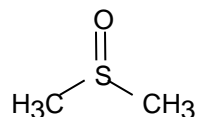
2-merkaptó-etanol



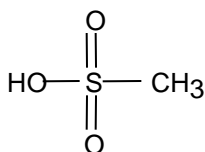
etil-metil-szulfid



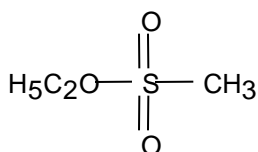
1-klór-2,3-epitio-  
propán



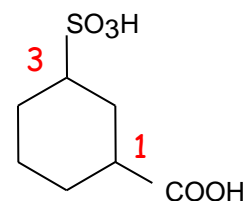
dimetil-szulfoxid



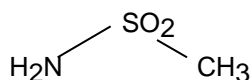
metánszulfonsav



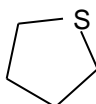
metánszulfonsav-  
etilészter



3-szulfo-1-  
ciklohexánkarbonsav



metánszulfonamid

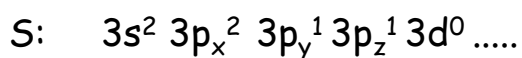


tetrametilén-szulfid

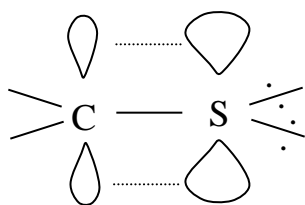
## Szerkezet

Elektronok	I. sor	C	N	O	F	$S_{EN(2,5)} < O_{EN(3,5)}$
	II. sor	Si	P	S	Cl	

- Jellegzetességek
- A. analógia oxigénnel
  - B. nagyobb sugarú vegyértékhéj  
kisebb EN  
kisebb bázicitás  
polározhatóság
  - C. különleges sztereokémia

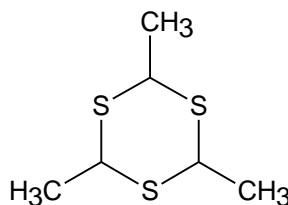
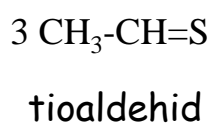


### 1 ligandumos kénvegyületek (tiovegyületek)

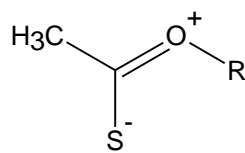
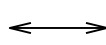
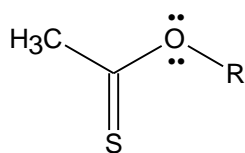


$\sigma$  kötés:  $C(2sp^2) - S(3sp^2)$   
 $\pi$  kötés:  $C(2p) - S(3p)$   
 nem stabil

Példa:



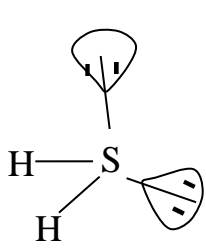
de:



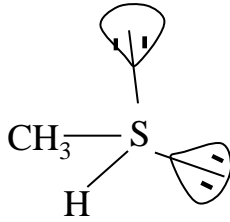
stabil

**tioészter: konjugált rendszer**

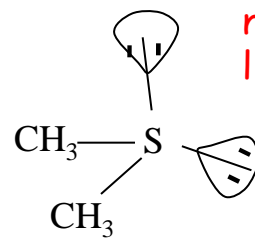
## 2 ligandumos kénvegyületek (tiol, tioéter)



HSH  $\sphericalangle$  92,5°  
HOH 104,5°



CSH  $\sphericalangle$  96,5°  
COH 105°



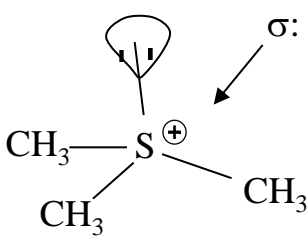
nem  
lineáris

CSC  $\sphericalangle$  98,5°  
COC 112°

$\sigma$ : H(s) - S(p);  
H - S: 335 kJ/mol  
H - O: 452 kJ/mol

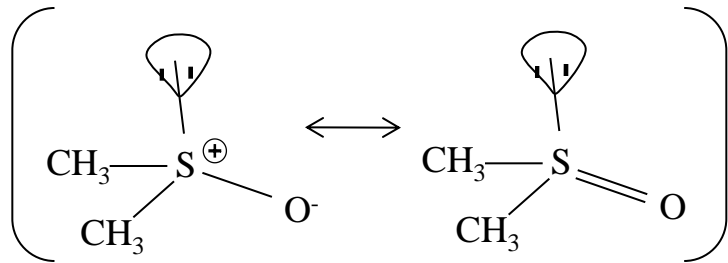
C(2sp<sup>3</sup>) - S(3p)  
C - S: 267 kJ/mol  
C - O: 347 kJ/mol

## 3 ligandumos kénvegyületek (szulfoxid, szulfóniumsó)



$\sigma$ : (3sp<sup>3</sup>) - (2sp<sup>3</sup>)

C - S: 1,83 Å  
CSC kötésszög: 103°  
piramisos, királis

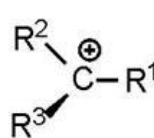


C - S: 1,81 Å  
CSC kötésszög: 96,4°  
piramisos, királis

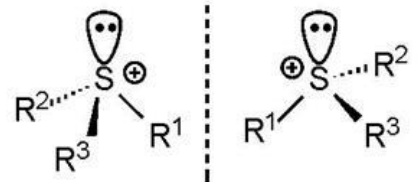
C - O: 1,47 Å  
CSO: 106,7°

$\sigma$ : C(2sp<sup>3</sup>) - S(3sp<sup>3</sup>)  
S(3sp<sup>3</sup>) - O(2sp<sup>2</sup>)  
 $\pi$ : S(3d) - O(2p)

### **Összevetés**

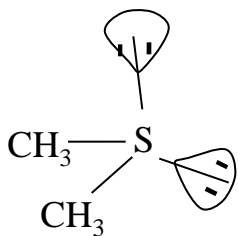


planáris, akirális

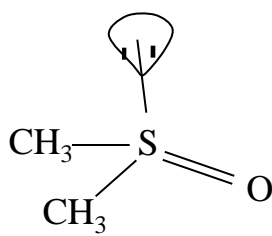


piramisos, királis

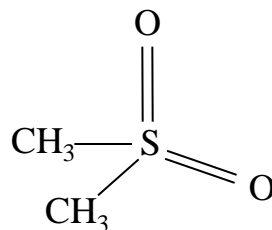
## Összegzés



szulfid



szulfoxid



szulfon

### Kötéshosszak:

C - S 1,82Å

C - S 1,81Å  
S = O 1,47Å

C - S 1,78Å  
S = O 1,44Å

### Kötésszögek:

CSC 98,5°

CSC 96,4°  
CSO 106,7°

CSC 103°  
CSO 108,7°  
OSO 118°

DE:

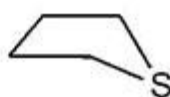
C-S-C 60°



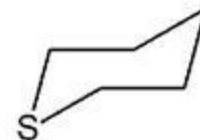
60°



78°



108°



100°

# Fizikai tulajdonságok

## A. Tiolok

1/10 millió

Forráspont (°C)	X=S	X=O
$H_2X^*$	- 62	100
$CH_3XH^*$	6	65
$CH_3CH_2XH^*$	35	78
$CH_3XCH_3$	37	- 24

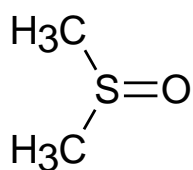
nincs H-híd kötés\*

illékonyág:  $CH_3CH_2CH_2SH$  hagyma  
 $CH_3(CH_2)_3SH$  görény

## B. Szulfoxidok, szulfonok



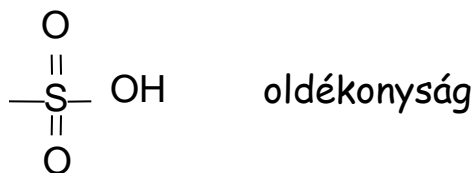
H-híd: akceptor



op: 18°C

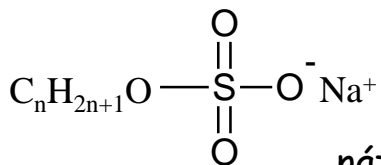
dipoláros, aprotikus oldószer

## C. Szulfonsavak (O-H sav)



oldékonyág

detergensek:



nátrium-alkilszulfát

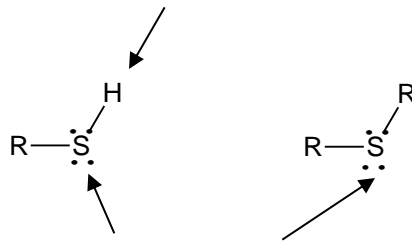


# Kémiai reakciók

## 1. Sav-bázis sajátság

Tiol, szulfid

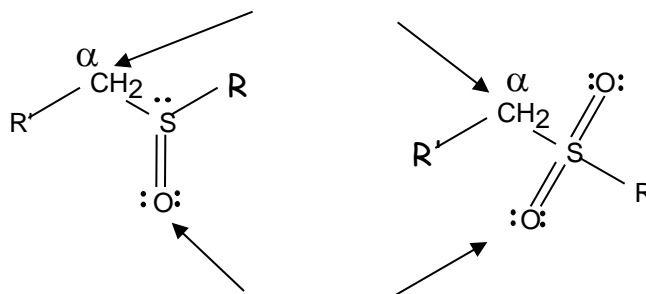
savas jelleg,  $pK_a=11$  (vö. OH  $pK_a=17$ )



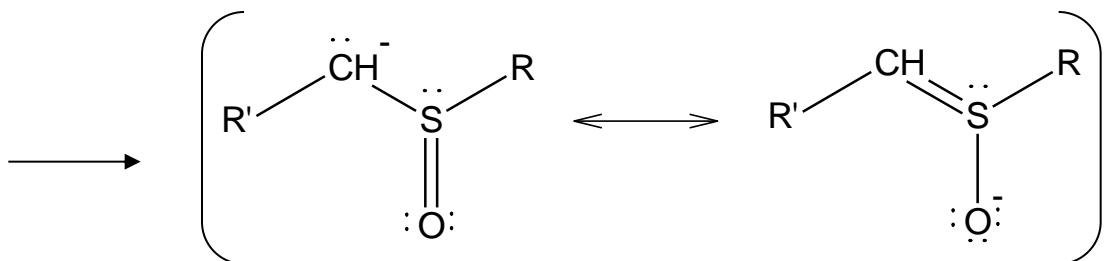
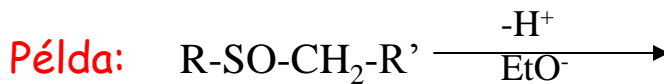
bázikus jelleg (gyengébb, mint  $:O:$ )

Szulfoxid, szulfon

savas jelleg



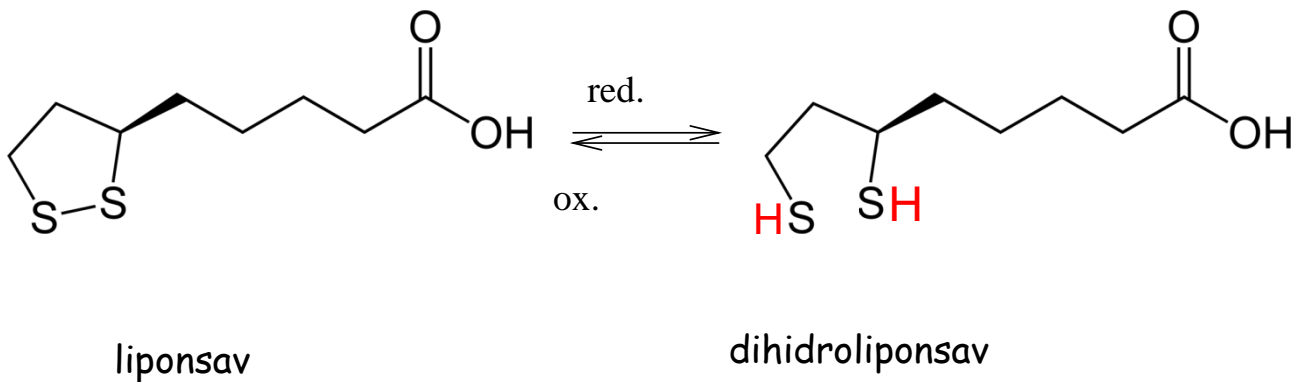
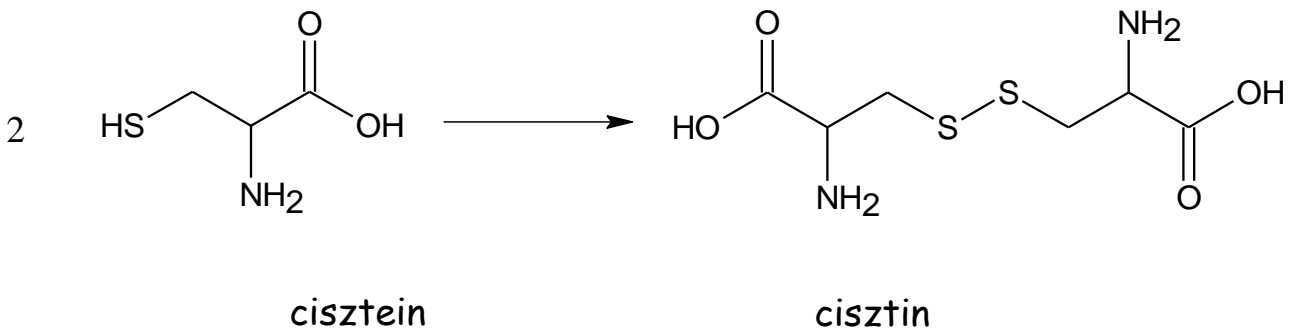
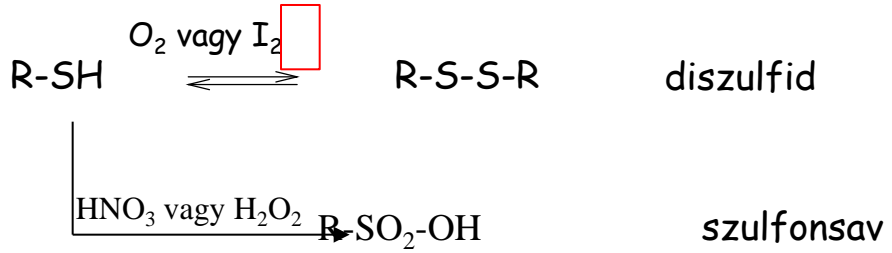
bázikus jelleg



konjugáció: delokalizált, nincs tautomerizáció!

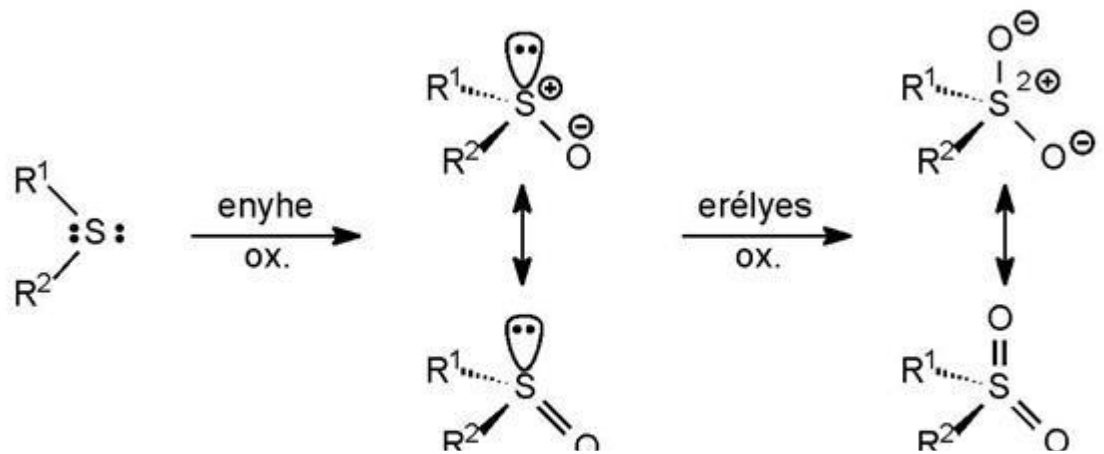
## 2. Oxidáció, redukció

### Tiol



királis karbonsav,  
kofaktor,  
piruvát-dehidrogenáz komplex része,  
antioxidáns

# Szulfid

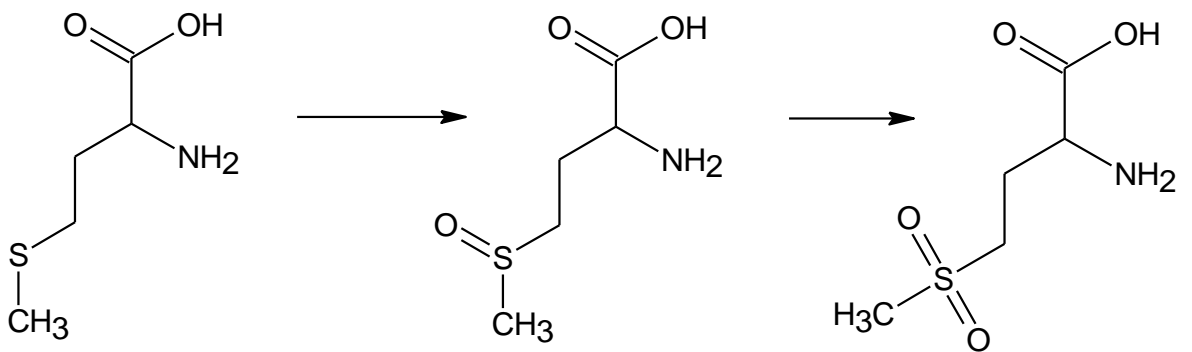


szulfid

szulfoxid

szulfon

Példa:



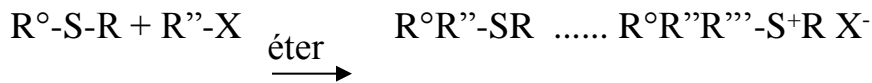
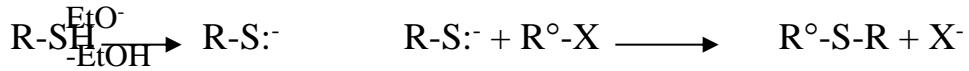
metionin

metionin  
szulfoxid

metionin  
szulfon

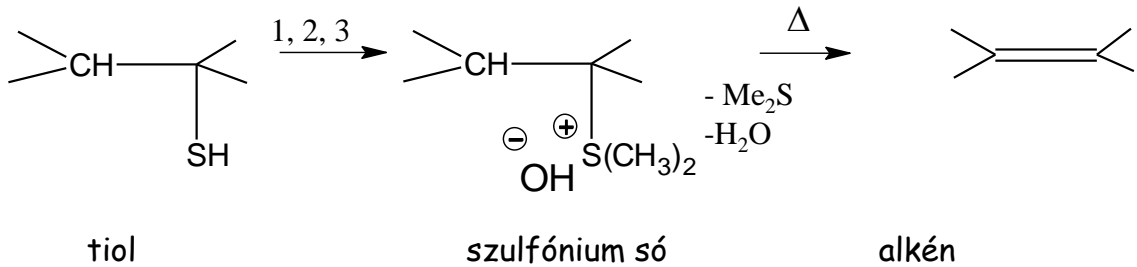
### 3. Nukleofil szubsztitúció

#### 3.1. Alkilezés (tiol, tioéter)



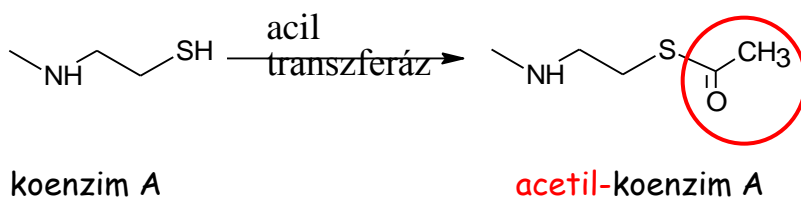
szulfóniumsó

#### Hofmann-analóg elimináció



1: EtO<sup>-</sup>, MeI; 2: MeI, éter; 3: Ag<sub>2</sub>O, H<sub>2</sub>O

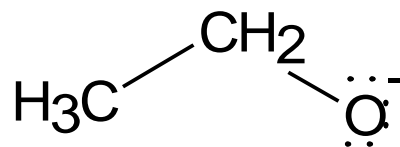
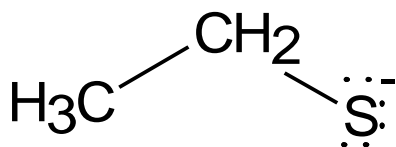
#### 3.2. Acilezés



# -SH vs -OH reaktivitása - összevetés

(tiol, merkaptán = „mercurium captans“)

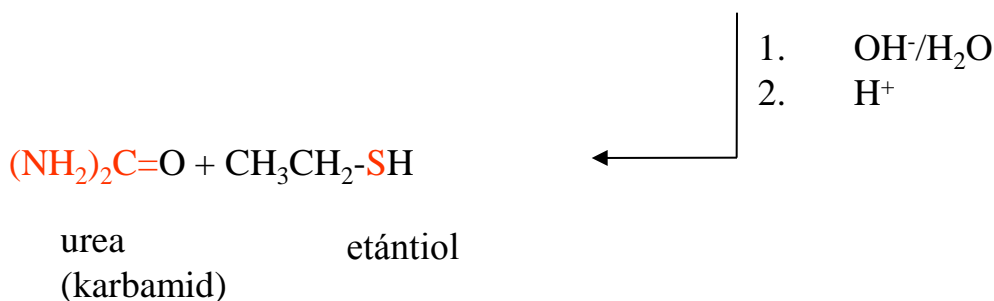
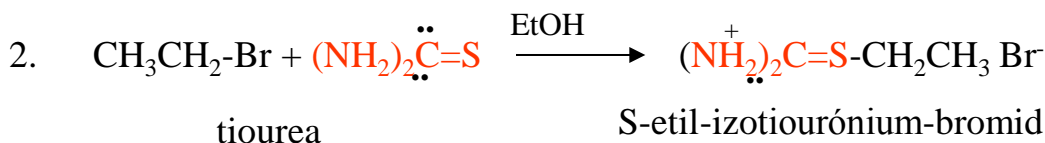
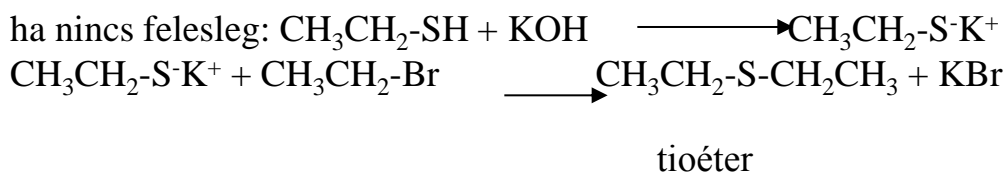
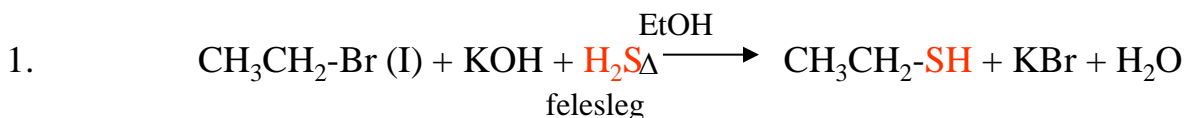
## 1. Nukleofil sajátság



2. Savi jelleg  $-\text{SH} > -\text{OH}$

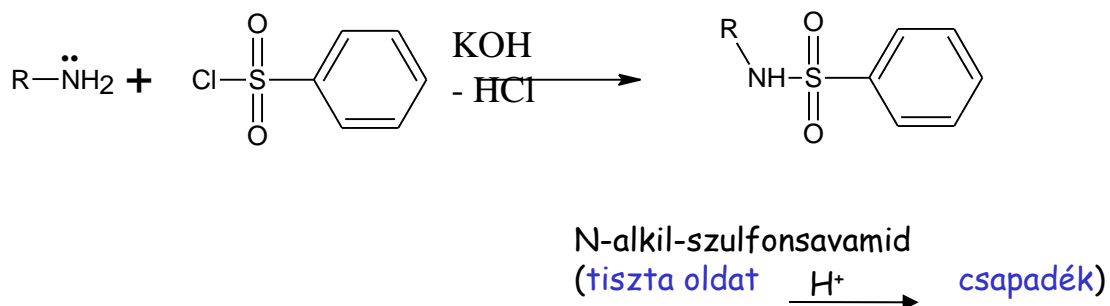
3. Oxidáció  $\text{R-SH} + \text{H}_2\text{O}_2 \longrightarrow \text{R-S-S-R} + 2 \text{H}_2\text{O}$

## Tiolok előállítása

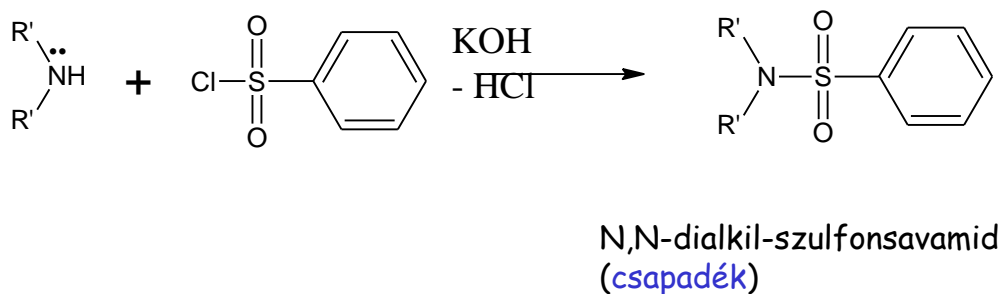


# Kimutatás: Aminok reakciója szulfonil-kloriddal (Hinsberg-reakció)

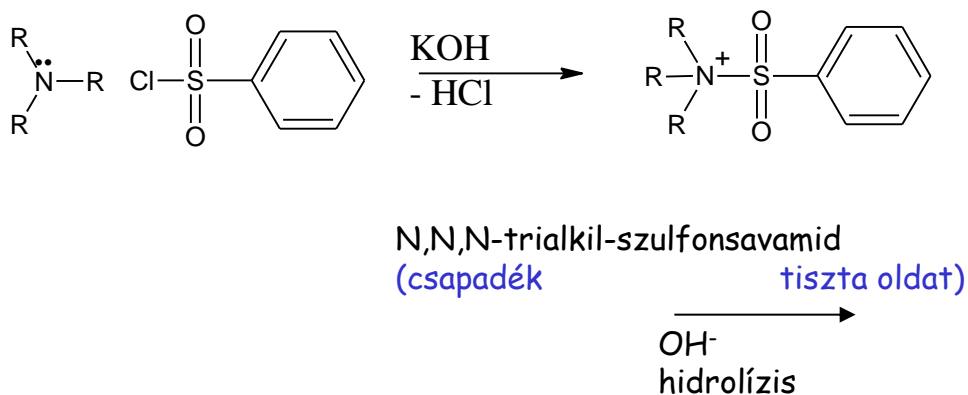
## 1. Primer amin



## 2. Szekunder-amin



## 3. Tercier-amin



# Antibiotikumok: szulfonamidok

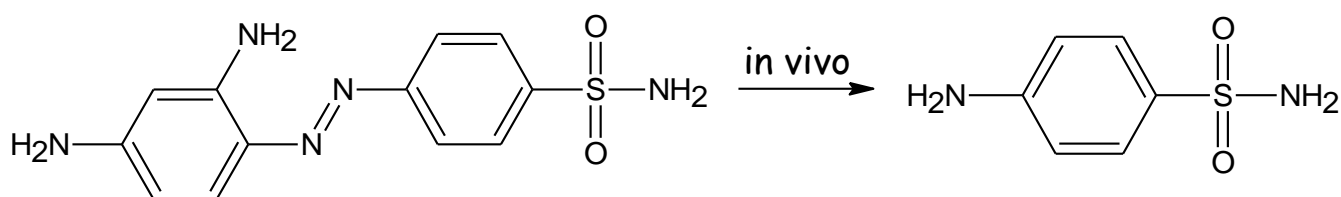


(1895 - 1964)

Gerhard Domagk (1932),  
patológus, bakteriológus

Münsteri Egyetem, I.G. Farben

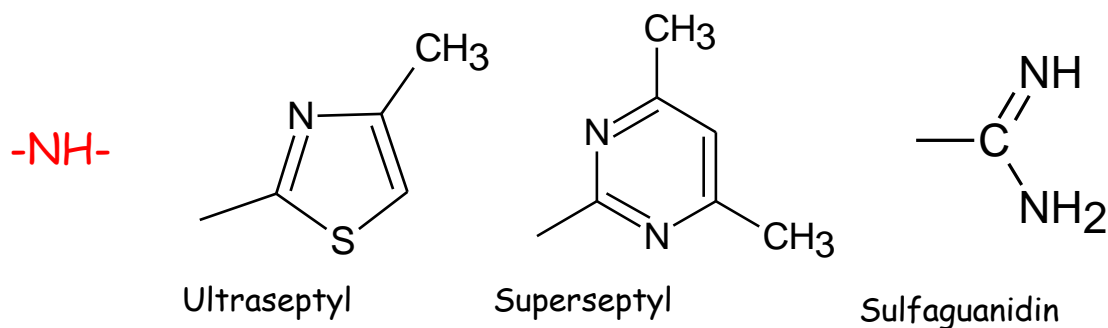
Nd. 1939→1947, az első kereskedelmi  
forgalomba is kerülő antibiotikumok,  
a szulfonamidok felfedezéséért



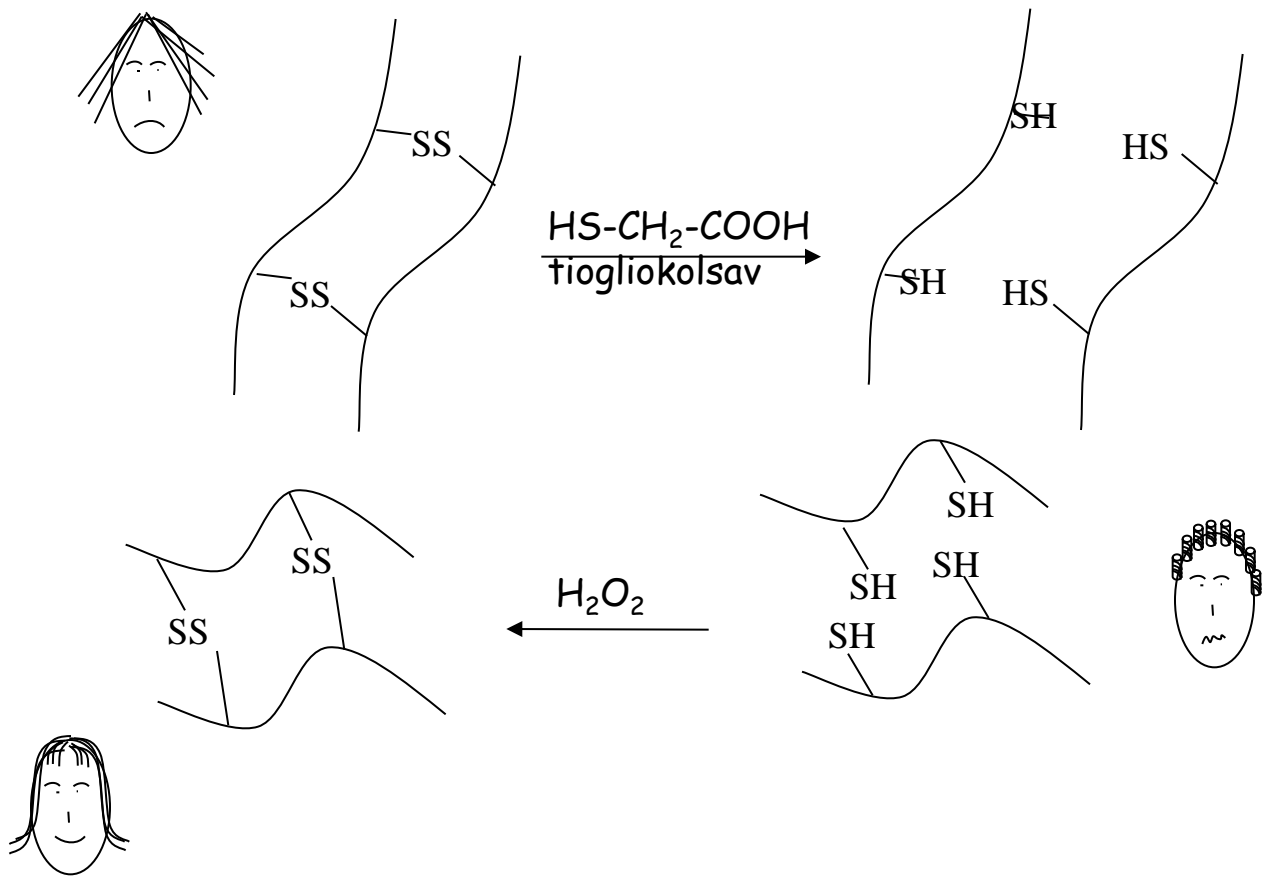
Prontosil (narancsvörös)

in vitro : „üvegben”  
in vivo: „életben”

para-amino-benzol-  
szulfonamid  
(PABS, fehér)  
(folsavsintézishez)

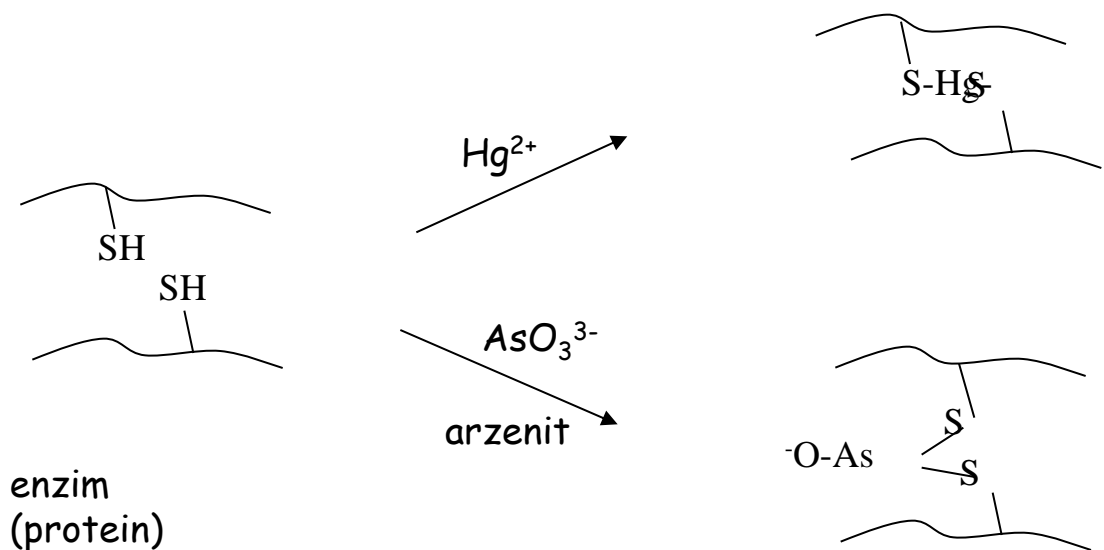


## A fodrásznál



## Mérgezés

(tiol, **merkaptán\*** jelentése = „mercurium captans”, capturing mercury )



\*1832, **William Christopher Zeise** , dán szerves kémikus, fémorganikus vegyületek



# Heterociklusos vegyületek

# HETEROCIKLUSOS VEGYÜLETEK

Felosztás:

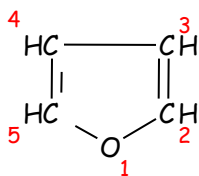
1. telített - telítetlen
2. heteroatomok száma
3. gyűrűk száma
4. heteroatomok milyensége (N, O, S, P, As, Si)

O oxa-

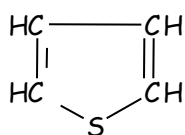
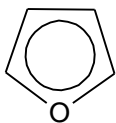
S tia-

N aza-

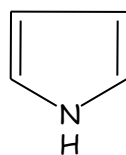
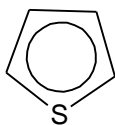
## I. Monociklusos, egy heteroatomos vegyületek



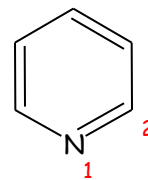
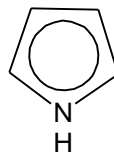
furán\*  
oxol



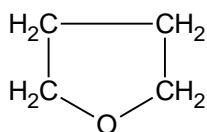
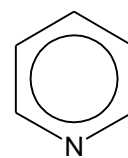
tiofén\*  
tiol



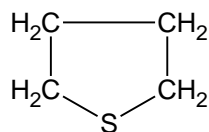
pirrol\*  
azol



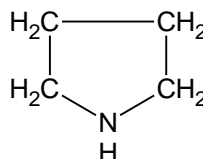
piridin\*  
azin



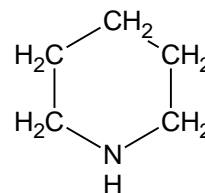
tetrahydrofurán\*  
oxolán



tetrahidrotiofén\*  
tiolán

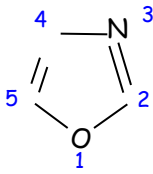


pirrolidin\*  
azolidin

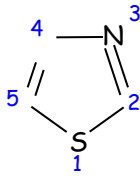


piperidin\*  
perhidroazin

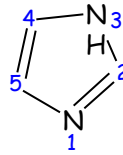
## II. Monociklusos, két heteroatomos vegyületek



oxazol

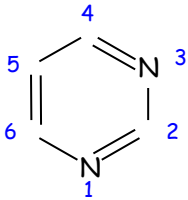


tiazol

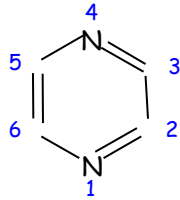


imidazol  
(hisztidinben)

Azolak:  
5-tagú gyűrű  
N + legalább 1  
más heteroatom



pirimidin (1,3-diazin)  
(DNS, RNS-ben)



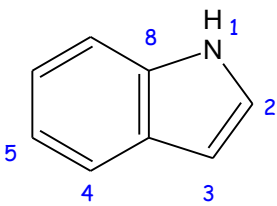
pirazin (1,4-diazin)

Azinok:  
6-tagú gyűrű  
N + legalább 1 más  
heteroatom (N)

piridazin (1,2-diazin)

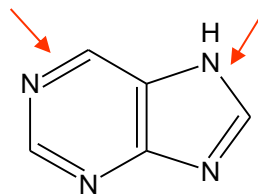
triazinok (3N), tetrazinok (4N)

## III. Biciklusos, kondenzált heteroatomos vegyületek



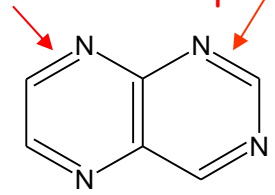
indol  
(triptofánban)

pirimidin



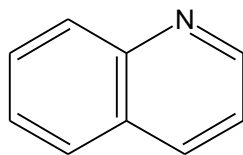
purin  
(DNS, RNS-ben)

imidazol pirazin

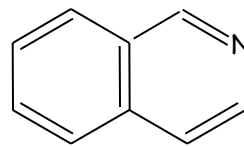


pteridin  
(folsavban)

pirimidin



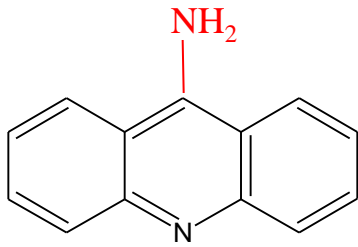
kinolin  
(benzopiridin)



izokinolin

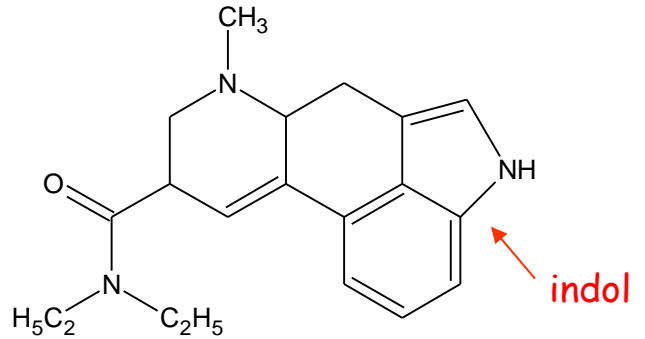
Festék alapanyag, tartósítószer, fertőtlenítő, oldószer, izokinolinvázas alkaloidok

#### IV. Tri-, ...-ciklusos, heteroatomos vegyületek



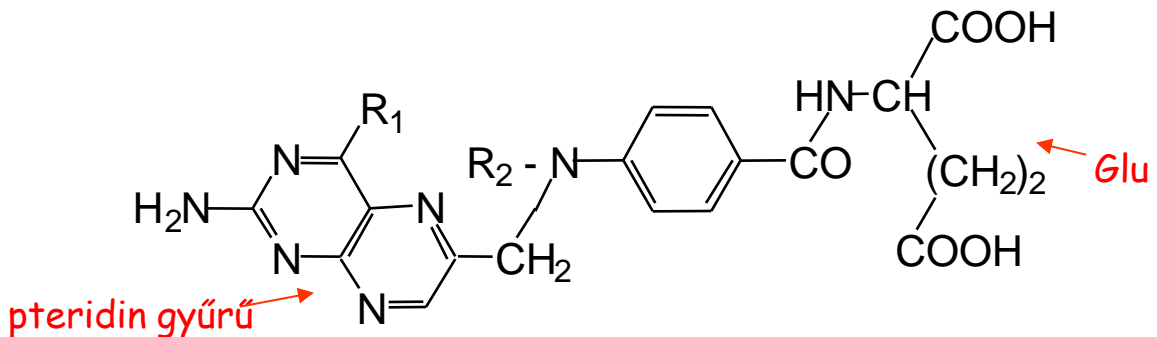
Akridin (váz)

**9-aminoakridin:**  
erős fertőtlenítő szer  
fluoreszcens tulajdonságú



lizergsav-dietilamid (LSD)  
op. 80-85°C  
(anyarozs alkaloid)

#### Folsav analógok



R<sub>1</sub> = OH, R<sub>2</sub> = H

R<sub>1</sub> = NH<sub>2</sub>, R<sub>2</sub> = H

R<sub>1</sub> = NH<sub>2</sub>, R<sub>2</sub> = CH<sub>3</sub>

folsav; B9-vitamin, M-vitamin.

aminopterin

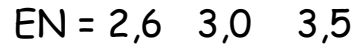
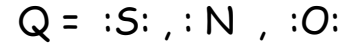
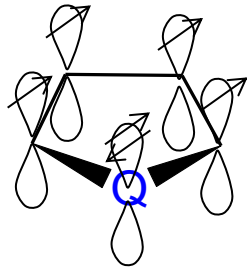
amethopterin, methotrexat

Folsav: terhesség korai szakaszában embrió gerinc, velőcsövet,  
fehérvérsejtek, vörösvértetek, vérlemezkék képzésében,  
az aminosavak és nukleinsavak anyagcseréjében

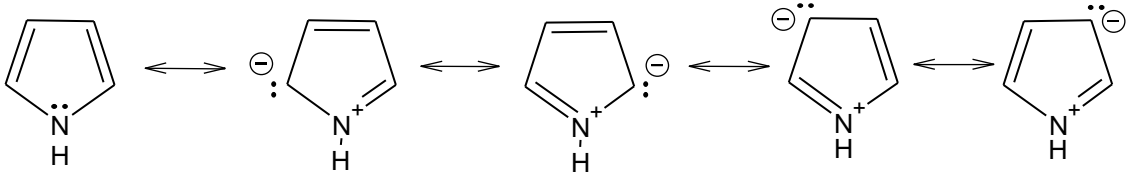
Metotrexát: tumorellenes szer,  
reumatoid artritisz

# Elektronszerkezet

Aromás jelleg (pirrol, furán, tiofén) (Hückel szabály:  $4n+2$  elektron)

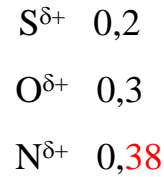
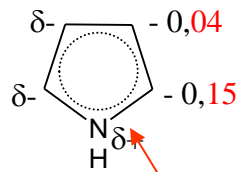
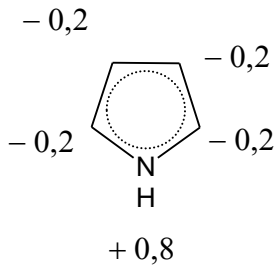


- I effektus (hetero atom EN-nak megfelelő mértékben vonzza az elektronokat) Tiofén hasonlít legjobban a benzolra, de az elektrofil szubsztitúciós reakció gyorsabbak.



K-effektus

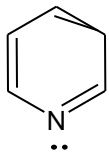
határszerkezetek!



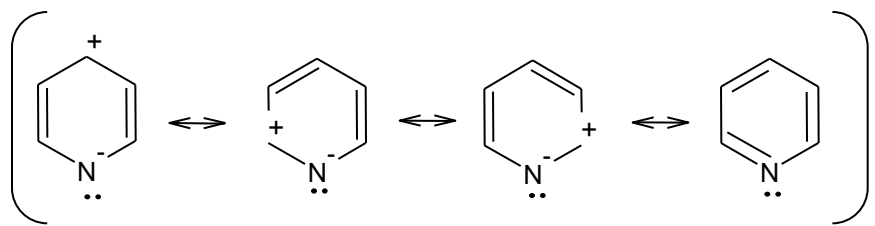
elektroneloszlás

csak határszerkezetekből

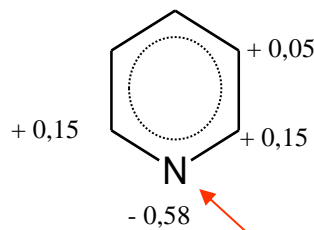
nem bázis, nem proton kedvelő



piridin



+ 0,18



bázis, proton kedvelő

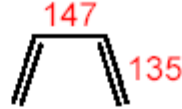
# Téralkat

kötéshosszak (pm)

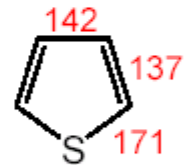
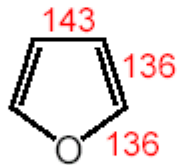
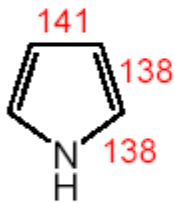
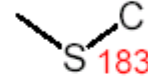
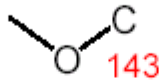
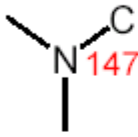
pm:  $10^{-12}$  m  
Å:  $10^{-10}$  m



izolált egyes kötés  
izolált kettős kötés

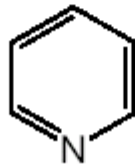


Konjugált kettős kötés  
esetén az egyes és  
kettős kötés hossza



aromás  
rendszer

Kötéshossz : S-C > N-C > O-C



C≡C (C<sub>6</sub>H<sub>6</sub>) 139

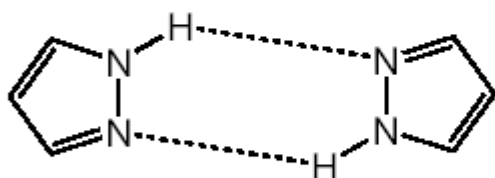
C-N 147

C=N 130

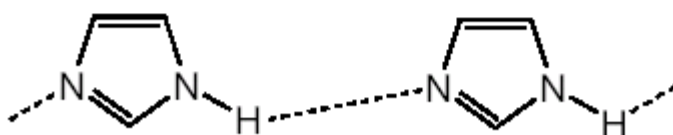
## Fizikai tulajdonságok

Ha a molekulában van H-donor (pl. N-H) és H-akceptor (pl. N), akkor tud H-kötést kialakítani

	fp. (°C)	H-kötés
benzol	80	-
tiofén	84	-
piridin	115	-
pirrol	131	+
pirazol	187	+ (dimer)
imidazol	256 (op. 90 °C)	+ (polimer)



pirazol



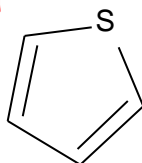
imidazol

# Kémiai reakciók

## 1A. Sav-bázis sajátság (egy heteroatom)

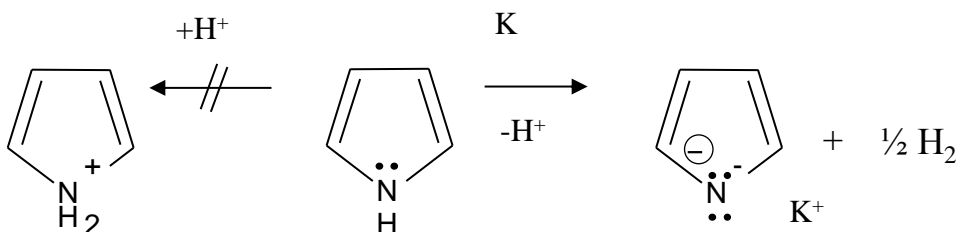
(sav: protont tud leadni; bázis: protont tud felvenni)

tiofén



nem bázis, nem sav (C-H nem proton donor, a kén atom EN nem elég nagy, hogy vonzza a H-t)

pirrol:

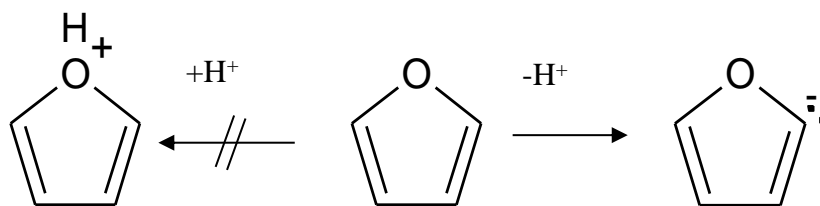


(pK = 15)

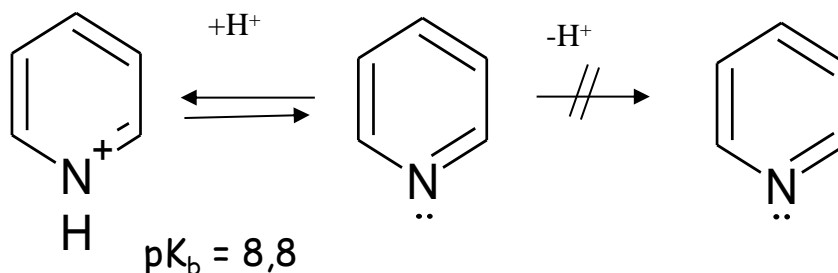
megszűnik az aromás jelleg

aromás marad (tehát gyenge N-H sav)

furán:



piridin:

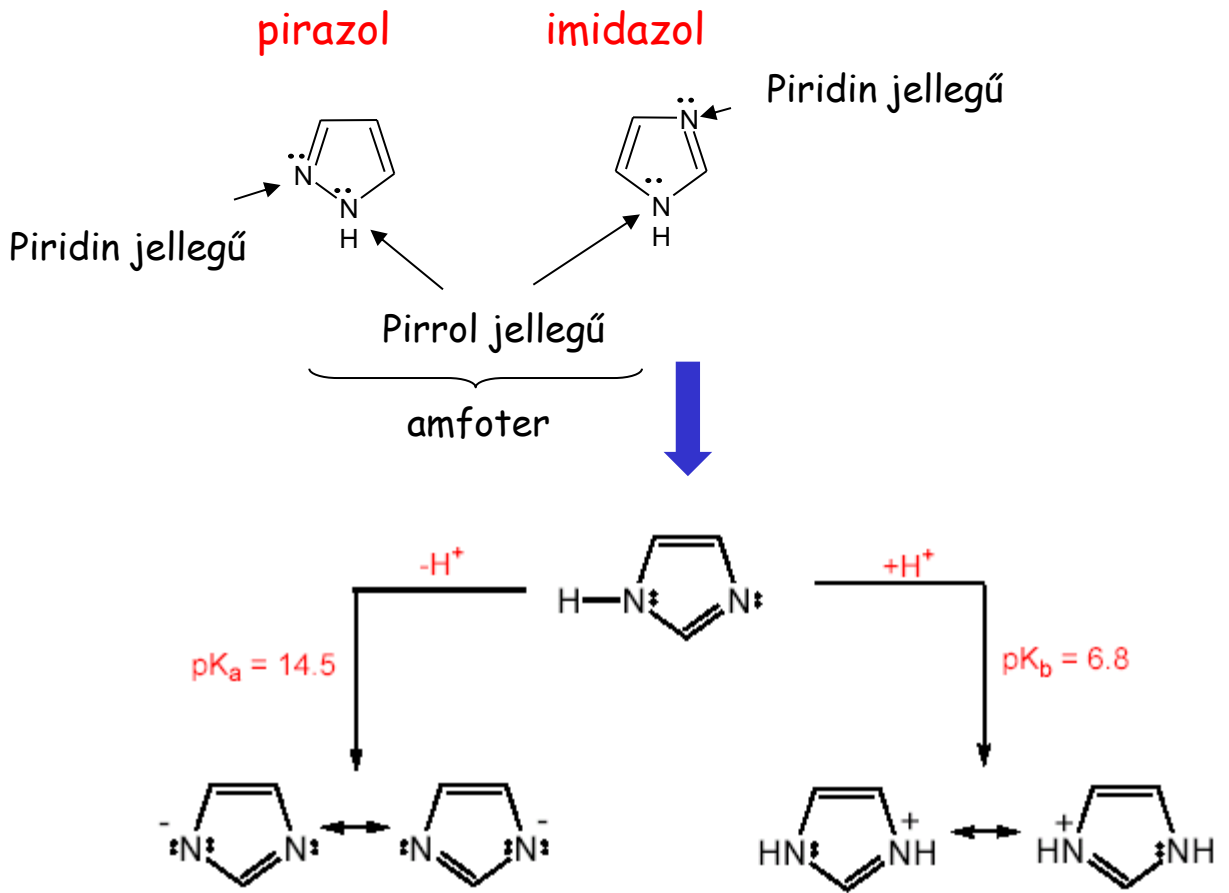


pK<sub>b</sub> = 8,8

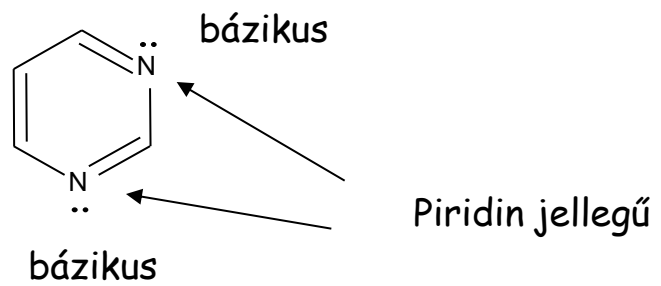
gyenge bázis



# 1B. Sav-bázis sajátság (két heteroatom)



## pirimidin



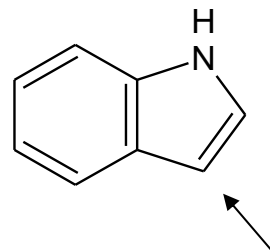
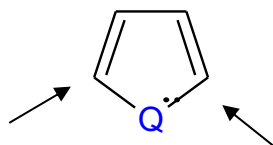
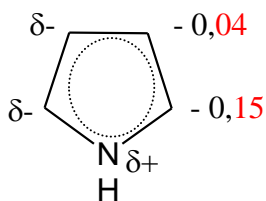
## 2. Elektrofil szubsztitúciók

Feltétel: elektronban „gazdag” gyűrűk

### A. pirrol, furán, tiofén, indol

pozitív töltés vagy parciális pozitív töltésű rész  
támad elektronban gazdag helyre

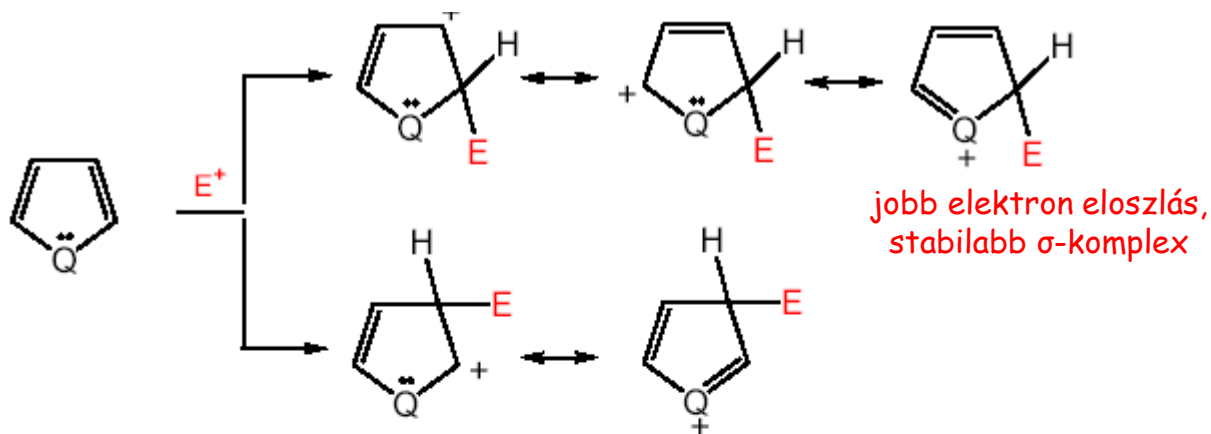
Irányítás



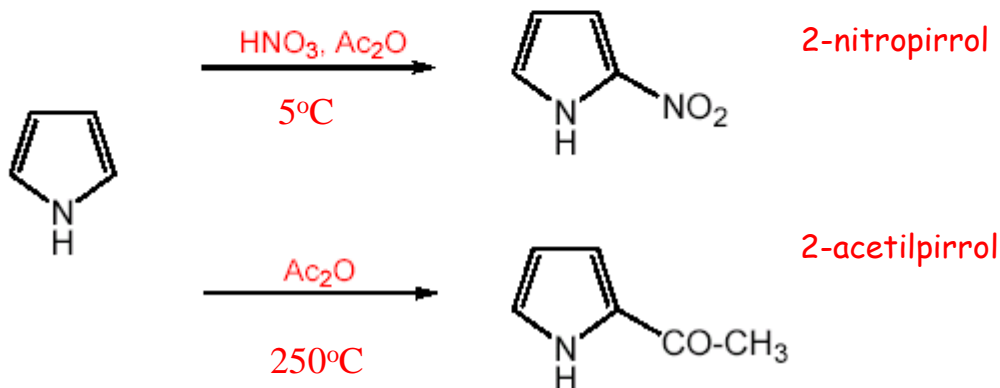
Reaktivitás



$\sigma$ -komplexek lehetséges határszerkezete 2-es és 3-as helyzetű szubsztitúció esetén:

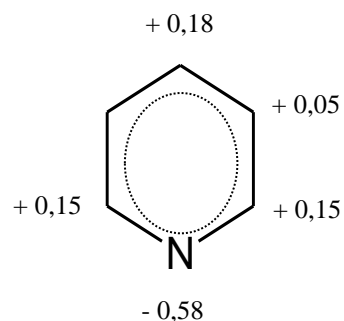
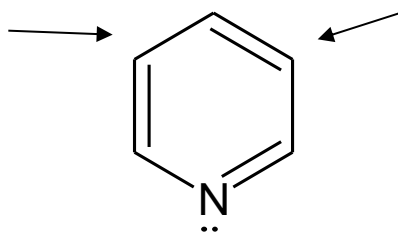


Példák



## B. piridin

Irányítás

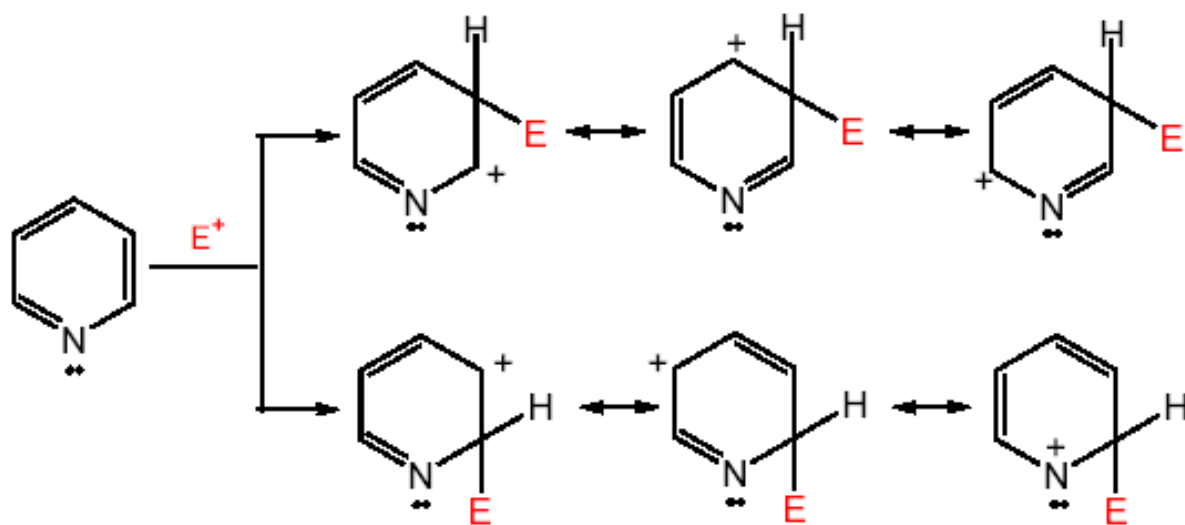


Reaktivitás

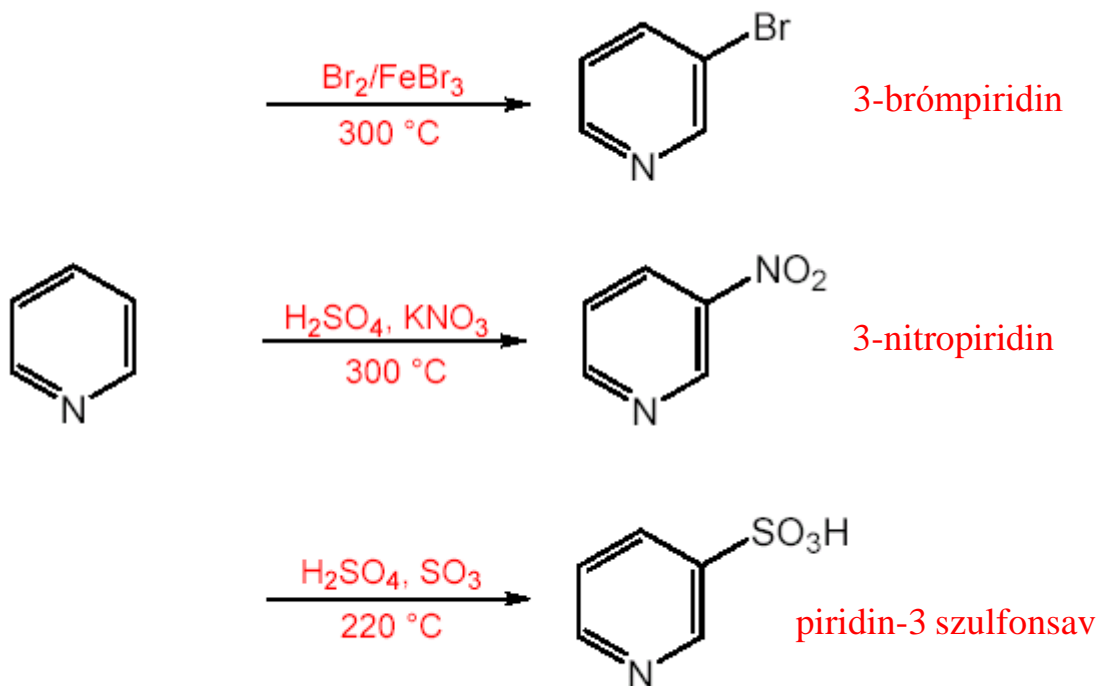
legkevésbé + helyre  
igyekszik kötődni



stabilabb  
 $\sigma$ -komplex



Példák (kénsav - protonálódás)

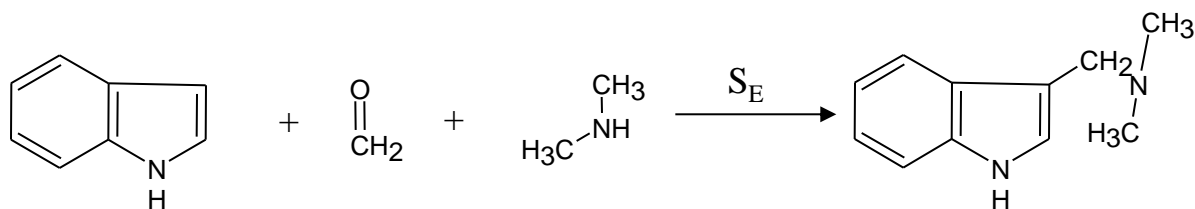


		pirrol	furán	tiofén	<sup>benzol</sup> ↓ piridin
nitrálás	NO <sub>2</sub> +	+	+	+	+*
szulfonálás	SO <sub>3</sub>	+	+	+	+*
diazo kapcsolás	Ar-N≡N	+	+		
Friedel- Crafts acilezés	CH <sub>3</sub> -CO-Q	+	+	+	
brómozás	Br <sub>2</sub>	+		+	+

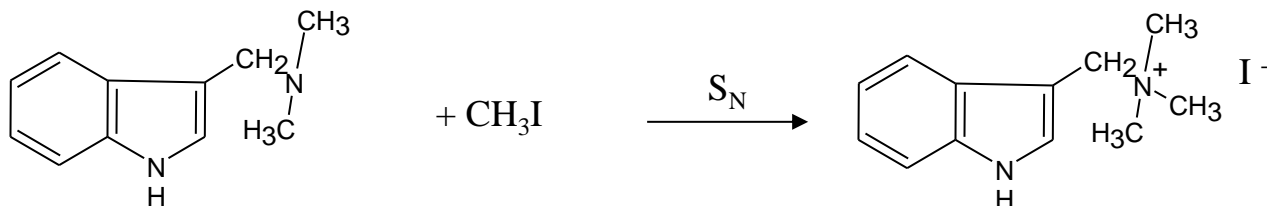
\* protonálás után

Példa: triptofán (Trp) szintézise (indol  $S_E$  reakció)

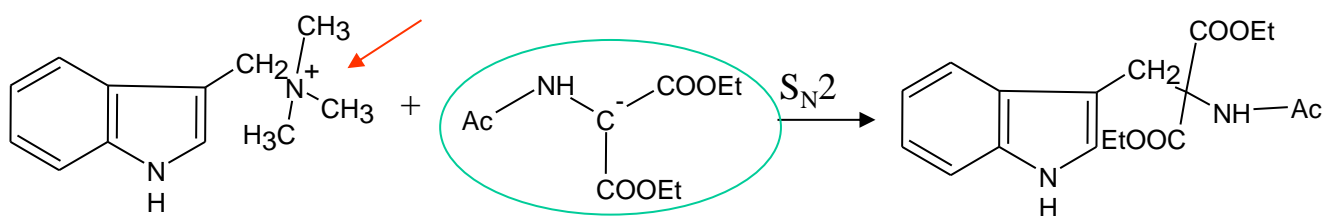
1. lépés Aminometilezés



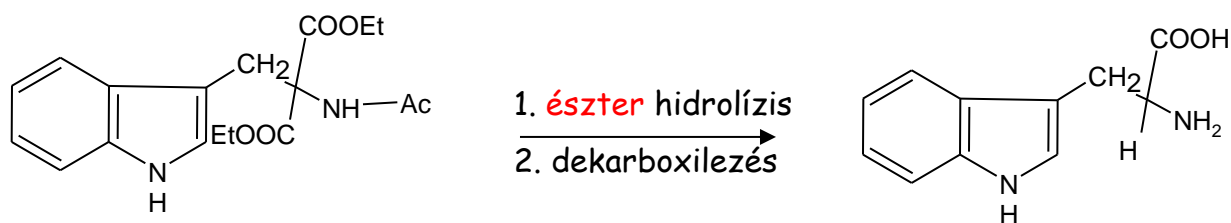
2. lépés Alkilezés



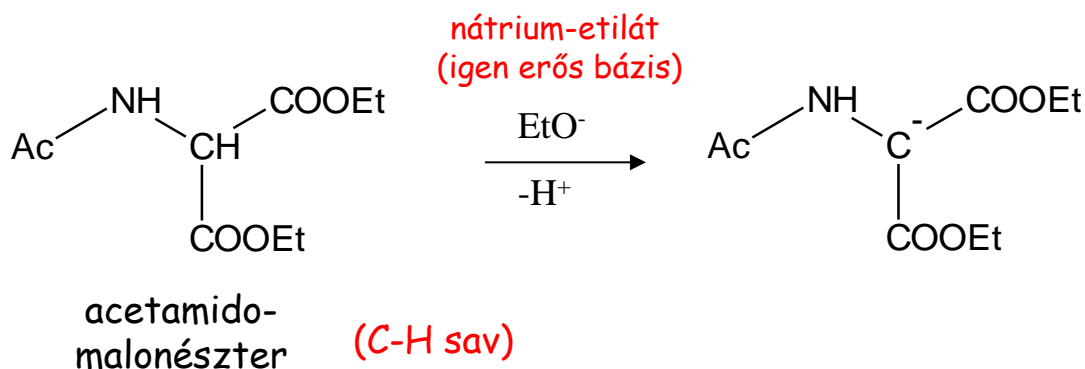
(jó távozó csoport, ld. Hoffman elimináció)



3. lépés Hidrolízis, dekarboxilezés

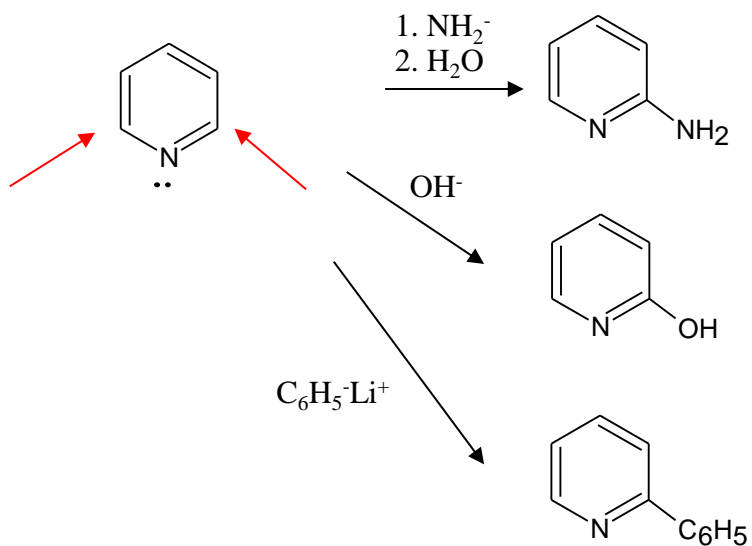


Triptofán (Trp)

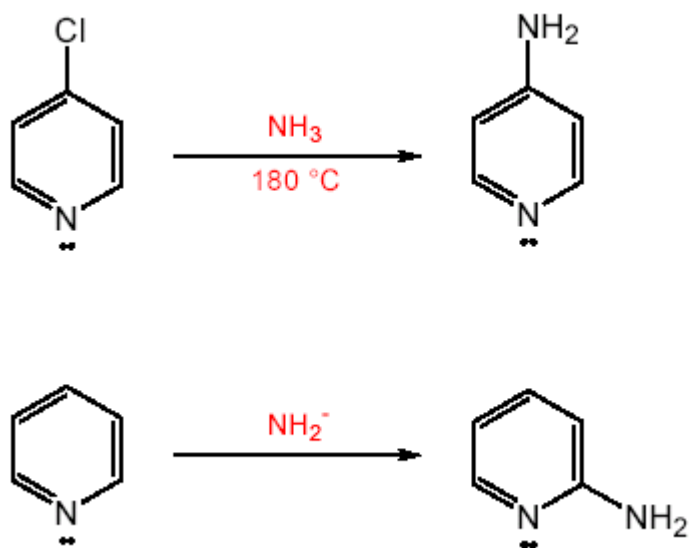


### 3. Nukleofil szubsztitúciók

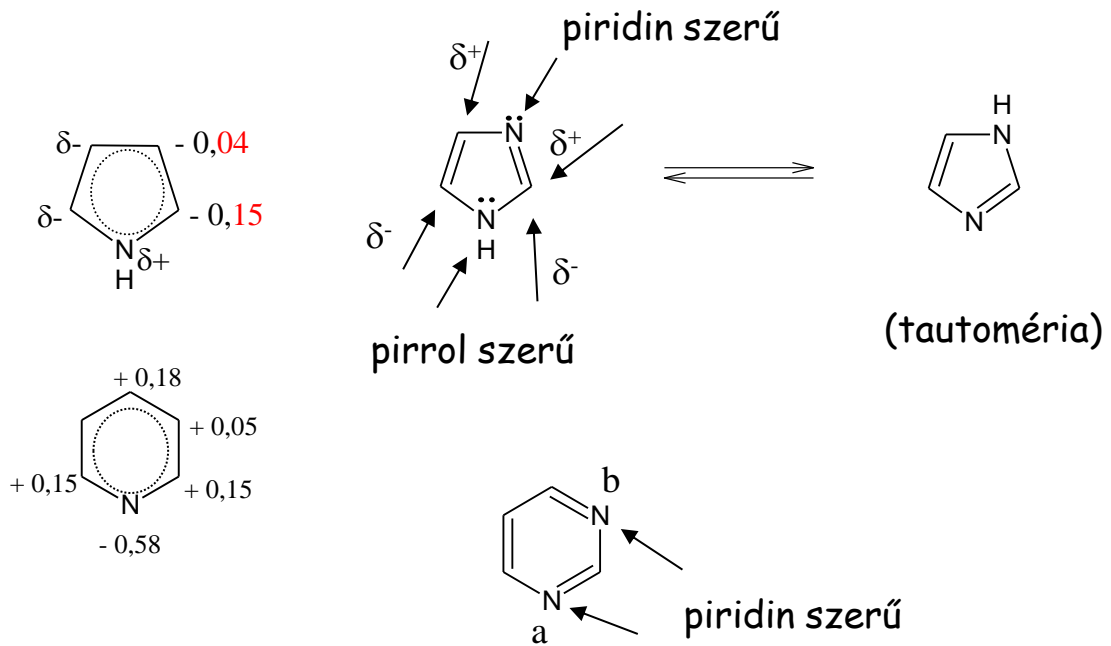
Feltétel: elektronban „szegény” gyűrűk



### Összehasonlítás



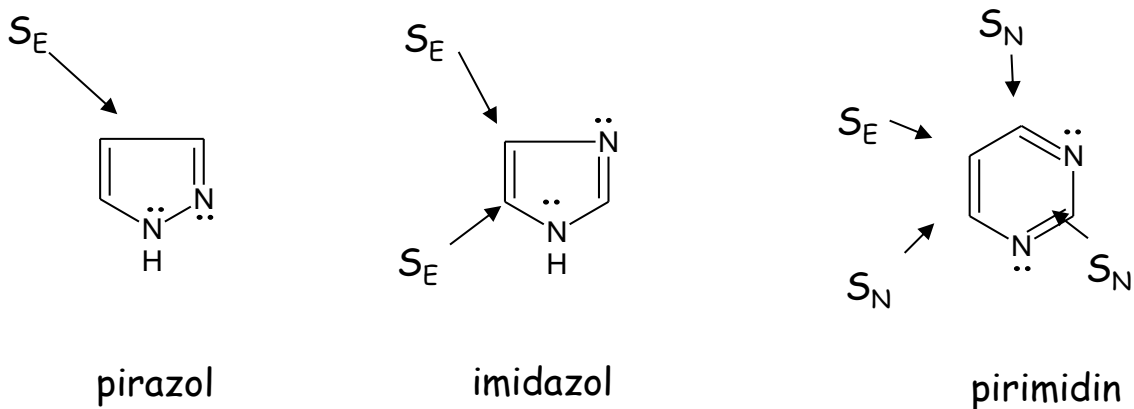
# Kétheteroatomos vegyületek reaktivitása



Pozíció	N <sub>a</sub>	N <sub>b</sub>
2	$\delta^+$	$\delta^+$
4	$\delta^+$	$\delta^+$
5	$\delta^-$	$\delta^-$
6	$\delta^+$	$\delta^+$

**Relatív elektronhiány:  $4 = 6 > 2 > 5$**

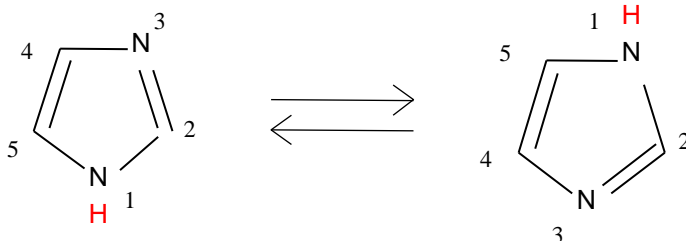
Magyarázat: a parciális töltések szuperponálódnak



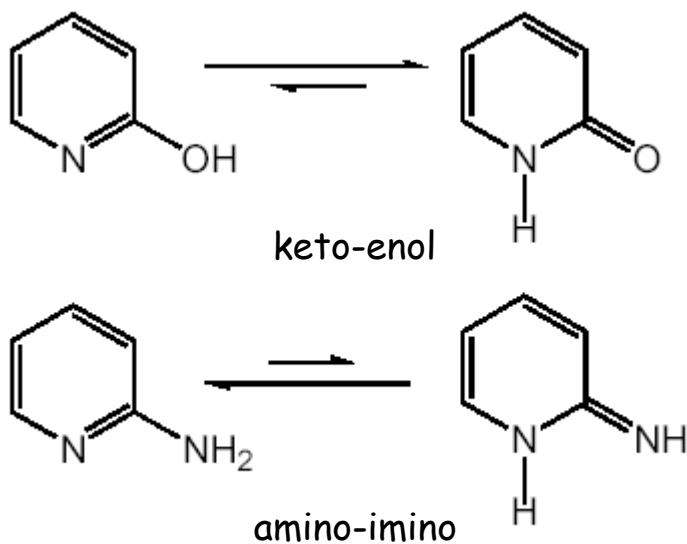
# Tautoméria

egy kettős kötés és egy proton helyzetének megváltozása

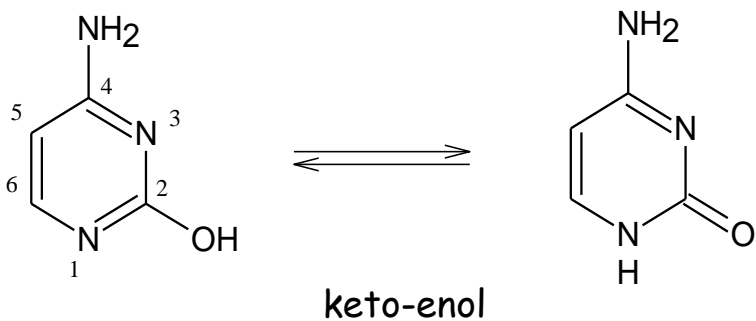
## Imidazol



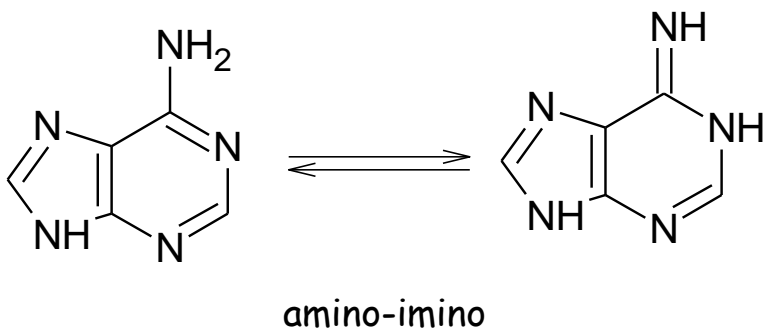
## Piridin származékok



## Pirimidin (citozin))

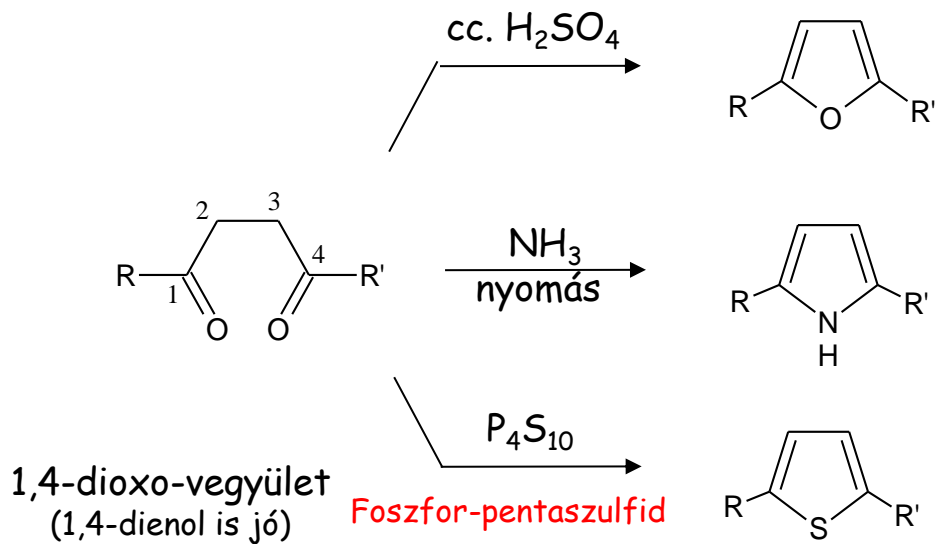


## Purin (adenin)

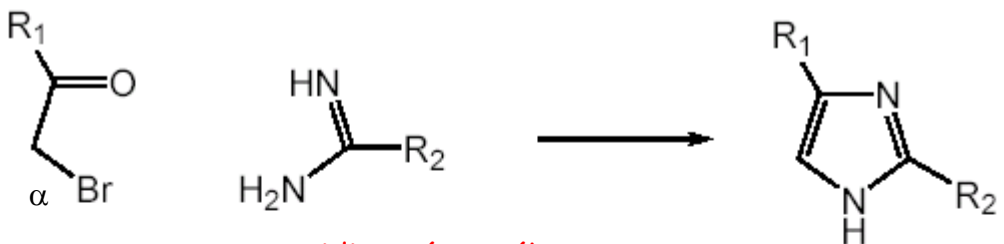




# Furán, tiofén, pirrol vázas vegyületek szintézise (Paal-Knorr)

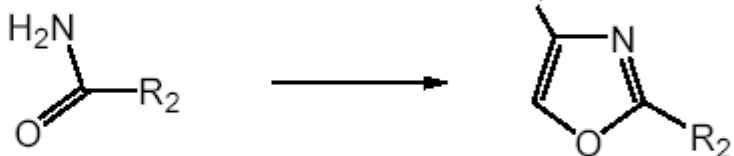
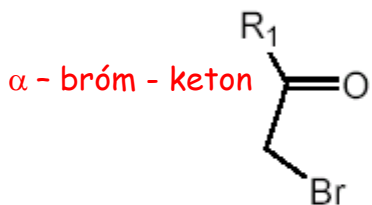


## Példák



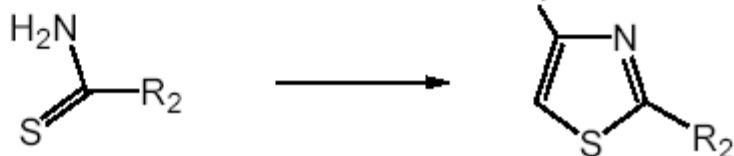
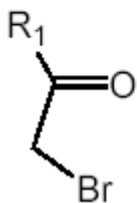
amidin-származék

imidazol-származék



karbonsavamid-származék

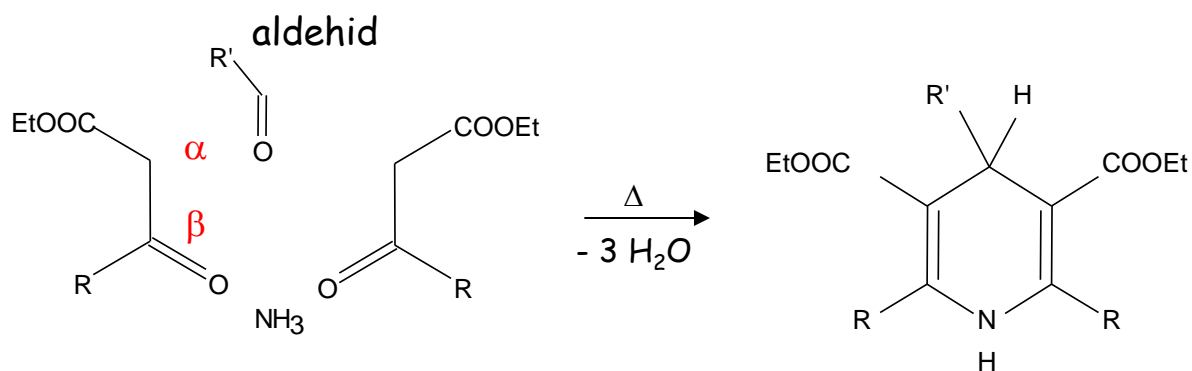
oxazol-származék



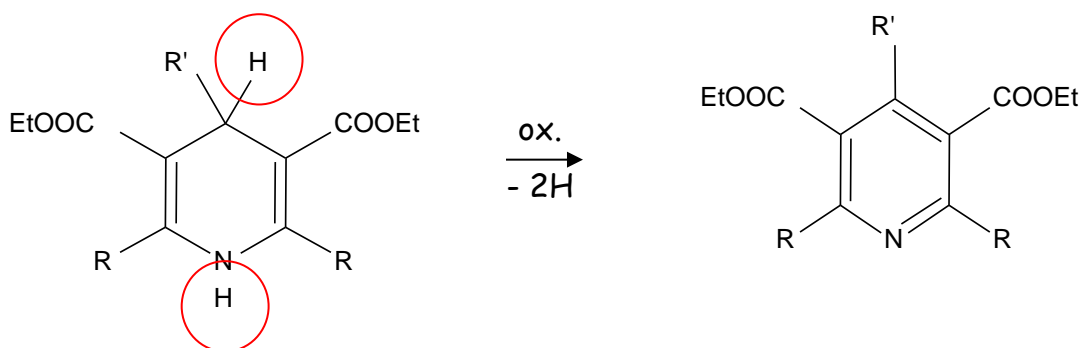
tioamid-származék

tiazol-származék

## Piridin szintézis (Hantzsch)

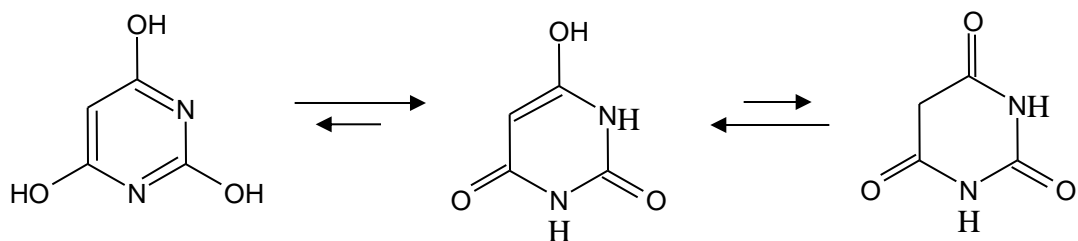


$\beta$ -oxo karbonsav észter



piridin-származék

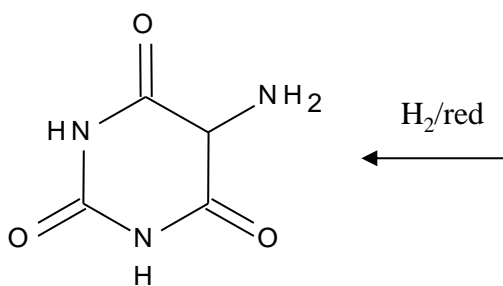
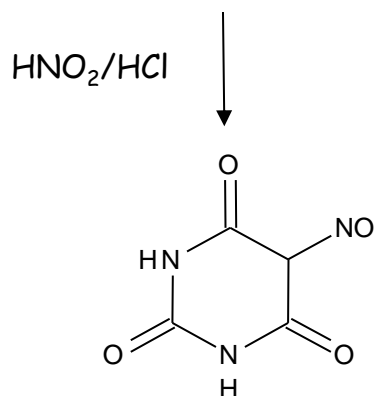
# Purin szintézis



2,4,6-trihidroxi-pirimidin  
(barbitursav)

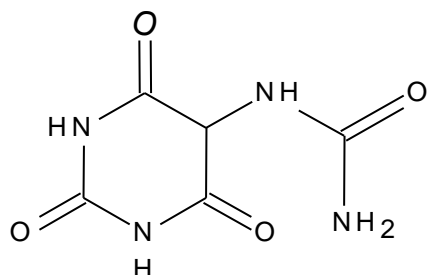
dilaktám-enol

dilaktám-keto

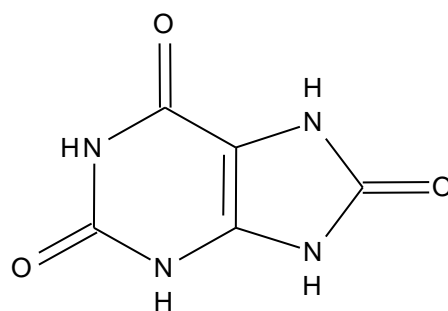
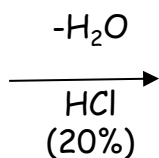


2,4,6-trihidroxi-5-amino-  
pirimidin

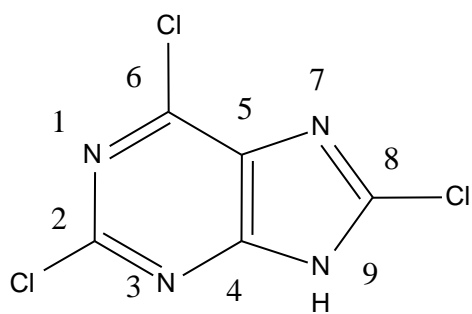
1. KOCN  
2. Wöhler-  
izomerizáció



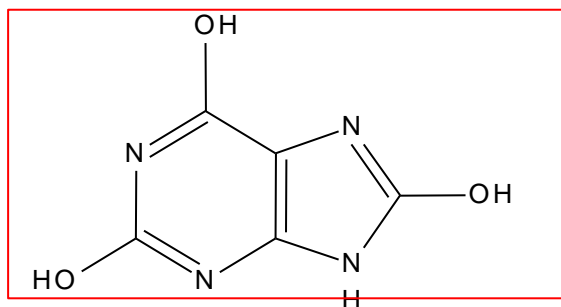
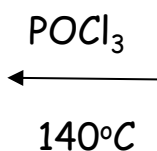
pszehudógysav



keto - enol  
tautoméria



2,6,8-triklór-purin

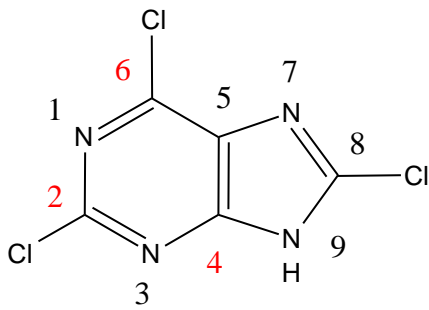


2,6,8-trihidroxi-purin (húgysav)

# Purin szintézis (folytatás)

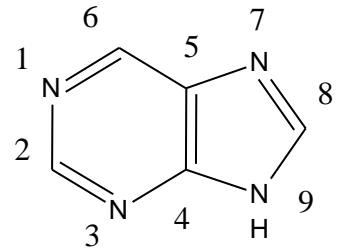
Reaktivitási sorrend

6 > 2 > 8



2,6,8-triklór-purin

Reduktív  
dehalogénezés

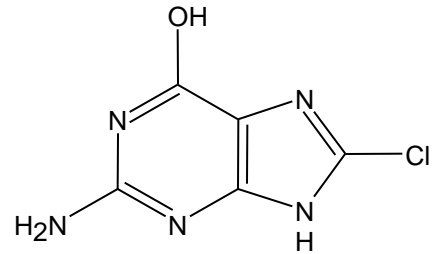
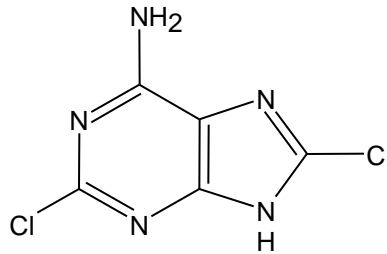
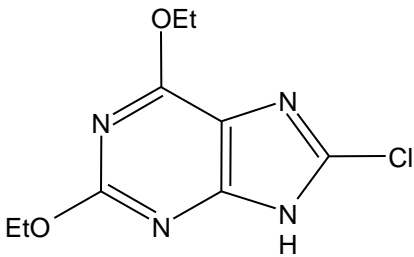


purin

+ 2 Na<sup>+</sup>EtO<sup>-</sup>

+ NH<sub>3</sub>

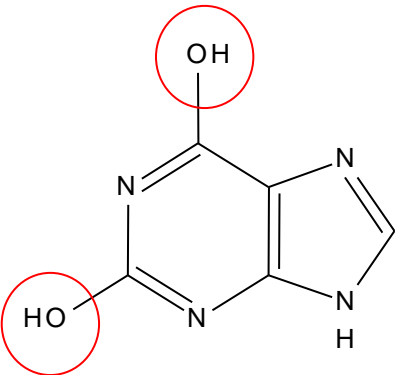
1. KOH  
2. NH<sub>3</sub>



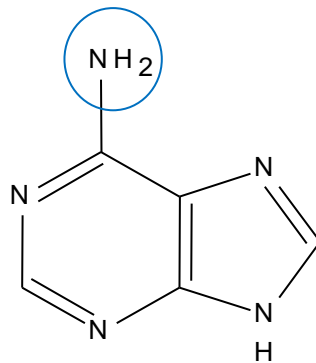
1. Elfőzés (cc. HCl)  
2. red.dehalogénezés

red. dehal.

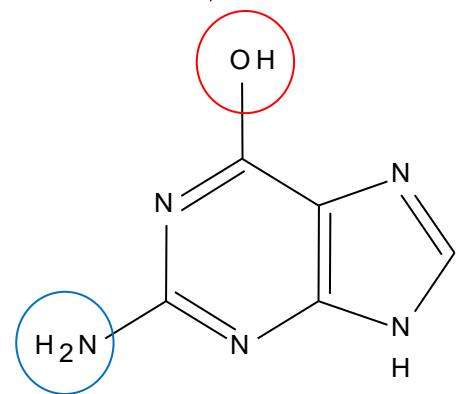
red. dehal.



xantin



6-aminopurin  
(adenin)



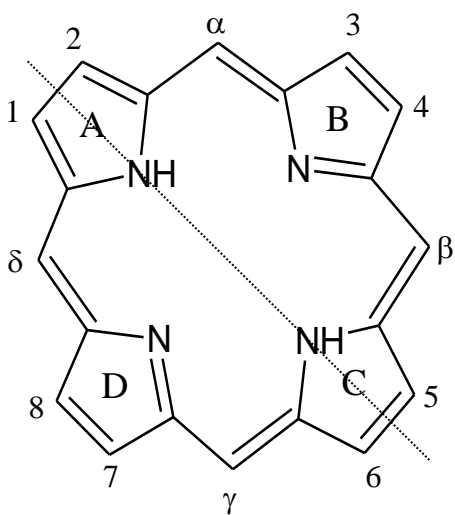
guanin

# Porfinvázak vegyületek

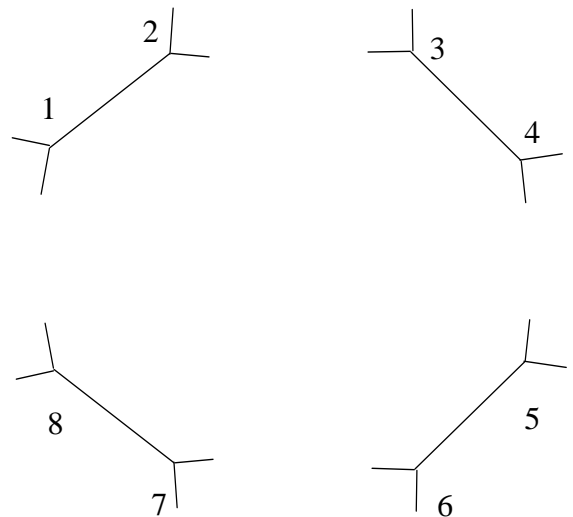
**Makrociklus:** ciklusba zárt molekula (nincs végcsoport)  
 vagy molekularészlet, amely  
 > 12 atomot tartalmaz

**Porfinvázis vegyületek:**

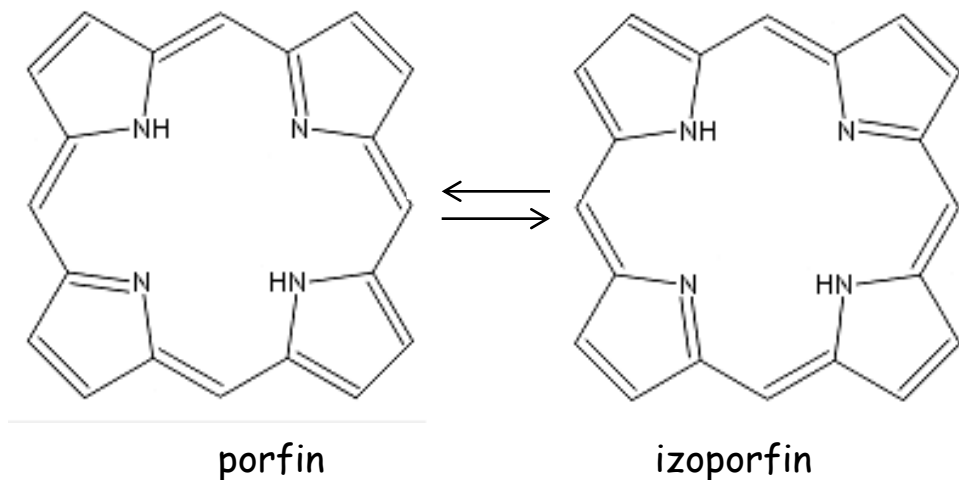
négy pirrol vagy részlegesen telített pirrolgyűrűt



porfin - váz



Egyszerűsített jelölésmód



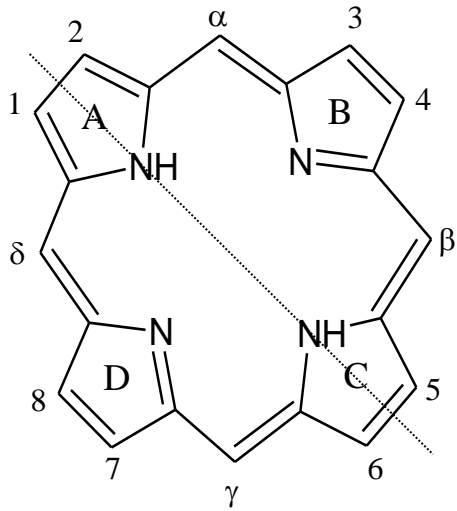
porfin

izoporphin

**Jellemzés:**

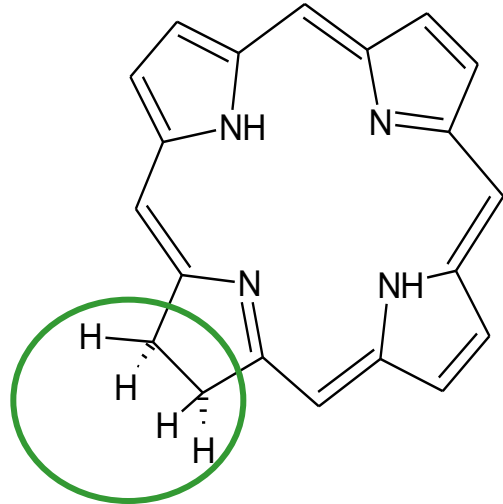
1. síkalkat,  $4n+2$  elektron (26) → aromás makrociklus
2. amfoter jelleg
  - a) NH → protonleadás
  - b) N: ← proton felvétel

# Porfinvázak



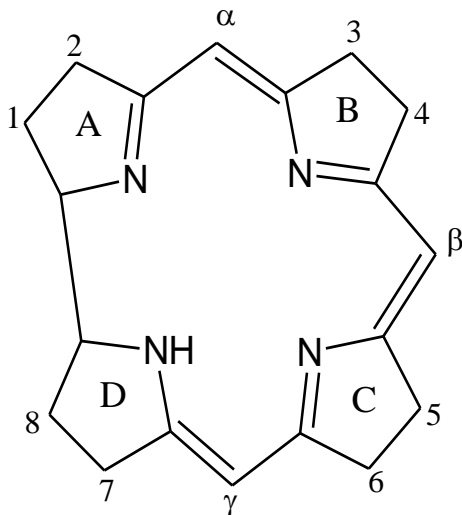
porfin - váz  
(hem-proteinek)

$Fe^{2+} / Fe^{3+}$



klorin (7,8-dihidro-porfin) - váz  
(klorofill)

$Mg^{2+}$



korrin  
( $B_{12}$  vitamin)

$Co^{3+}$

- Funkció: 1.  $\text{CO}_2$  asszimiláció (pl. klorofill)  
2. Biológiai oxidáció (pl. hemoglobin)

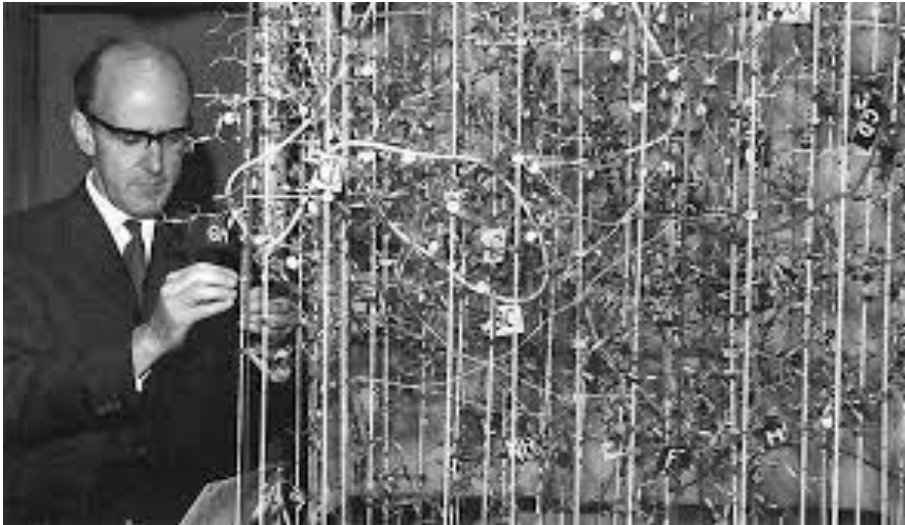
## Csoportosítás

1. Kromoproteidek (protein + prosztetikus csoport)
  - 1.1 Hemoglobin (gerincesek)
  - 1.2 Mioglobin (izomsejtek, gerincesek/gerinctelenek)
  - 1.3 Eritrokruorin (gerinctelenek, 150 hem)
  - 1.4 Kataláz, peroxidáz (protoporfirin,  $\text{Fe}^{3+}$ )
  - 1.5 Citokrómok (terminális oxidáció,  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ )
2. Klorofill (zöld növények)
3. Cianokobalamin (B12 vitamin)



## 1.1. Hemoglobin (1862, kristályos)

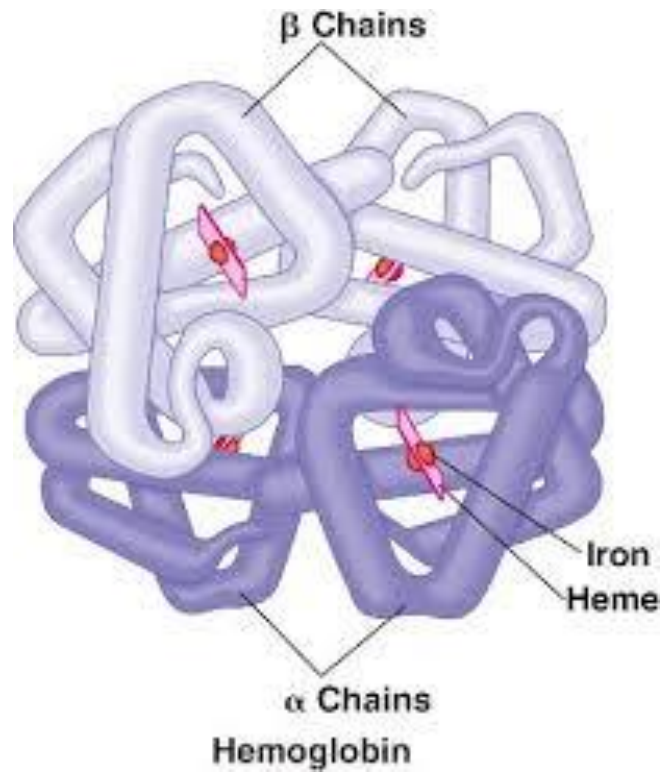
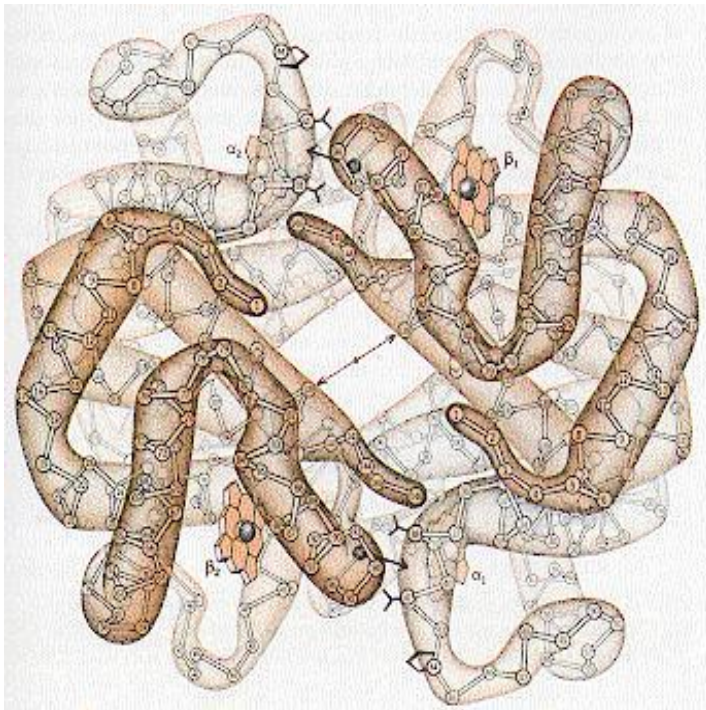
Prosztetikus csoport (**vörös**) +  
globin (4 polipeptid lánc, Mt: 17 000)



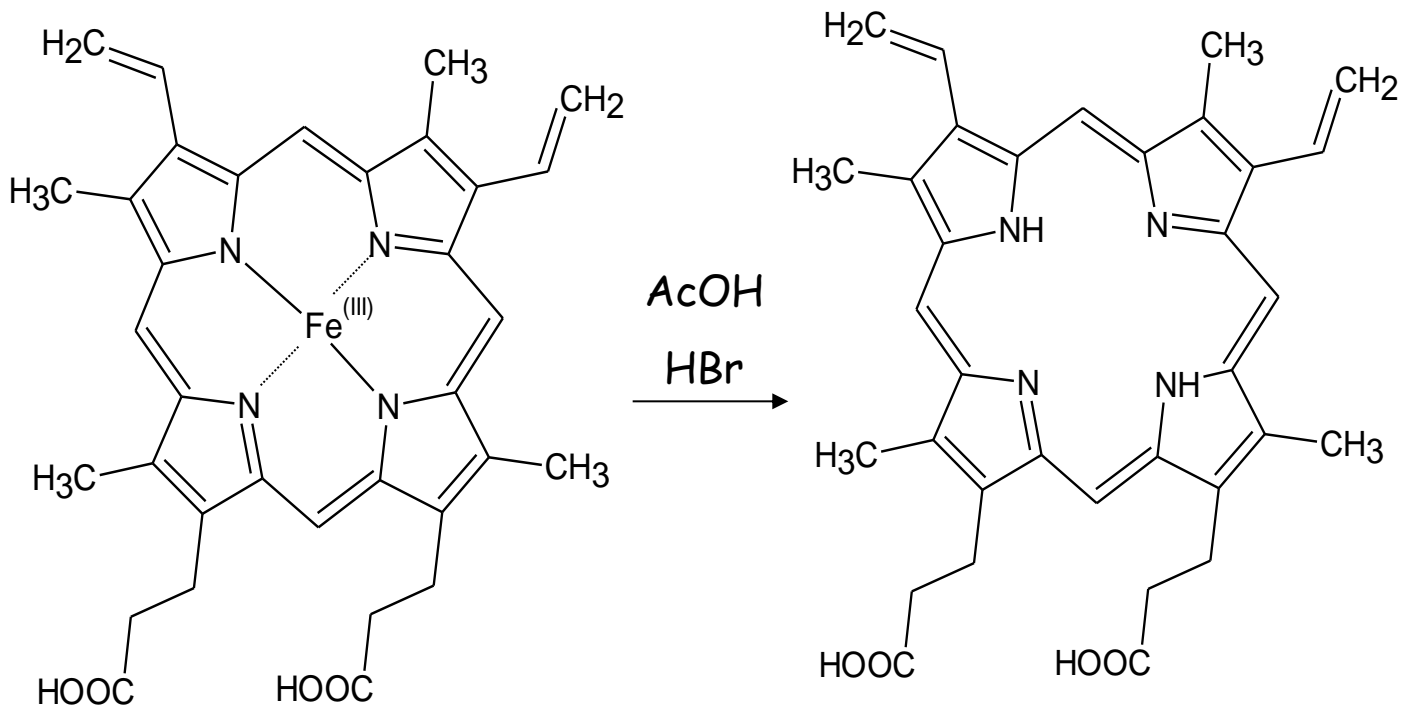
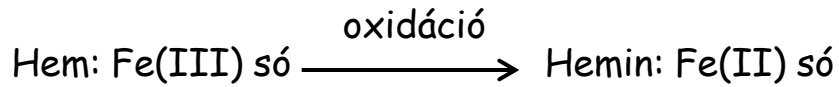
Max F. Perutz, 1960

Nobel díj, (J. Kendrew) 1962

[www.mfpl.ac.at](http://www.mfpl.ac.at)



[phm.utoronto.ca](http://phm.utoronto.ca)

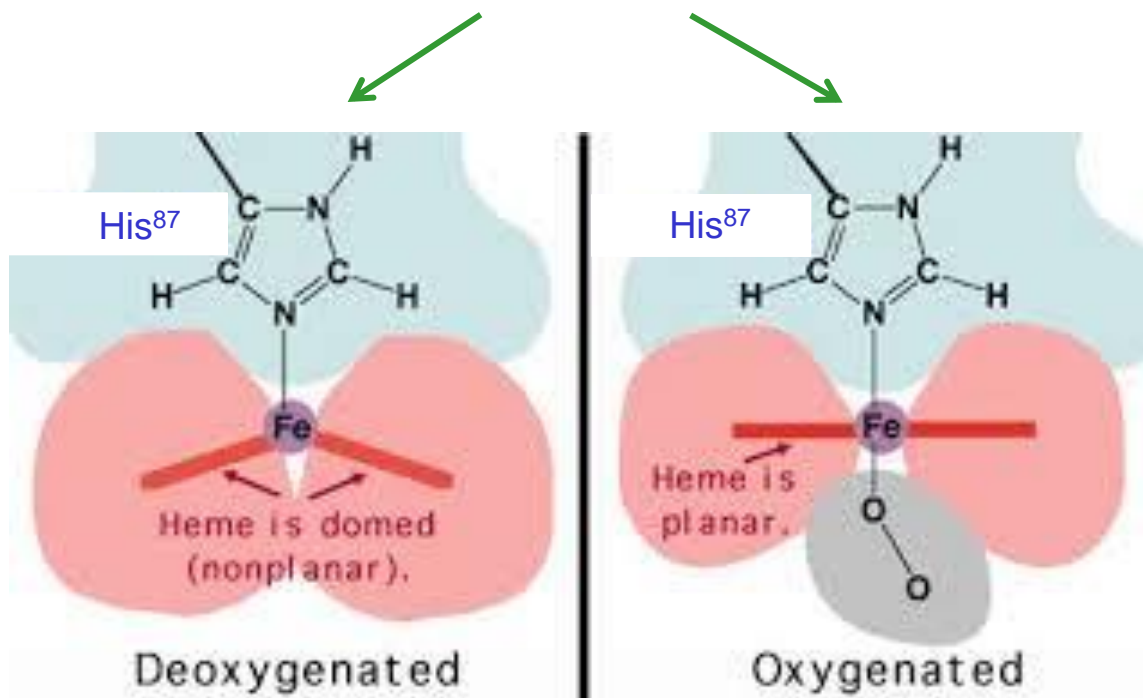


Protoporfirin  
(vas mentes)

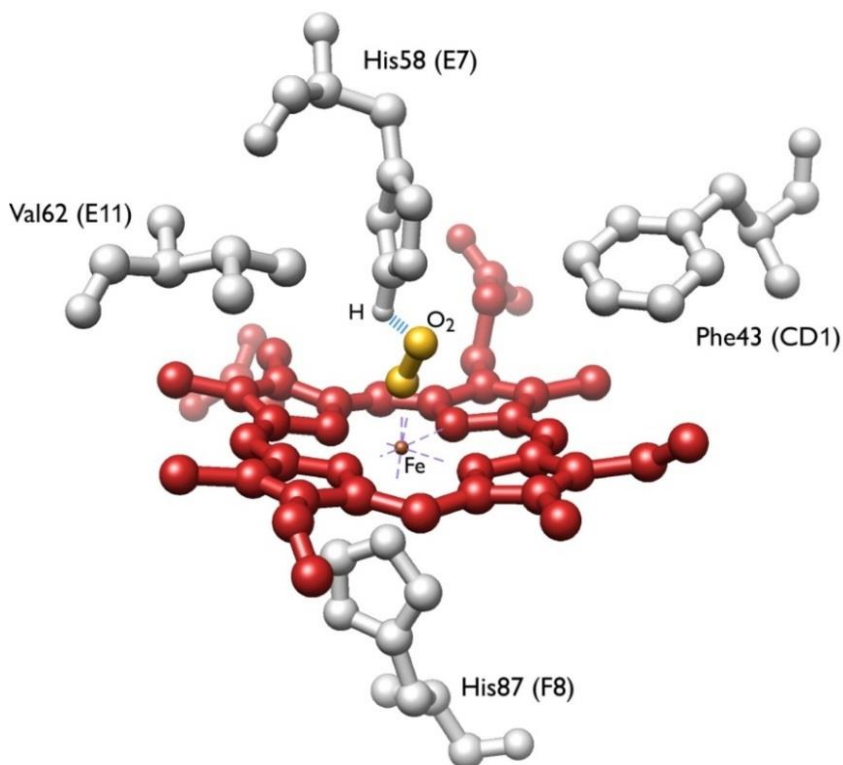
### Jellemzés:

1. porfin származékok
2. sötétvörös, kristályos
3. síkalkat,  $4n+2$  elektron  $\rightarrow$  aromás makrociklus
4. amfoter jelleg
  - a) NH  $\rightarrow$  protonleadás
  - b) N:  $\leftarrow$  proton felvétel
5. hem totálszintézise: H. Fischer, 1929

globin



[www.chemistry.wustl.edu](http://www.chemistry.wustl.edu)



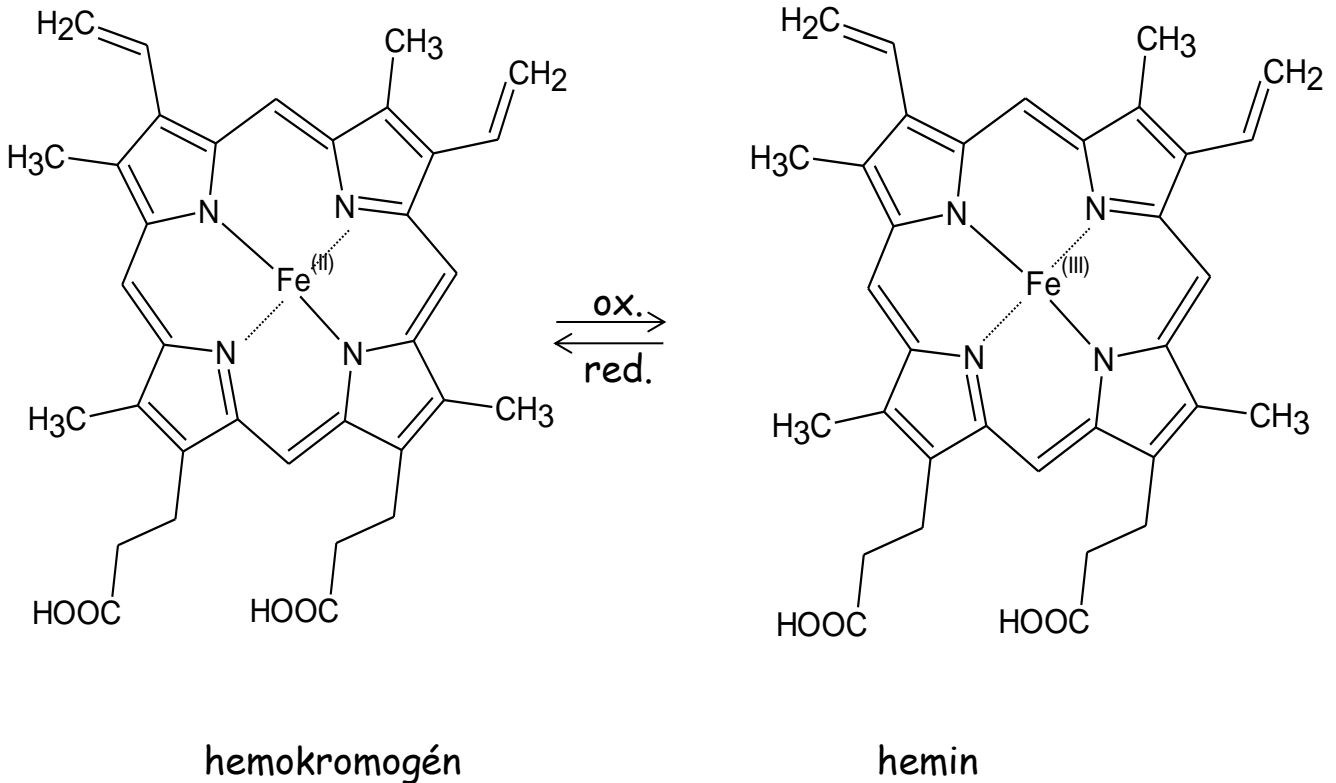
[http://ttktamop.elte.hu/online-tananyagok/a\\_biokemia\\_es\\_molekularis\\_biologiai\\_alapjai/ch07s03.html](http://ttktamop.elte.hu/online-tananyagok/a_biokemia_es_molekularis_biologiai_alapjai/ch07s03.html)

Paál. G. A fehérjeműködés paradigmája: mioglobin és hemoglobin

## 1.2. Mioglobin

Prosztetikus csoport (vörös) + globin (1 polipeptidlánc)

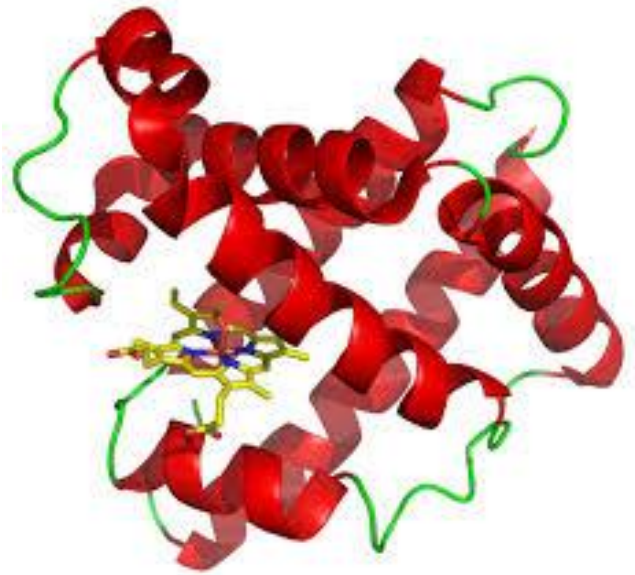
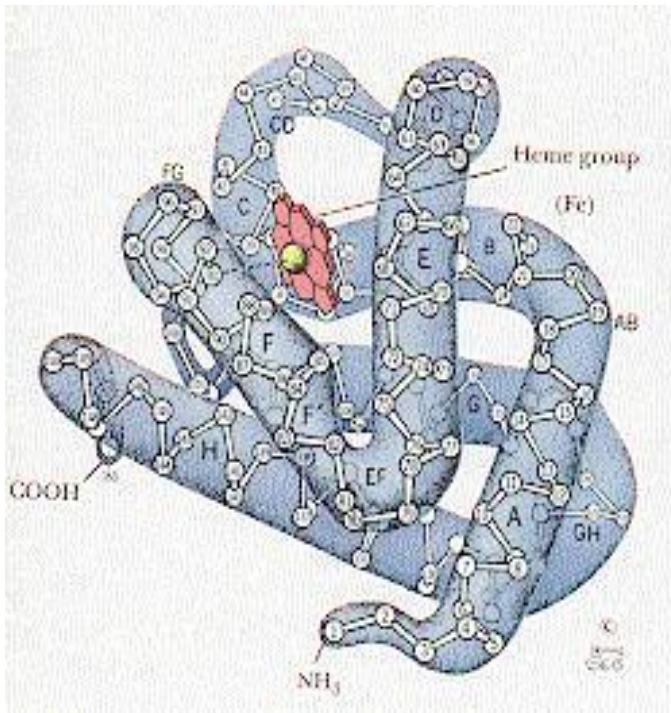
153 aminosav



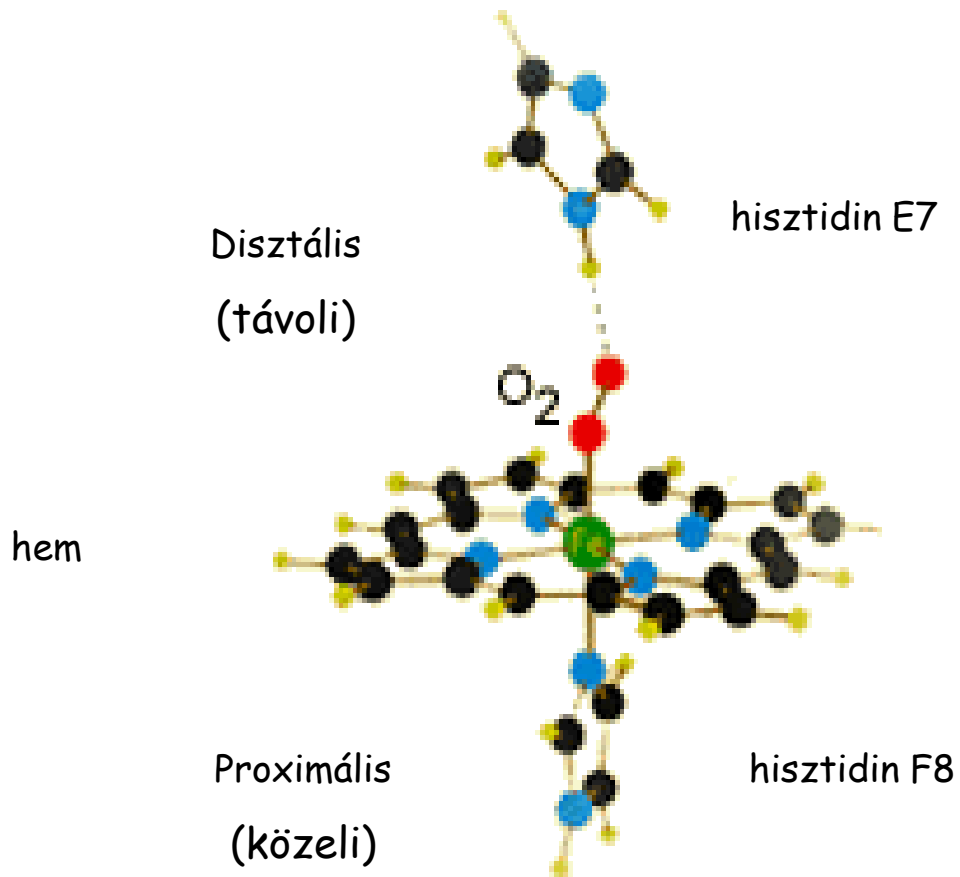
Jellemzés:

1. izomban fordul elő
2.  $O_2$  megkötés (nagyobb, mint hemoglobin)
3. térszerkezet (J. Kendrew, Nobel díj)  
első fehérje, 1958
1. hem - protein zseb (His szerepe)

# A mioglobin és $O_2$ kötőhelye



[guweb2.gonzaga.edu](http://guweb2.gonzaga.edu)



## Mioglobin, hemoglobin összehezés

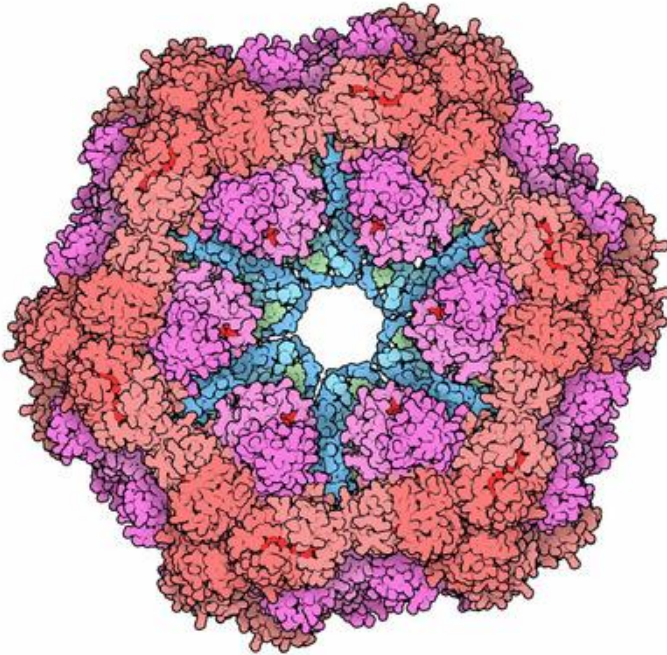
váz	fémion	prosztetikus csoport	protein	funkció
Proto-porfirin	$Fe^{2+}$	hem	ferrohemoglobin (hemoglobin)	$O_2$ kötés
	$Fe^{3+}$	hemin	ferrihemoglobin (hemoglobin)	$H_2O$
	$Fe^{2+}$	hem	oximioglobin	$O_2$ kötés
	$Fe^{3+}$	hemin	ferrimioglobin	$H_2O$
	$Fe^{2+}$	hem	dezoximioglobin	$O_2$ kötés

humán hemoglobin

	F1	F2	F3	F4	F5	F6	F7	F8	F9
$\alpha$ lánc	Leu	Ser	Ala	Leu	Ser	Asp	Leu	His	Ala
$\beta$ lánc	Phe	Ala	Thr	Leu	Ser	Glu	Leu	His	Cys
ámbráscet mioglobin	Leu	Lys	Pro	Leu	Ala	Gln	Ser	His	Ala

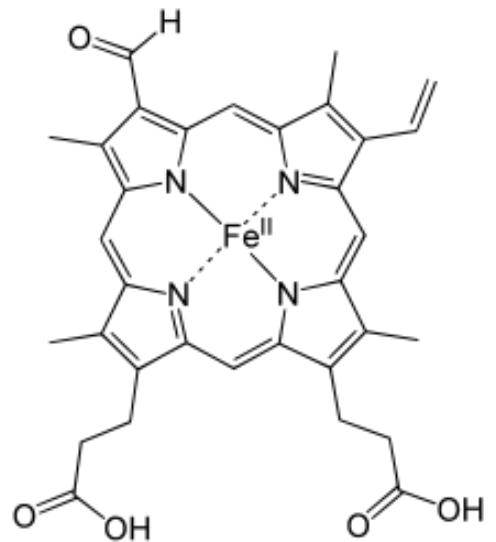
### 1.3. Eritrokrutorin és klorokrutorin

Oxigén szállító, hem-tartalmú fehérjék (M<sub>t</sub> > 3,5 millió Da)  
Gyűrűsférgek, soksertéjűek (Polychaeta)



Eritrokrutorin (4 × 36 globin)

<http://www.rcsb.org/pdb/101/motm.do?momID=159>

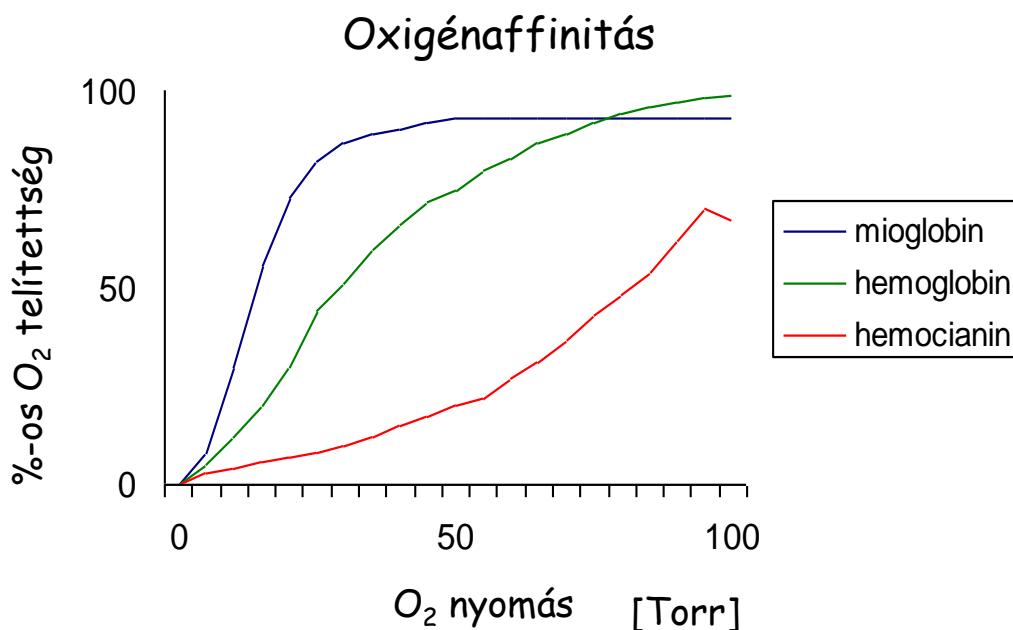


Prosztetikus csoport  
klorokrutorin

## Légzési színezékek (kiegészítés)

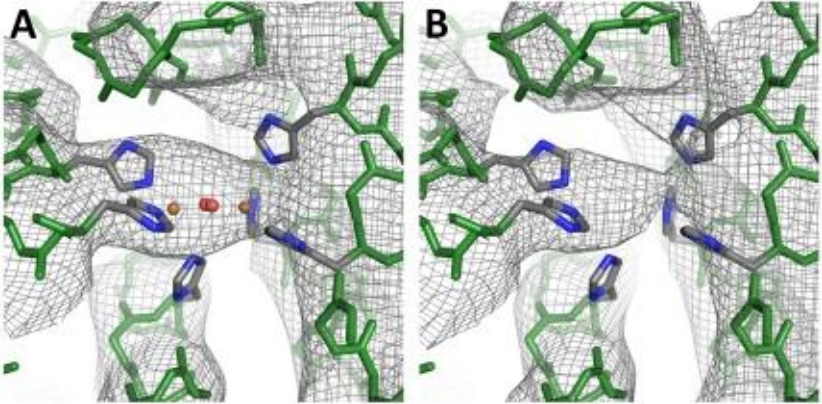
O<sub>2</sub> diffúzió: 2 mm mélység ⇒ „szállítófolyadék”

	szín	fémion	molekula tömeg	példa
hemoglobin	világospiros	Fe <sup>3+</sup>	70.000	gerinces
	↓	↕	20.000	körszájúak
	sötétvörös	Fe <sup>2+</sup>	400.000	rákok, férgek
mioglobin	világospiros	Fe <sup>3+</sup>	20.000	gerinces
	↓	↕	3.000.000	gyűrűs férgek
	sötétpiros	Fe <sup>2+</sup>		
klorokruorin	zöld	Fe <sup>3+</sup>	3.000.000	soksertéjű
	↓	↕		férgék
	zöld	Fe <sup>2+</sup>		
hemocianin	kék	Cu <sup>2+</sup>	400.000	rákok
	↓	↓		(languszták)
	színtelen	Cu <sup>+</sup>	7.000.000	tőrfarkúak





# Hemocianin (metalloprotein)



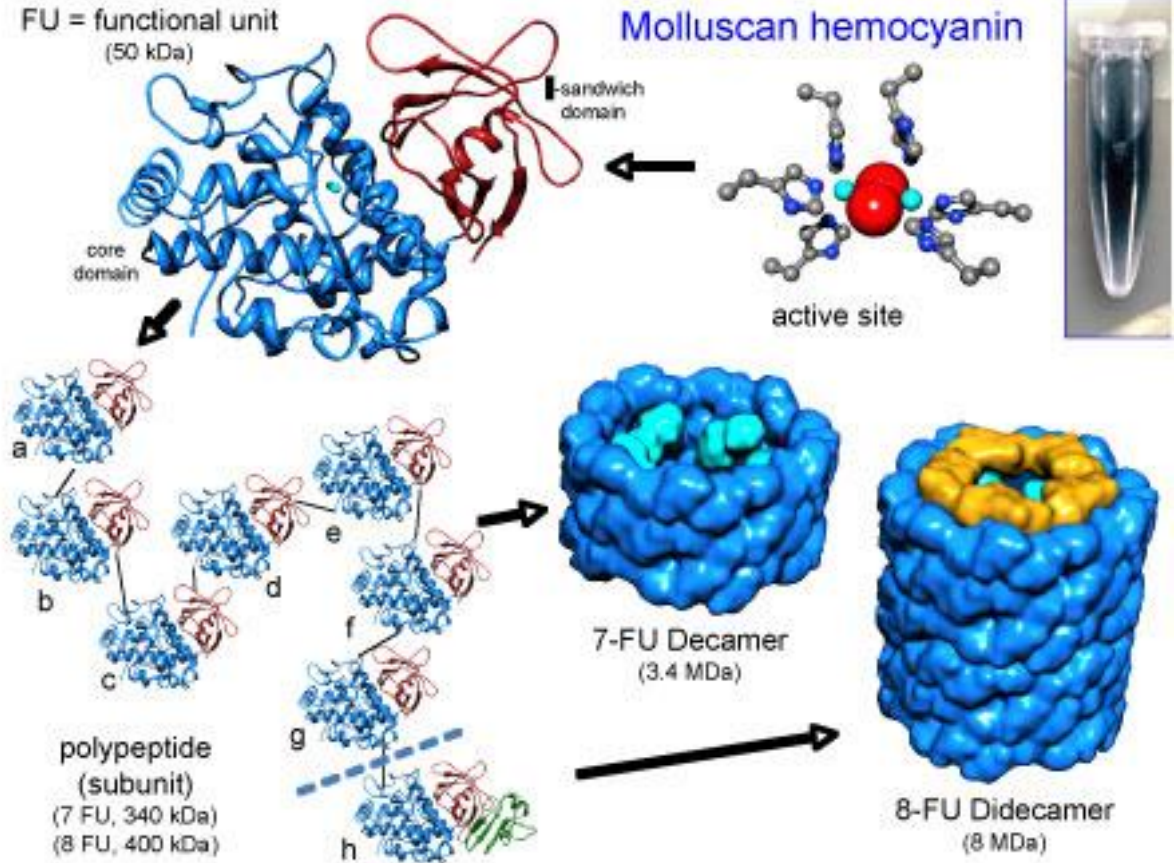
Cu = narancs, O = vörös

*Megathura crenulata*  
(keyhole limpet)



Hemocianin from *Pandinus imperator*

E. Jaenicke et al. PLoS One 2012, 7(3) e 32548



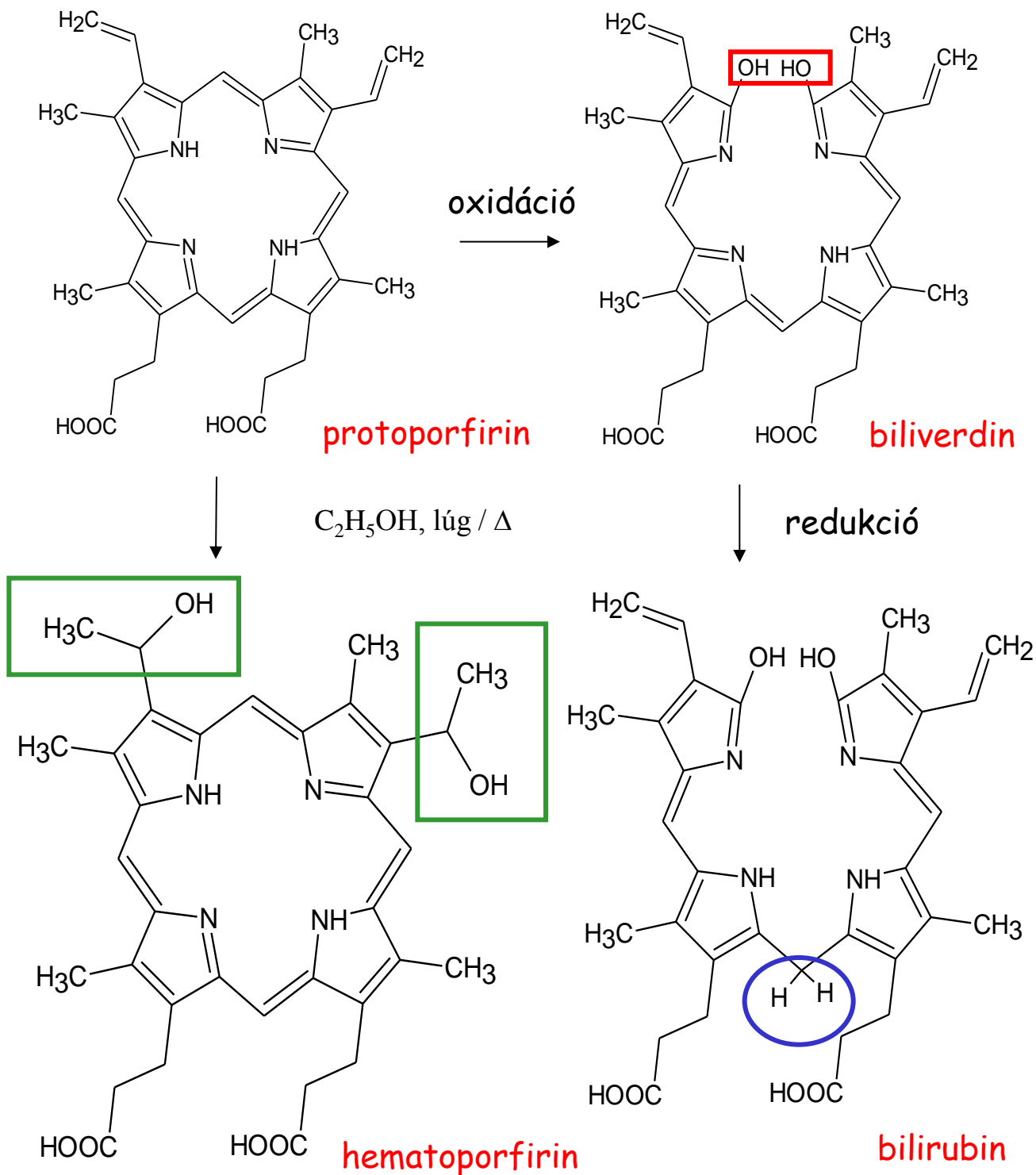
# Epefestékek

hemoglobin hem részének bomlástermékei

A. biliverdin, zöld (máj)

B. bilirubin, sárga (máj).

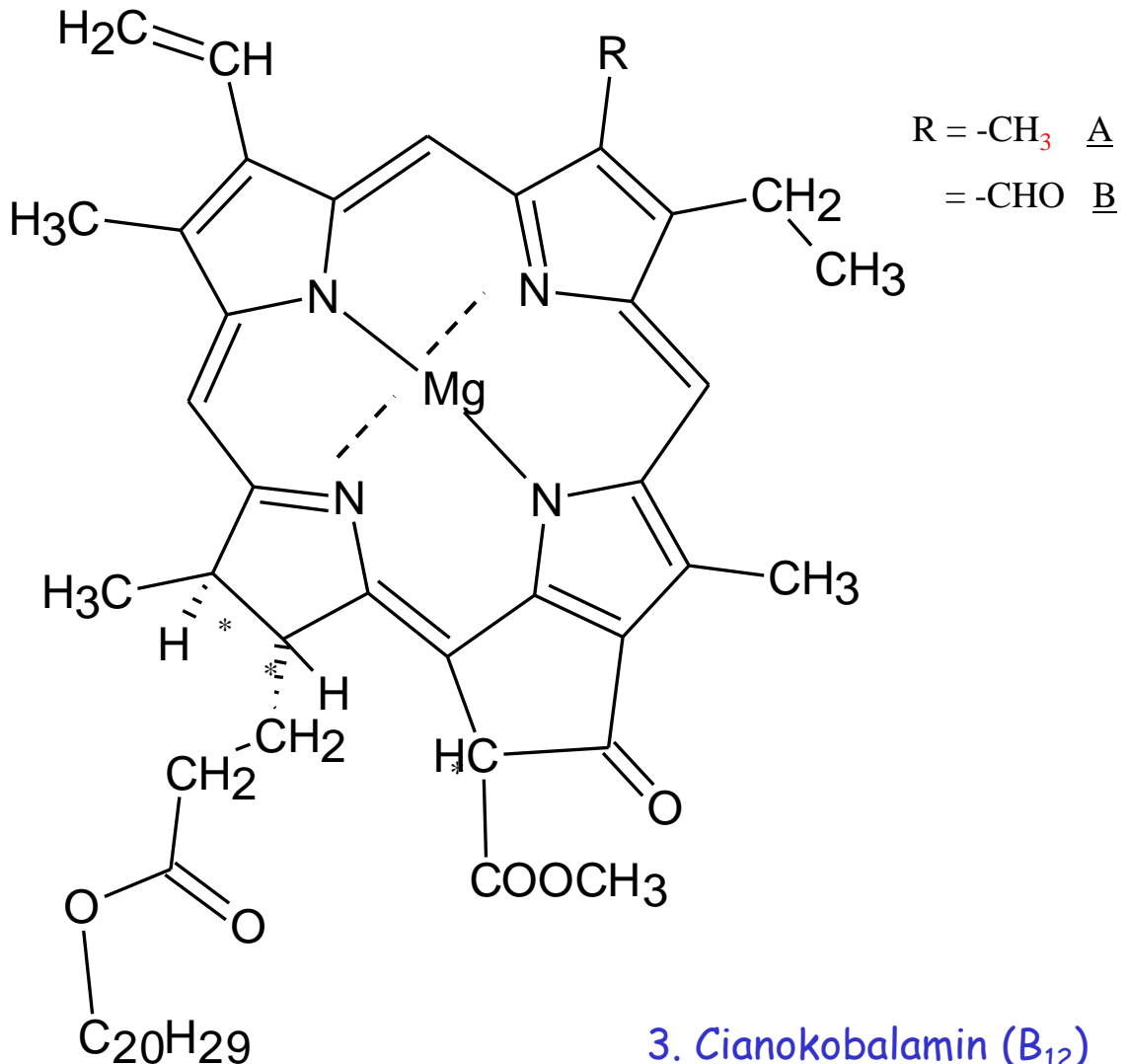
Legrégebben ismert; biliverdin oxidációja. vér c = 0,5 mg/100 ml → sárgaság,  
máj → epe → bélrendszer 250 mg/nap



## 2. Klorofill

zöld szemcsék (kloroplasztok) pigmentje  
izolálás: Willstätter (1904-13)  
szerkezet: Fischer (1940)  
szintézis: Woodward (1960)

Összetétel: klorofill A + klorofill B = 3:1 + Mg



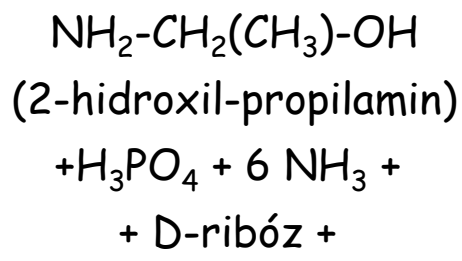
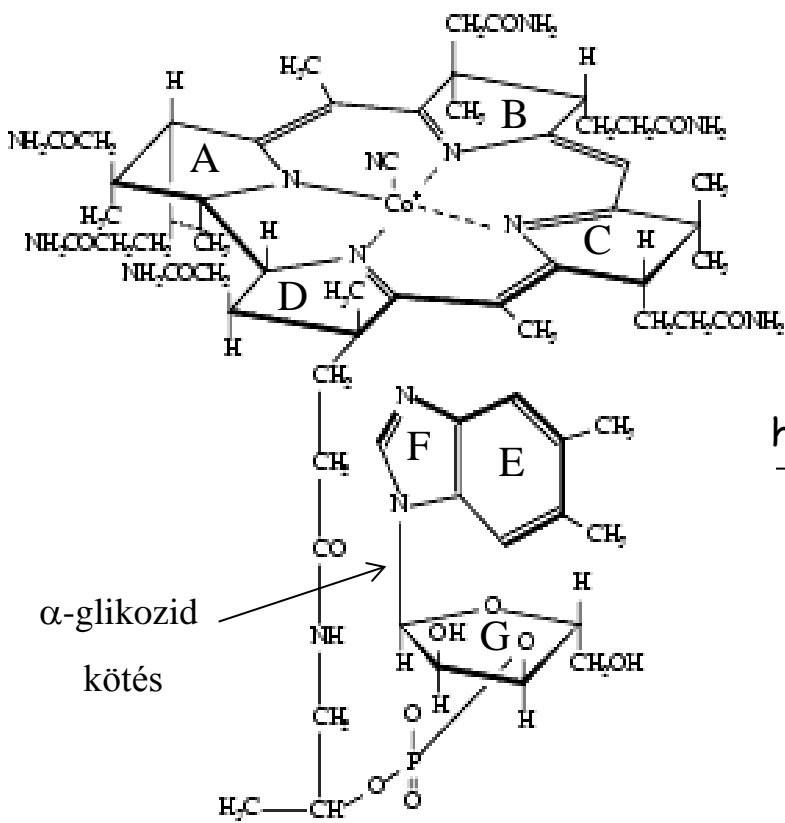
## 3. Cianokobalamin (B<sub>12</sub>)

Co<sup>3+</sup>, 4,3% kobalt

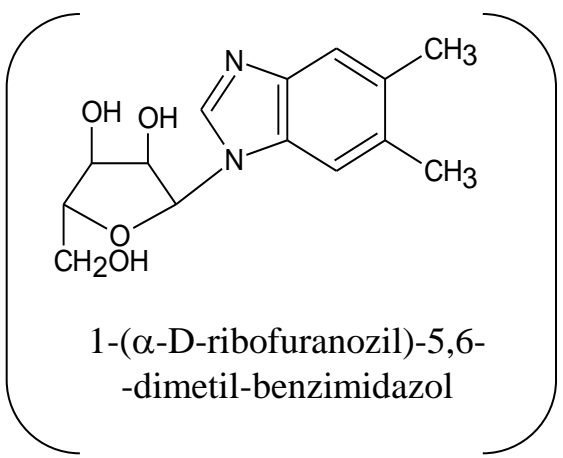
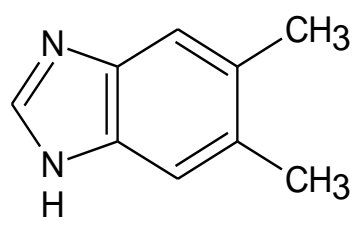
C<sub>68</sub>H<sub>88</sub>O<sub>14</sub>N<sub>14</sub>Co

(C<sub>20</sub>H<sub>29</sub>) fitol észter

Cisz-7(R)-11 (R)-3,7,11,15-tetrametil-2-hexadecén-1-ol



hidrolízis  
 $\xrightarrow{\text{H}^+}$



- Variációk:
- CN       $\text{B}_{12}$
  - OH      $\text{B}_{12a}$
  - $\text{NO}_2$     $\text{B}_{12c}$

- 1926: májkivonat - vészes vérszegénység (Minot, Murphy)
- 1947: mikrobák növekedési faktora (Shoriz)
- 1948: izolálás tengeri algákból (Folkers, Smith)
- 1954-56: térszerkezet (Hodgkin)