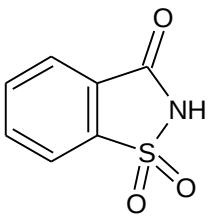
10. Előadás

Szerves vegyületek kénatommal. Heterociklusos (porfinvázas) vegyületek.

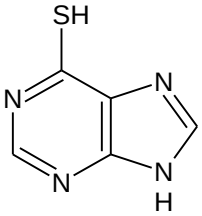
SZERVES VEGYÜLETEK KÉNATOMMAL

Példák:

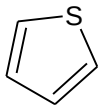
$CH_2=CH-CH_2-S-S-CH_2-CH=CH_2$ diallil-diszulfid (fokhagyma olaj)



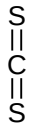
szacharin



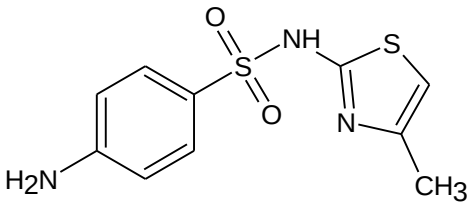
merkapto-purin



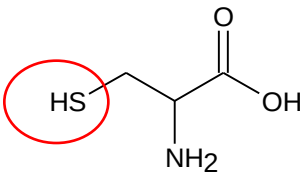
tiofén



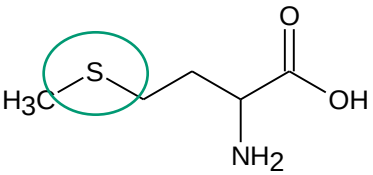
szén-diszulfid



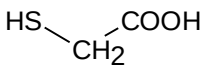
szulfonamid
(Ultraseptyl)



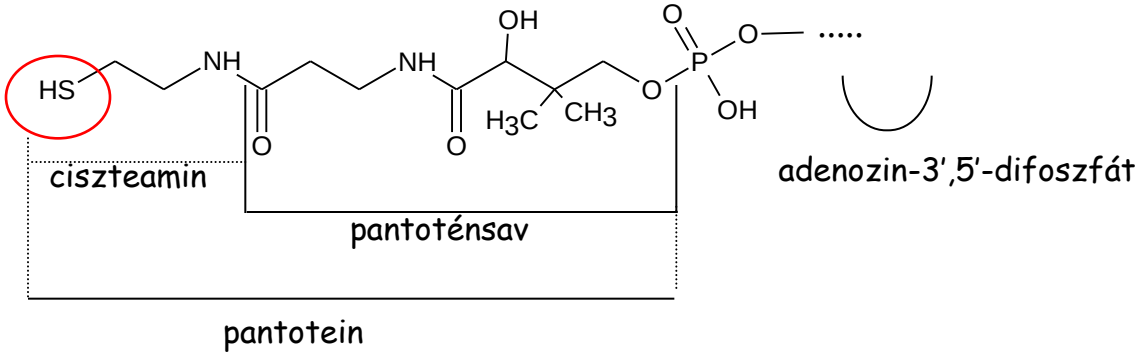
cisztein (Cys)



metionin (Met)



tio-glikolsav
(merkaptoecetsav,
szulfhidril-ecetsav)

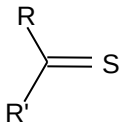


KOENZIM A

Áttekintés

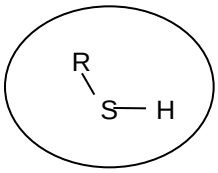
A kénatomhoz kapcsolódó ligandumok száma

[1]

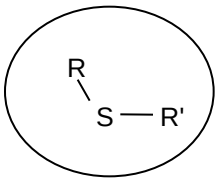


tiovegyület
(pl. tioketon)

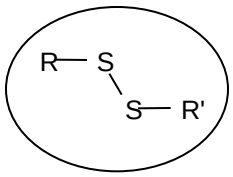
[2]



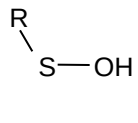
tiol



szulfid

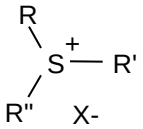


diszulfid

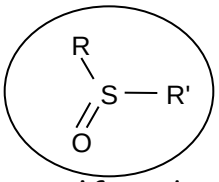


szulfénsav

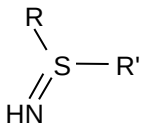
[3]



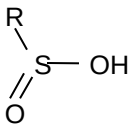
szulfóniumsó



szulfoxid

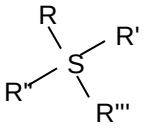


szulfilimin

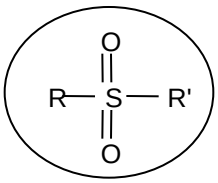


szulfinsav

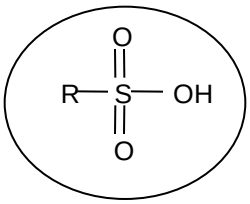
[4]



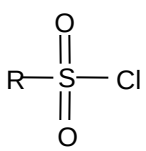
szulfurán



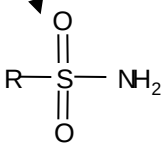
szulfon



szulfonsav

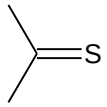


szulfonil-klorid



szulfon(sav)amid

Csoportok:

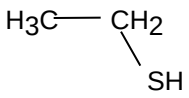


tiokarbonil

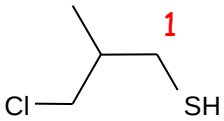
-SH

merkapto-
(szulfhidril)

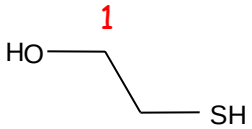
Nomenklatúra, példákkal



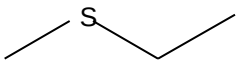
etán-tiol
(etil-hidrogénszulfid,
etil-merkaptán)



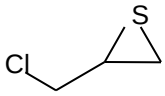
3-klór-2-metil-1-
propántiol



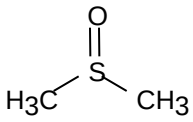
2-merkapto-etanol



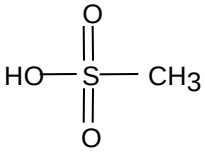
etil-metil-szulfid



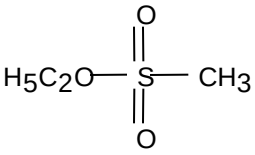
1-klór-2,3-epitio-
propán



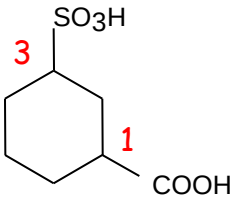
dimetil-szulfoxid



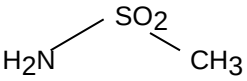
metánszulfonsav



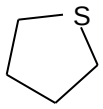
metánszulfonsav-
etilészter



3-szulfo-1-
ciklohexánkarbonsav



metánszulfonamid



tetrametilén-szulfid

Szerkezet

Elektronok

I. sor C N O F
II. sor Si P S Cl

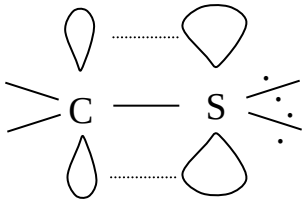
$S_{EN}(2,5) < O_{EN}(3,5)$

Jellegzetességek

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

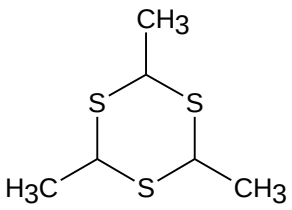
S: $3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1\ 3d^0$ .....

<u>1 ligandumos kénvegyületek (tiovegyületek)</u>



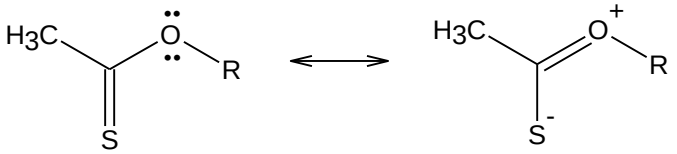
σ kötés: C($2sp^2$) – S($3sp^2$)
π kötés: C(2p) – S(3p)
nem stabil

Példa: 3 CH_3-CH=S ⟶



tioaldehid

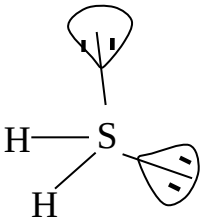
de:



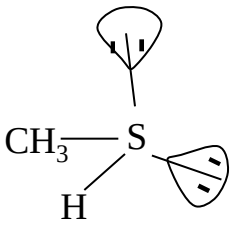
stabil

tioészter: konjugált rendszer

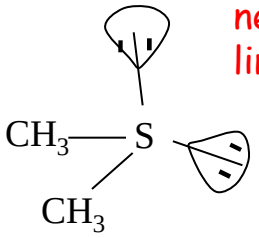
2 ligandumos kénvegyületek (tiol, tioéter)



HSH ∢ 92,5°
HOH 104,5°



CSH ∢ 96,5°
COH 105°



nem lineáris

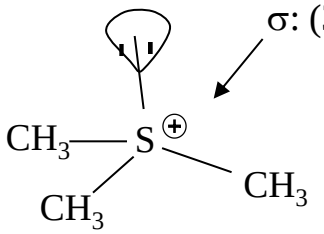
CSC ∢ 98,5°
COC 112°

σ: H(s) – S(p);
H - S: 335 kJ/mol
H – O: 452 kJ/mol

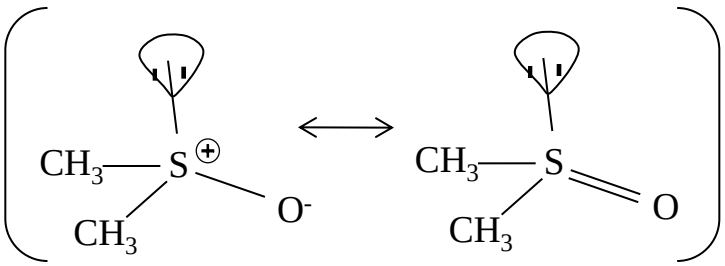
C(2sp³) – S(3p)
C - S: 267 kJ/mol
C – O: 347 kJ/mol

3 ligandumos kénvegyületek (szulfoxid, szulfóniumsó)

σ: $(3sp^3) – (2sp^3)$



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

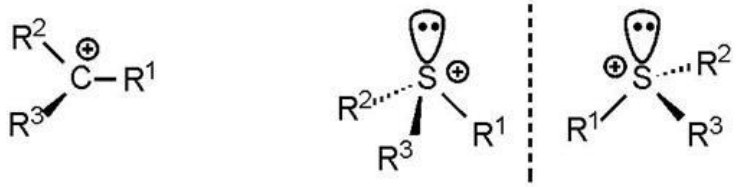


C – S: 1,81 Å
CSC kötésszög: 96,4°
piramisos, királis

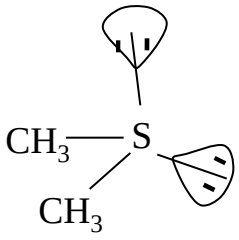
C – O: 1,47 Å
CSO: 106,7°

σ: $C(2sp^3) – S(3sp^3)$
$S(3sp^3) – O(2sp^2)$
π: S(3d) – O(2p)

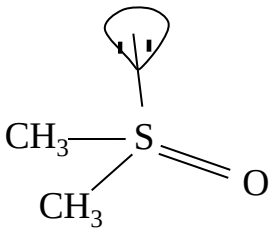
Összevetés



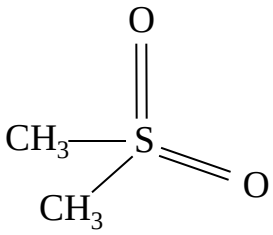
Összegzés



szulfid



szulfoxid



szulfon

Kötéshosszak:

C – S 1,82Å

C – S 1,81Å
S = O 1,47Å

C – S 1,78Å
S = O 1,44Å

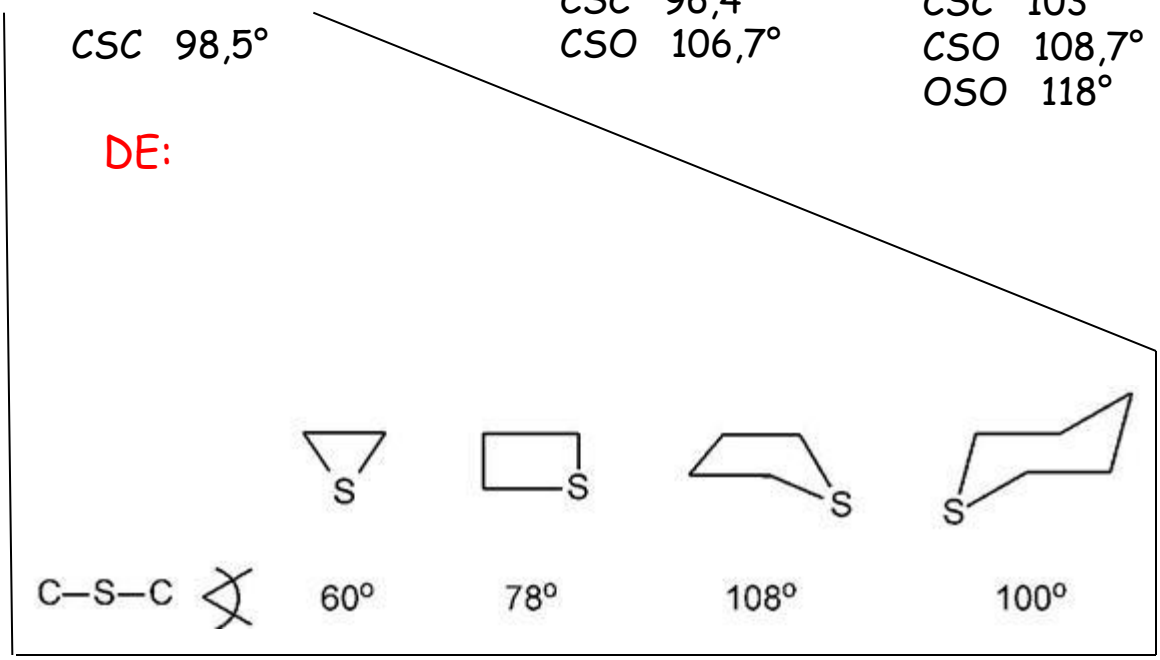
Kötésszögek:

CSC 98,5°

CSC 96,4°
CSO 106,7°

CSC 103°
CSO 108,7°
OSO 118°

DE:



Fizikai tulajdonságok

A. Tiolok

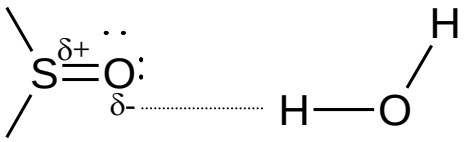
Forráspont (°C)	X=S	X=O
H_2X*	- 62	100
CH_3XH*	6	65
CH_3CH_2XH*	35	78
CH_3XCH_3	37	- 24

1/10 millió

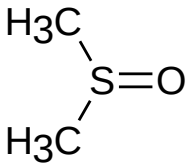
nincs H-híd kötés*

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

B. Szulfoxidok, szulfonok



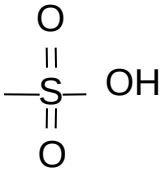
H-híd: akceptor



op: 18°C

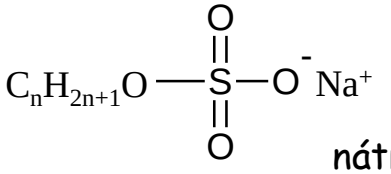
dipoláros, aprotikus oldószer

C. Szulfonsavak (O-H sav)



oldékonyság

detergensek:



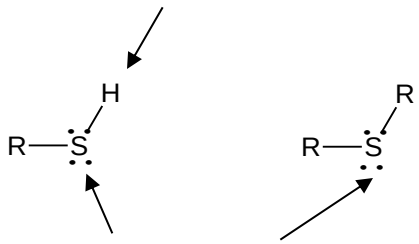
nátrium-alkilszulfát

Kémiai reakciók

1. Sav-bázis sajátság

Tiol, szulfid

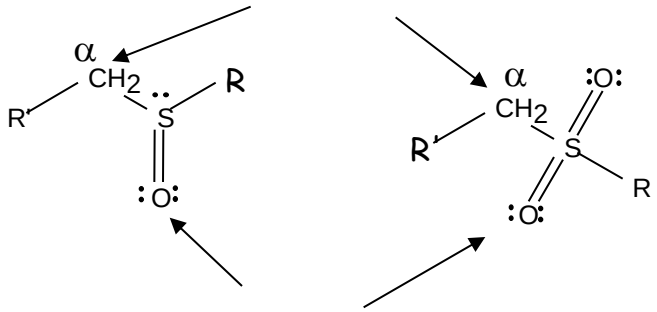
savas jelleg, pK_a=11 (vö. OH pK_a=17)



bázikus jelleg (gyengébb, mint :O:)

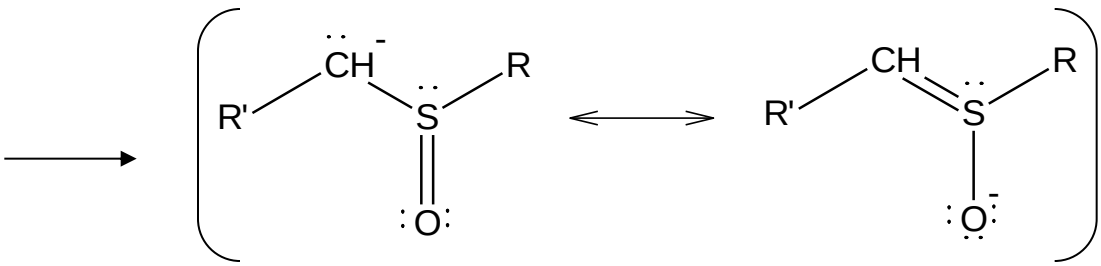
Szulfoxid, szulfon

savas jelleg



bázikus jelleg

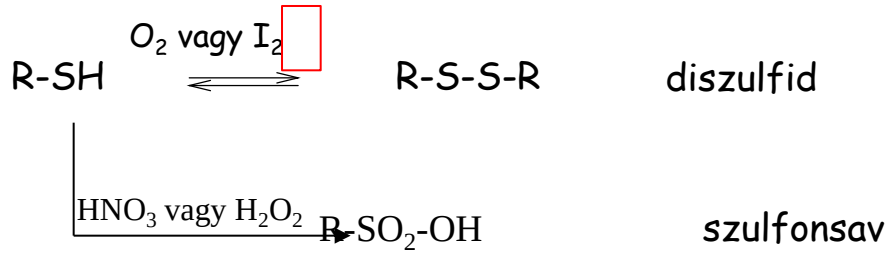
Példa: R-SO-CH_2-R' $\xrightarrow[EtO^-]{-H^+}$

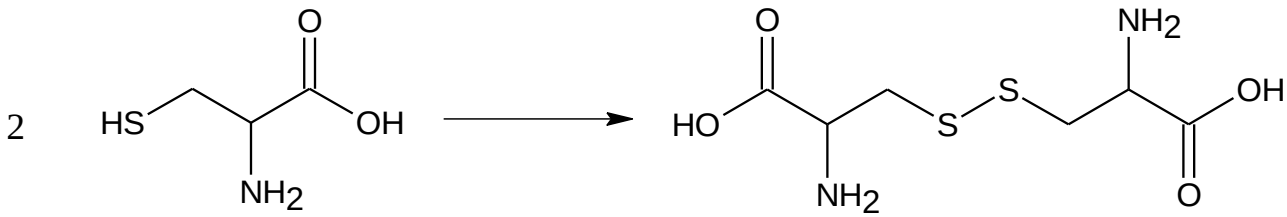


konjugáció: delokalizált, nincs tautomerizáció!

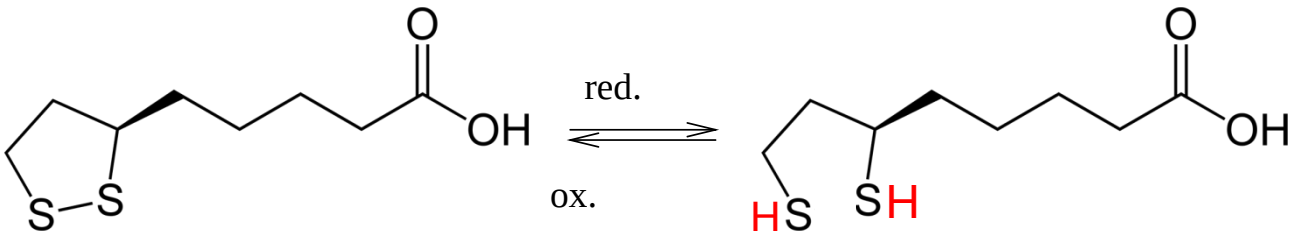
2. Oxidáció, redukció

Tiol





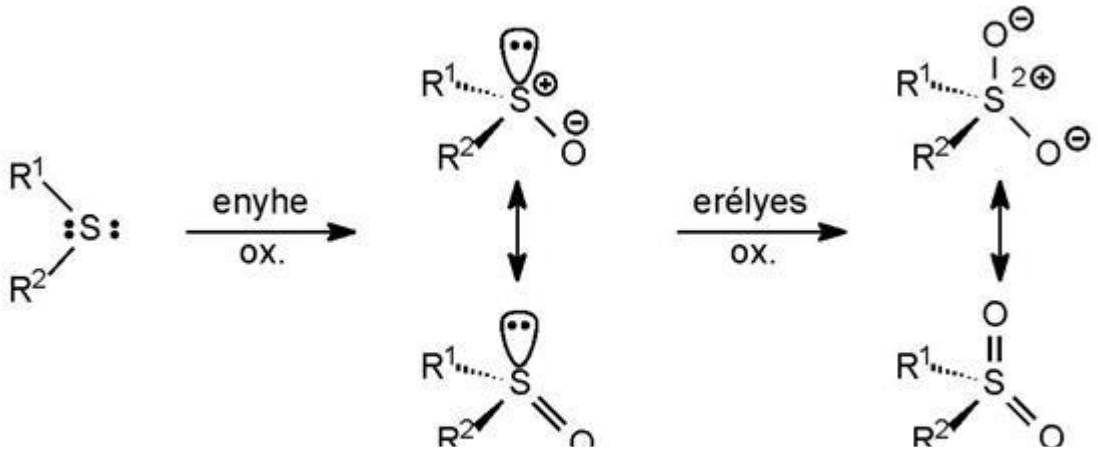
cisztein cisztin



liponsav dihidroliponsav

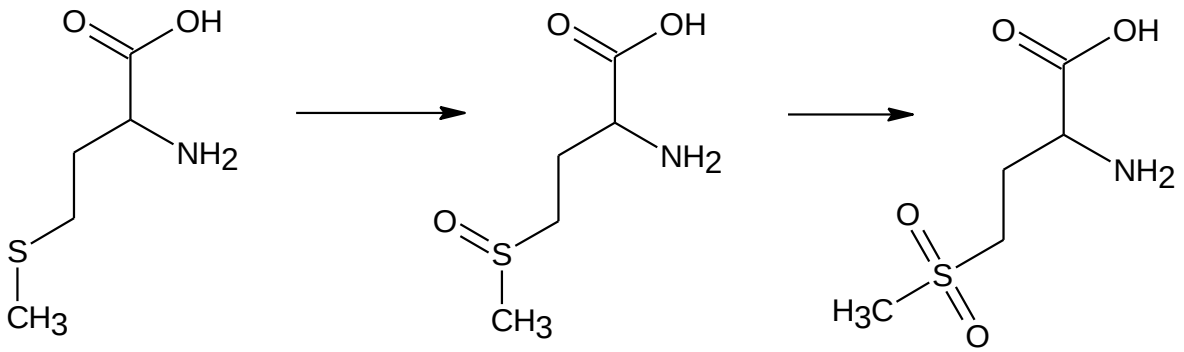
királis karbonsav,
kofaktor,
piruvát-dehidrogenáz komplex része,
antioxidáns

Szulfid



szulfid szulfoxid szulfon

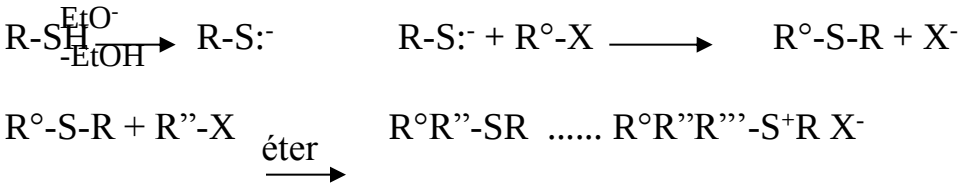
Példa:



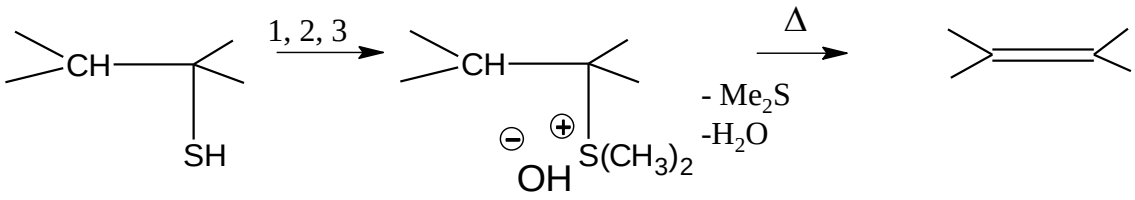
metionin metionin szulfoxid metionin szulfon

3. Nukleofil szubsztitúció

3.1. Alkilezés (tiol, tioéter)



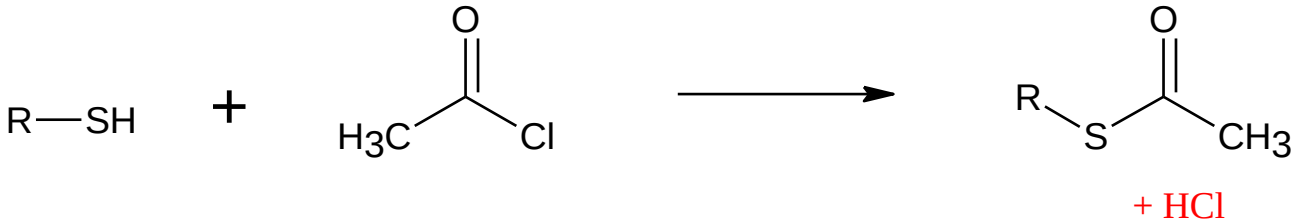
Hofmann-analóg elimináció



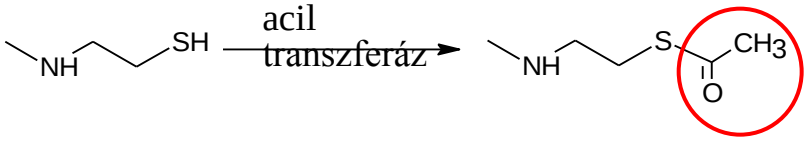
tiol szulfónium só alkén

1: EtO^-, MeI; 2: MeI, éter; 3: Ag_2O, H_2O

3.2. Acilezés



acetil-klorid alkil-tioacetát

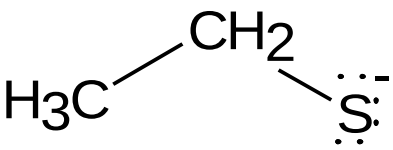


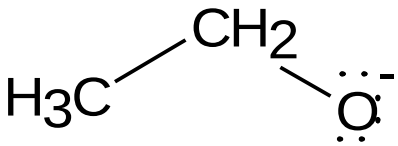
koenzim A acetil-koenzim A

-SH vs -OH reaktivitása - összevetés

(tiol, merkaptán = „mercurium captans")

1. Nukleofil sajátság





2. Savi jelleg -SH > -OH

3. Oxidáció $R\text{-}SH + H_2O_2 \longrightarrow R\text{-}S\text{-}S\text{-}R + 2\ H_2O$

Tiolok előállítása

1. $CH_3CH_2\text{-}Br\ (I) + KOH + \underset{\text{felesleg}}{H_2S} \xrightarrow[\Delta]{\text{EtOH}} CH_3CH_2\text{-}SH + KBr + H_2O$

ha nincs felesleg: $CH_3CH_2\text{-}SH + KOH \longrightarrow CH_3CH_2\text{-}S^-K^+$

$CH_3CH_2\text{-}S^-K^+ + CH_3CH_2\text{-}Br \longrightarrow CH_3CH_2\text{-}S\text{-}CH_2CH_3 + KBr$

tioéter

2. $CH_3CH_2\text{-}Br + (NH_2)_2\ddot{C}\text{=}S \xrightarrow{\text{EtOH}} (\overset{+}{N}H_2)_2C\text{=}S\text{-}CH_2CH_3\ Br^-$

tiourea

S-etil-izotiourónium-bromid

1. OH^-/H_2O
2. H^+

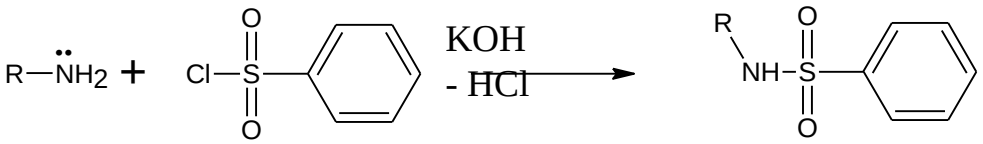
$(NH_2)_2C\text{=}O + CH_3CH_2\text{-}SH$

urea (karbamid)

etántiol

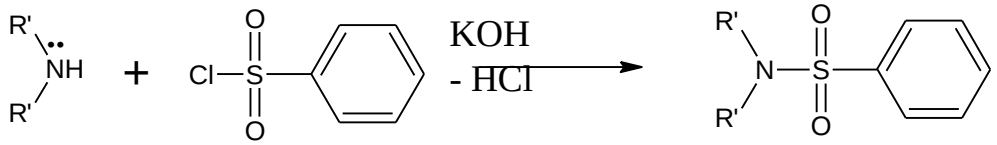
Kimutatás: Aminok reakciója szulfonil-kloriddal (Hinsberg-reakció)

1. Primer amin



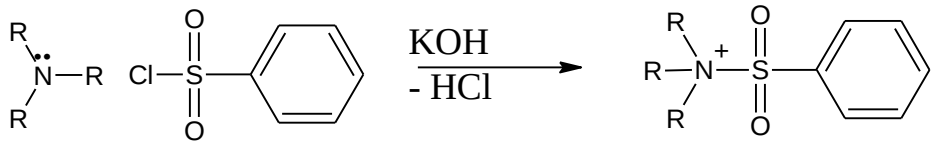
N-alkil-szulfonsavamid
(tiszta oldat $\xrightarrow{H^+}$ csapadék)

2. Szekunder-amin



N,N-dialkil-szulfonsavamid
(csapadék)

3. Tercier-amin



N,N,N-trialkil-szulfonsavamid
(csapadék $\xrightarrow[\text{hidrolízis}]{OH^-}$ tiszta oldat)

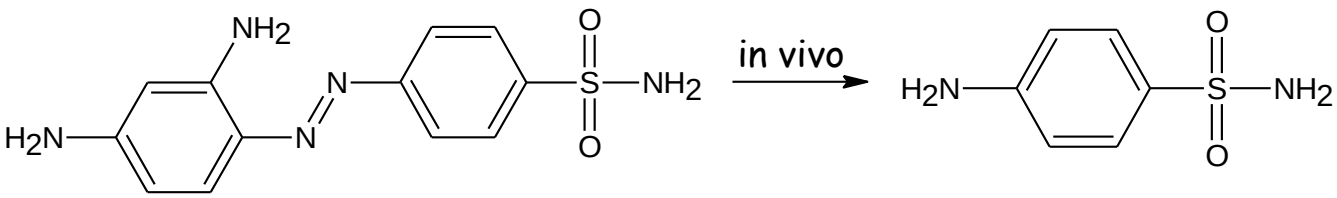
Antibiotikumok: szulfonamidok

(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

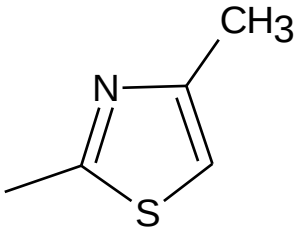


Prontosil (narancsvörös)

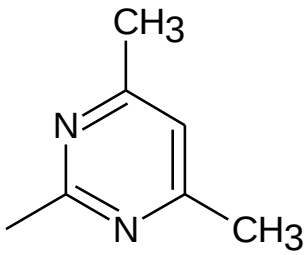
in vitro : „üvegben"
in vivo: „életben"

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

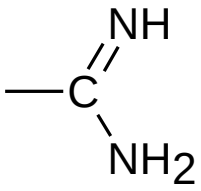
-NH-



Ultraseptyl

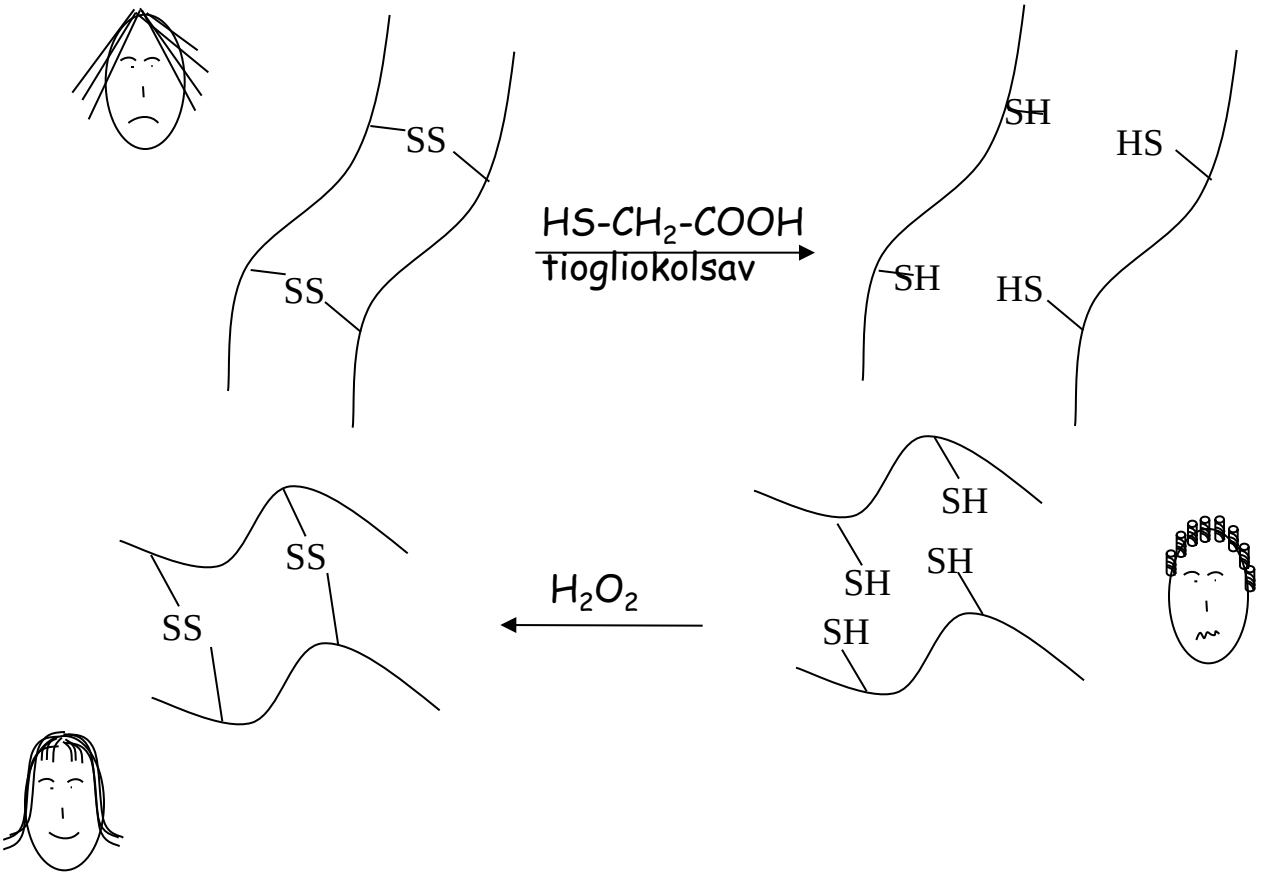


Superseptyl



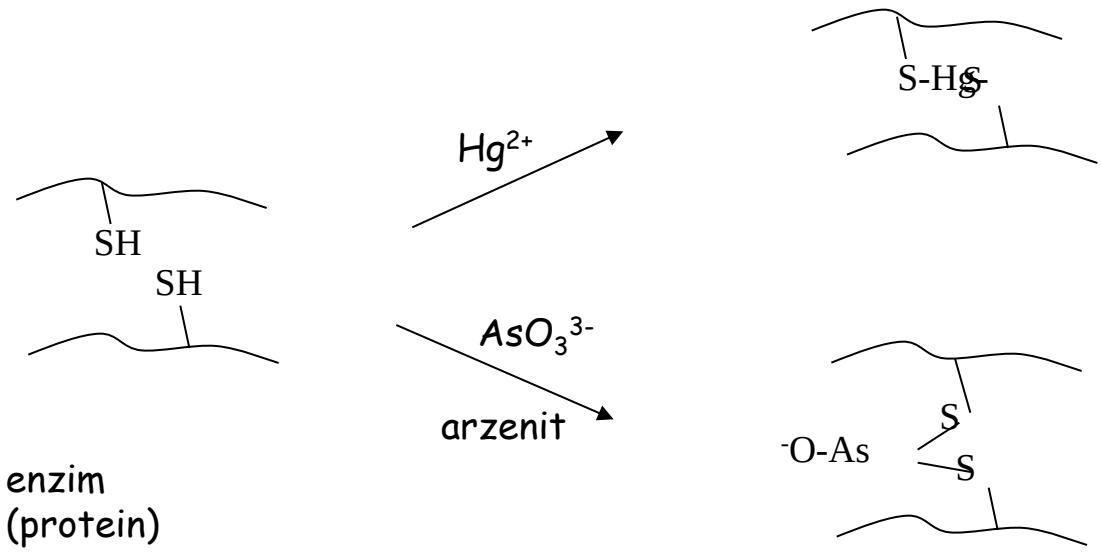
Sulfaguanidin

A fodrásznál



Mérgezés

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



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

Heterociklusos vegyületek

HETEROCIKLUSOS VEGYÜLETEK

Felosztás:

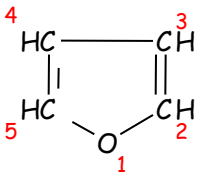
O oxa-

S tia-

N aza-

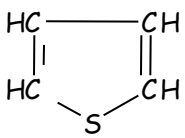
1. telített – telítetlen
2. heteroatomok száma
3. gyűrűk száma
4. heteroatomok milyensége (N, O, S, P, As, Si)

I. Monociklusos, egy heteroatomos vegyületek



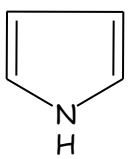
furán*

oxol



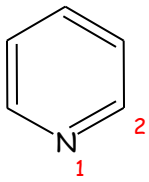
tiofén*

tiol



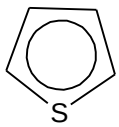
pirrol*

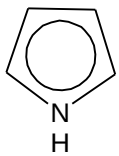
azol

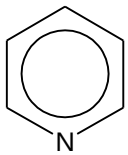


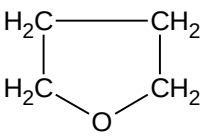
piridin*

azin



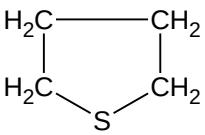






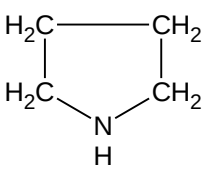
tetrahidrofurán*

oxolán



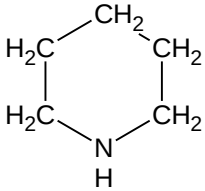
tetrahidrotiofén*

tiolán



pirrolidin*

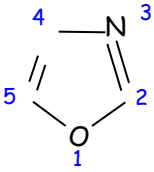
azolidin



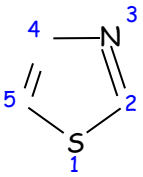
piperidin*

perhidroazin

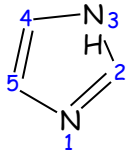
II. Monociklusos, két heteroatomos vegyületek



oxazol

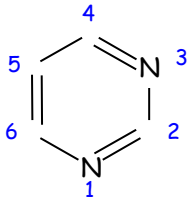


tiazol



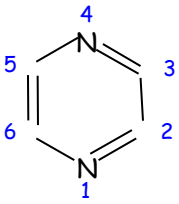
imidazol
(hisztidinben)

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



pirimidin (1,3-diazin)

(DNS, RNS-ben)



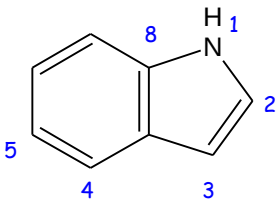
pirazin (1,4-diazin)

piridazin (1,2-diazin)

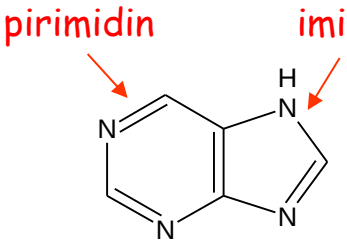
triazinok (3N), tetrazinok (4N)

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

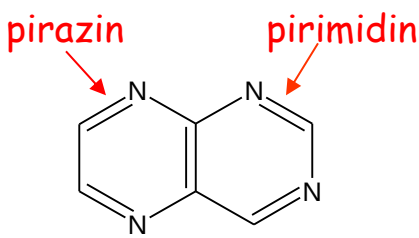
III. Biciklusos, kondenzált heteroatomos vegyületek



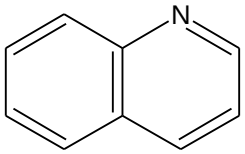
indol
(triptofánban)



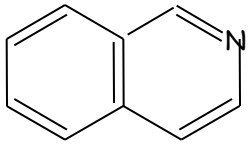
purin
(DNS, RNS-ben)



pteridin
(folsavban)



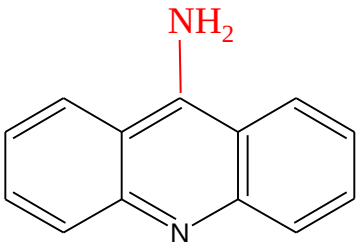
kinolin
(benzopiridin)



izokinolin

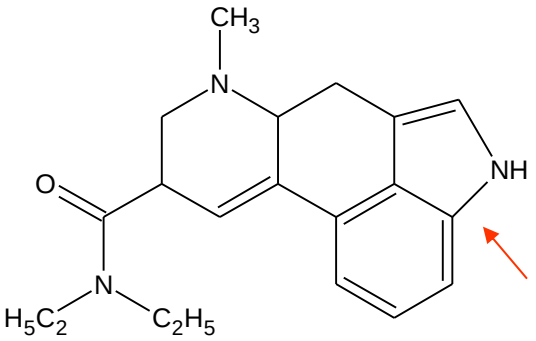
Festék alapanyag, tartósítószer, fertőtlenítő, oldószer, izokinolinvázas alkaloidok

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



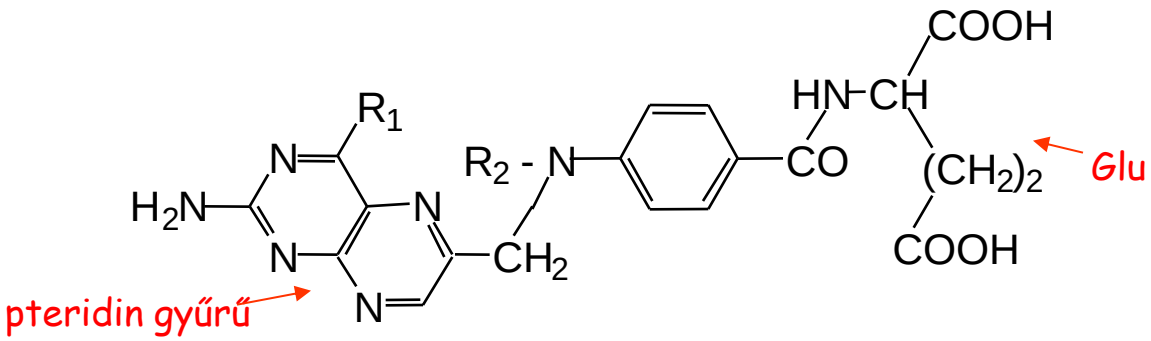
Akridin (váz)

9-aminoakridin:
erős fertőtlenítő szer
fluoreszcens tulajdonságú



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

Folsav analógok



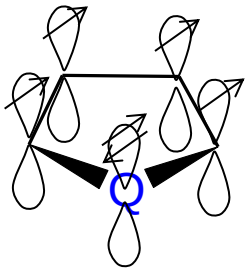
$R_1 = OH, \quad R_2 = H$	folsav; B9-vitamin, M-vitamin.
$R_1 = NH_2, \quad R_2 = H$	aminopterin
$R_1 = NH_2, \quad R_2 = CH_3$	amethopterin, methotrexat

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

Metotrexát: tumorellenes szer, reumatoid artritisz

Elektronszerkezet

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



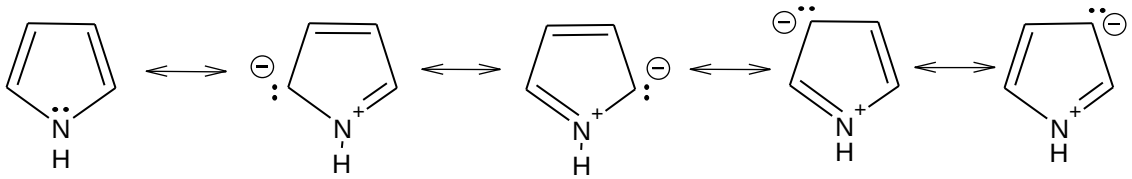
Q = :S: , : N , :O:

EN = 2,6 3,0 3,5

S < N < O

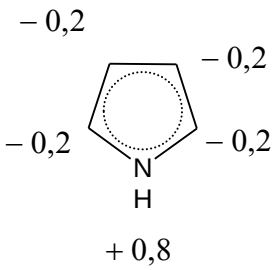
- I effektus (hetero atom EN-nak megfelelő mértékben vonzza az elektronokat)

Tiofén hasonlít legjobban a benzolra,de az elektrofil szubsztitúciós reakció gyorsabbak.

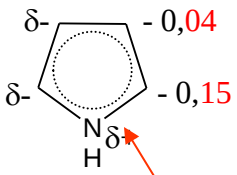


K-effektus

határszerkezetek!



„egyenletes"



valóságos

$S^{\delta+}$ 0,2

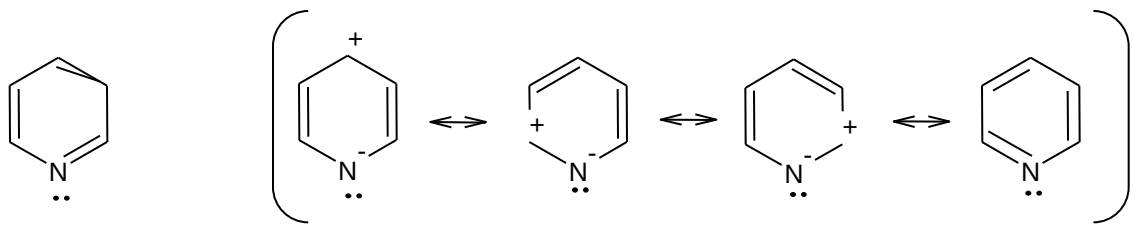
$O^{\delta+}$ 0,3

$N^{\delta+}$ 0,38

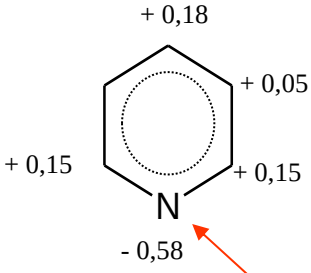
elektroneloszlás

csak határszerkezetekből

nem bázis, nem proton kedvelő



piridin



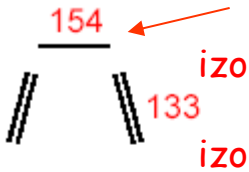
bázis, proton kedvelő

Téralkat

kötéshosszak (pm)

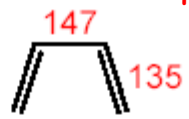
Konjugált kettős kötés esetén az egyes és kettős kötés hossza

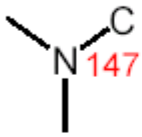
pm: 10^{-12} m
Å: 10^{-10} m

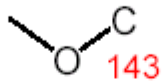


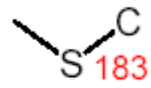
izolált egyes kötés

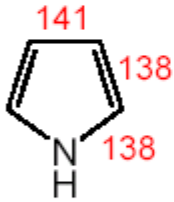
izolált kettős kötés

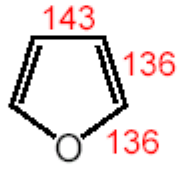


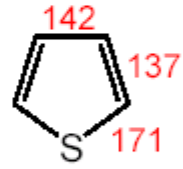






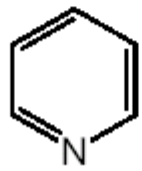






aromás rendszer

Kötéshossz : S-C > N-C > O-C

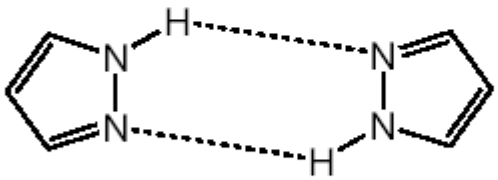


C=C (C_6H_6)	139
C—N	147
C≡N	130

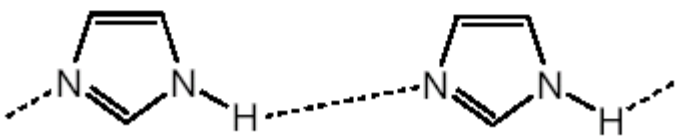
Fizikai tulajdonságok

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



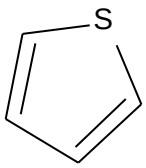
imidazol

Kémiai reakciók

1A. Sav-bázis sajátság (egy heteroatom)

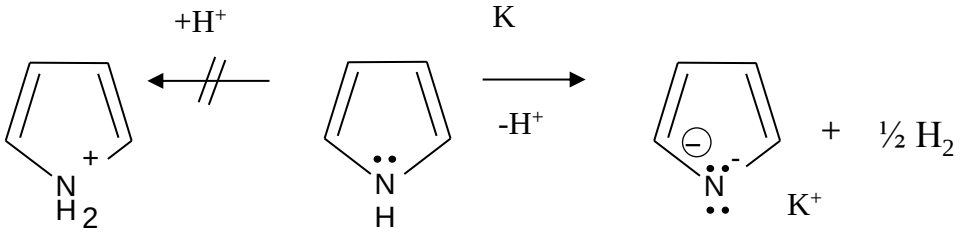
(sav: protont tud leadni; bázis: protont tud felvenni)

tiofén



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

pirrol:

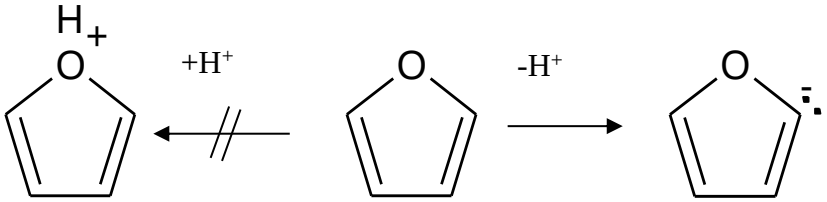


(pK = 15)

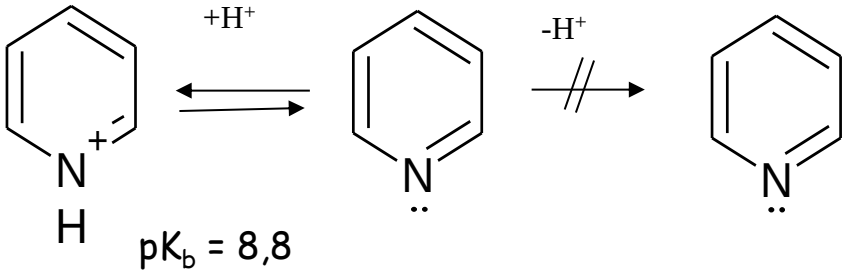
megszűnik az aromás jelleg

aromás marad (tehát gyenge N-H sav)

furán:



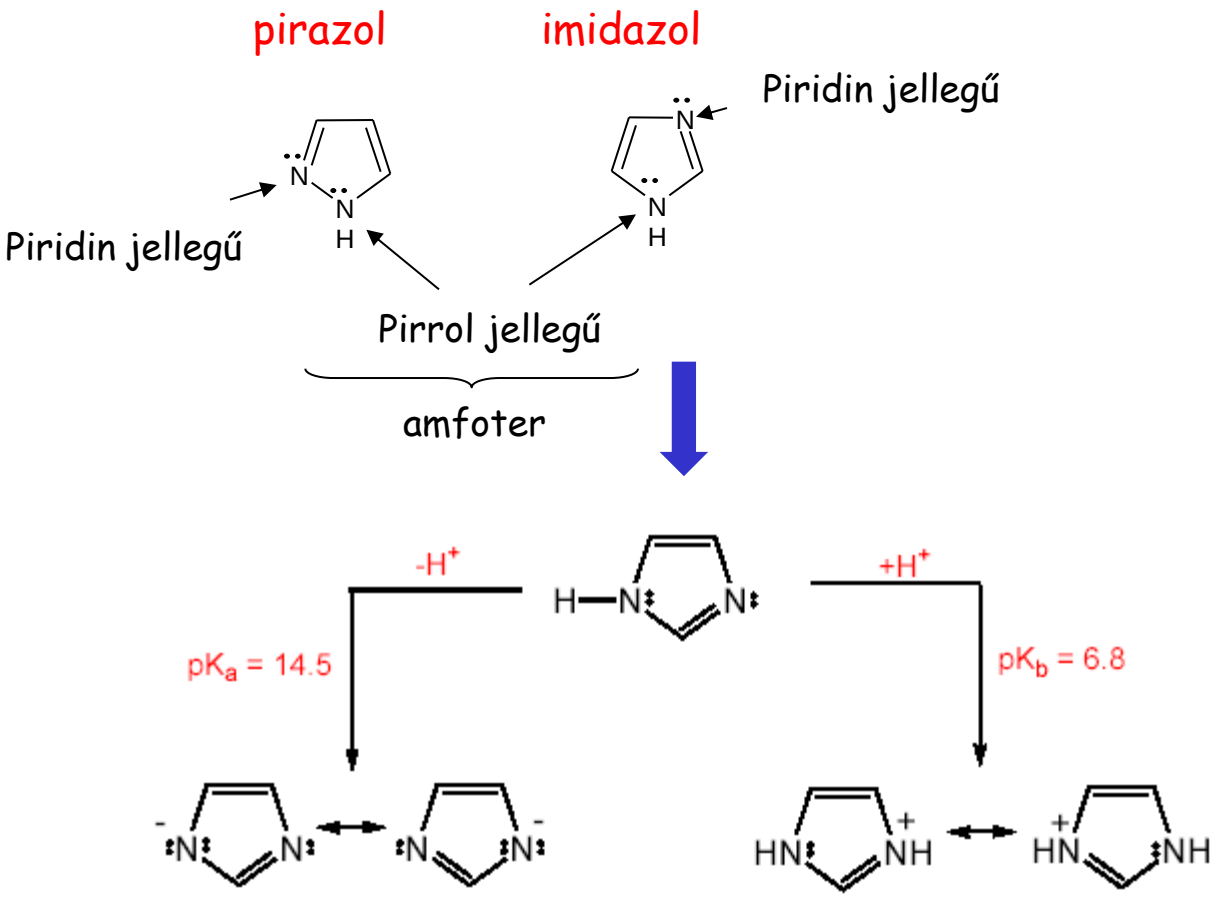
piridin:



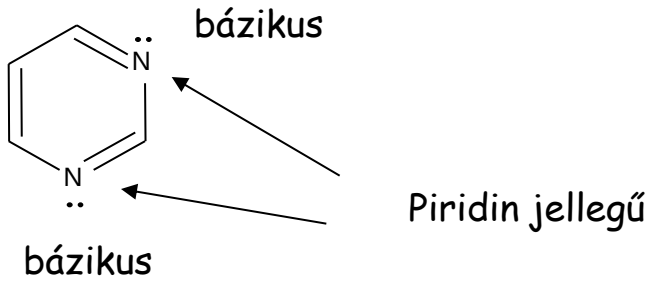
pK_b = 8,8

gyenge bázis

1B. Sav-bázis sajátság (két heteroatom)



pirimidin



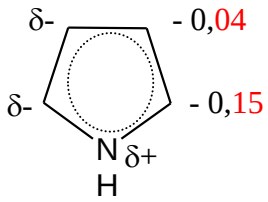
2. Elektrofil szubsztitúciók

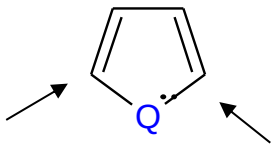
Feltétel: elektronban „gazdag” gyűrűk

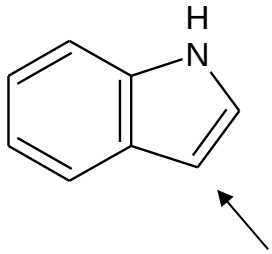
A. pirrol, furán, tiofén, indol

pozitív töltés vagy parciális pozitív töltésű rész
támad elektronban gazdag helyre

Irányítás

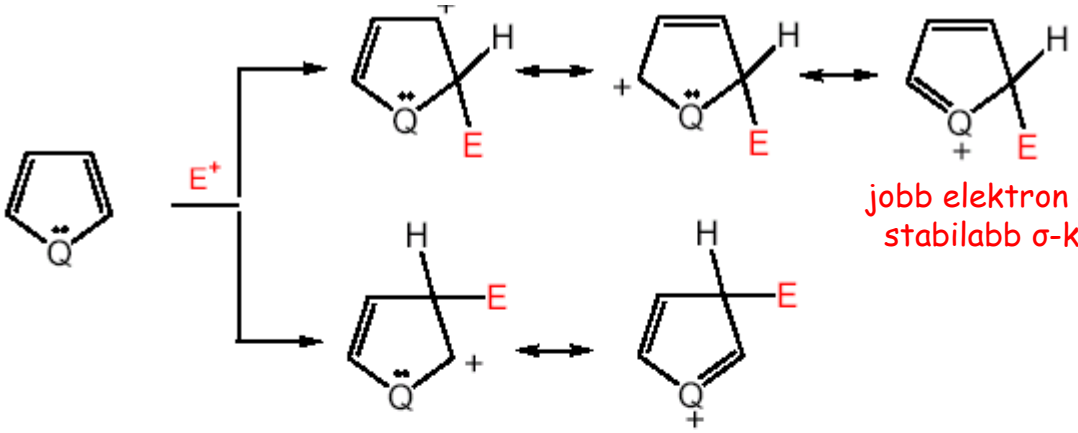




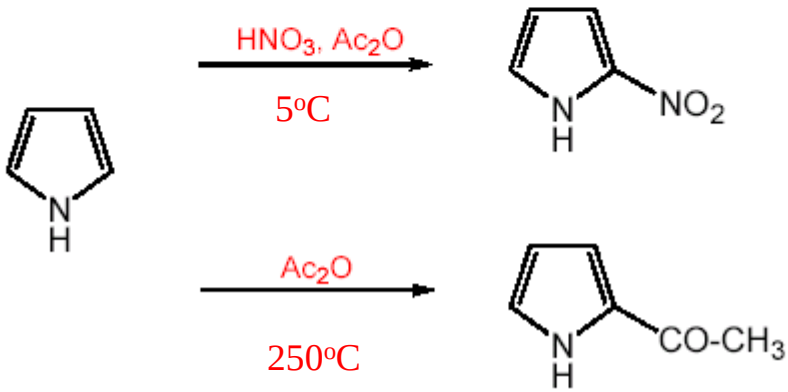


Reaktivitás

σ-komplexek lehetséges határszerkezete 2-es és 3-as helyzetű szubsztitúció esetén:

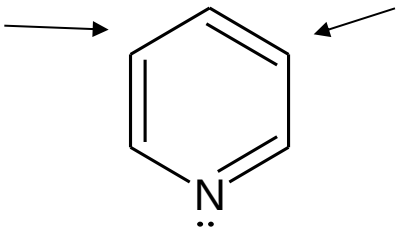


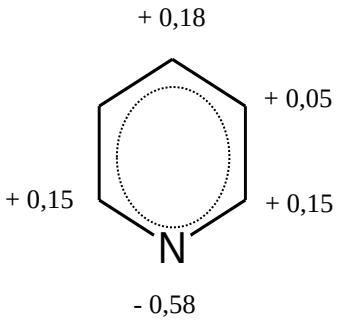
Példák



B. piridin

Irányítás

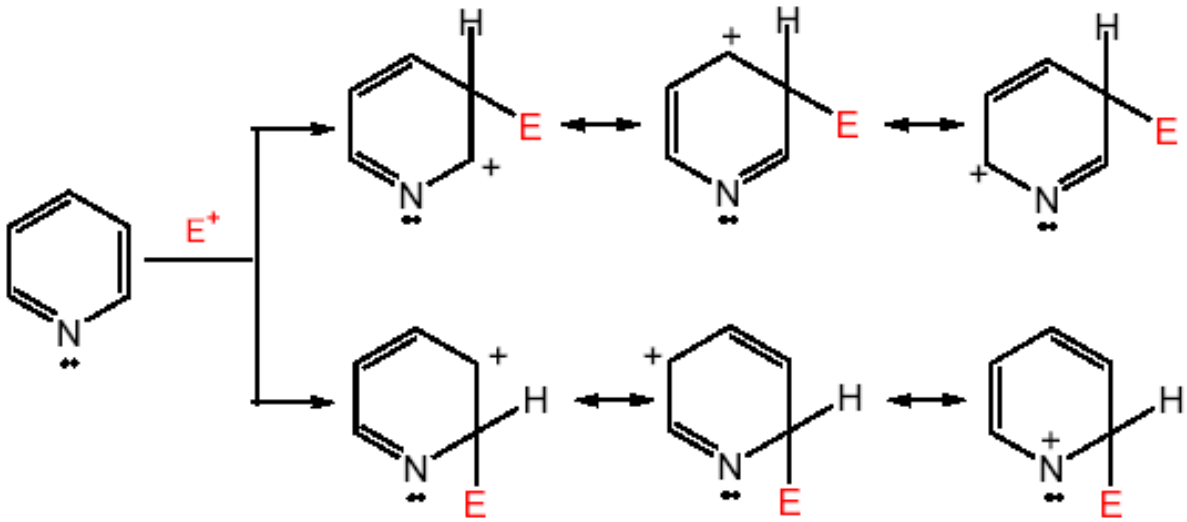




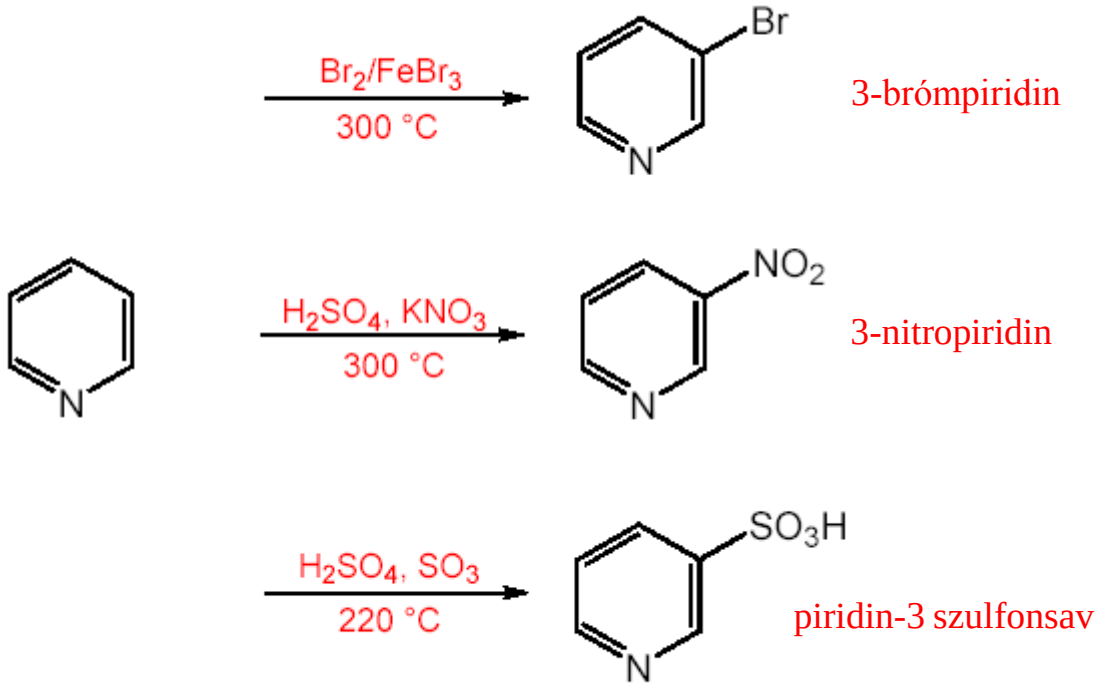
Reaktivitás

legkevésbé + helyre igyekszik kötődni

stabilabb σ-komplex



Példák (kénsav – protonálódás)

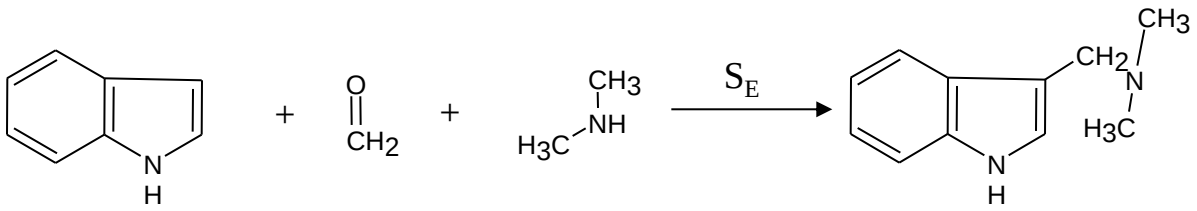


		pirrol	furán	tiofén	benzol ↓ piridin
nitrálás	NO_2^+	+	+	+	+*
szulfonálás	SO_3	+	+	+	+*
diazo kapcsolás	Ar-N≡N	+	+		
Friedel-Crafts acilezés	CH_3-CO-Q	+	+	+	
brómozás	Br_2	+		+	+

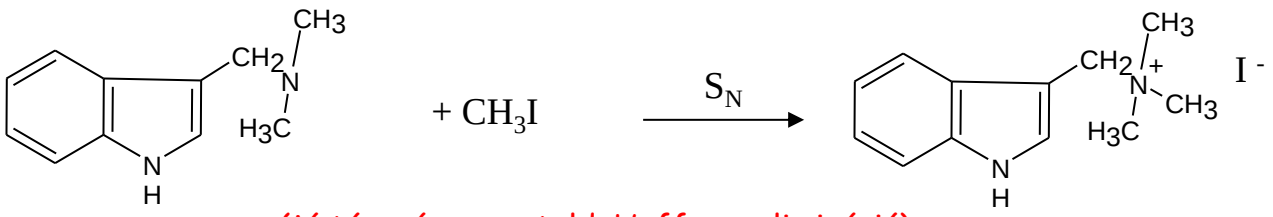
* protonálás után

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

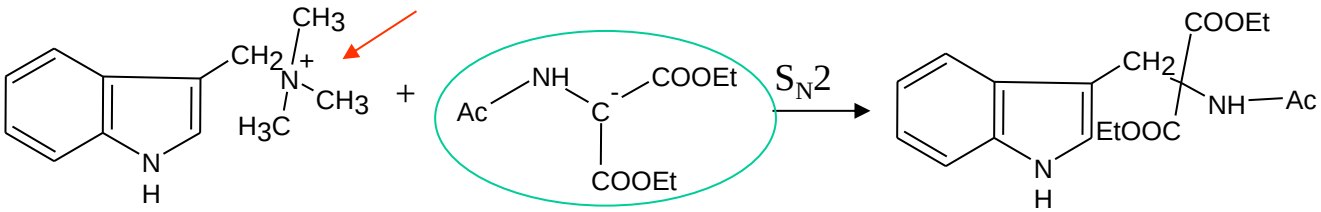
1. lépés Aminometilezés



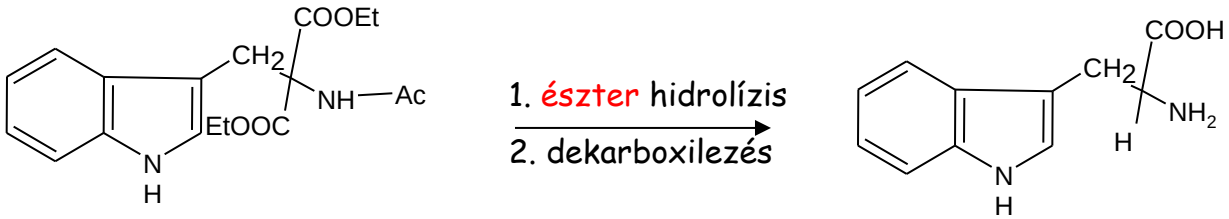
2. lépés Alkilezés



(jó távozó csoport, ld. Hoffman elimináció)



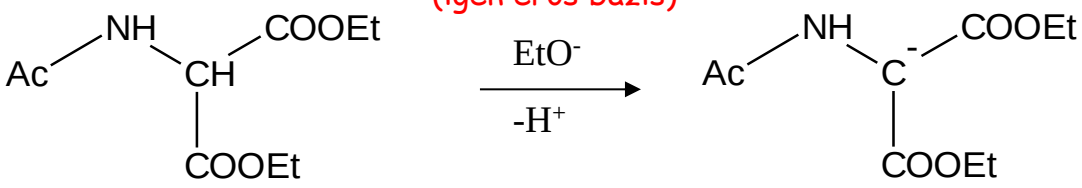
3. lépés Hidrolizis, dekarboxilezés



Triptofán (Trp)

---

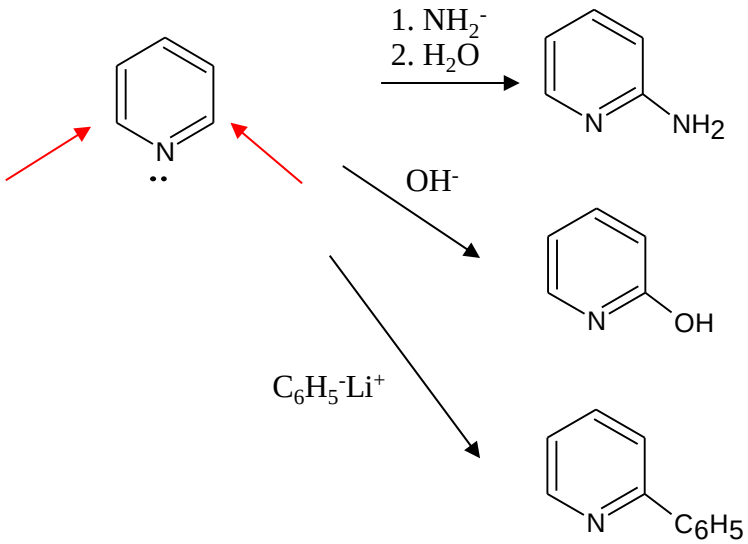
nátrium-etilát
(igen erős bázis)



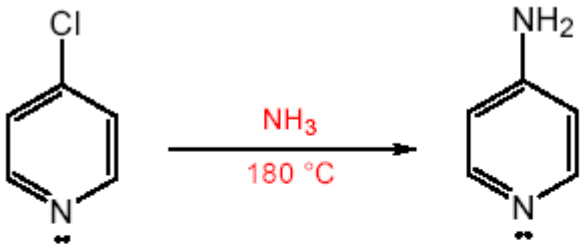
acetamido-malonészter (C-H sav)

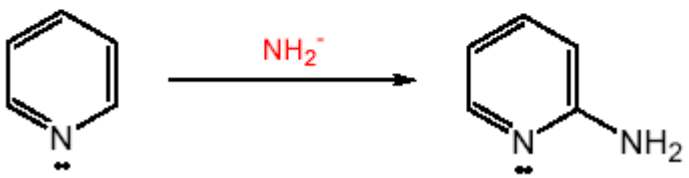
3. Nukleofil szubsztitúciók

Feltétel: elektronban „szegény” gyűrűk

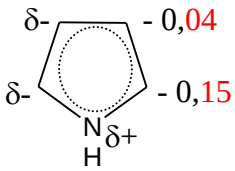


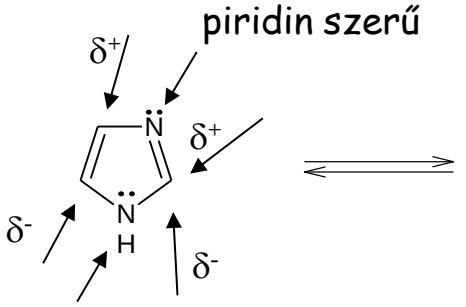
Összehasonlítás



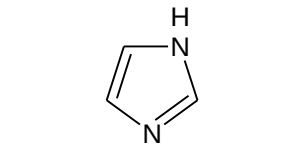


Kétheteroatomos vegyületek reaktivitása

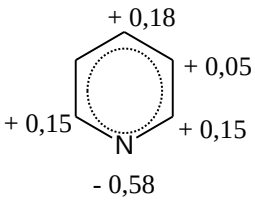


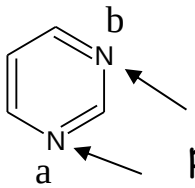


pirrol szerű



(tautoméria)



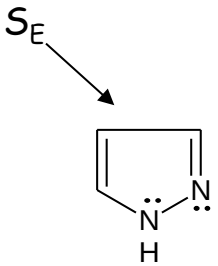


piridin szerű

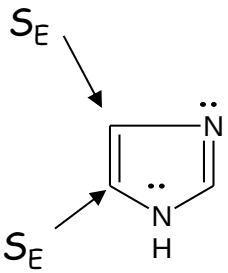
Pozíció	N_a	N_b
2	δ+	δ+
4	δ+	δ+
5	δ-	δ-
6	δ+	δ+

Relatív elektronhiány: 4 = 6 > 2 > 5

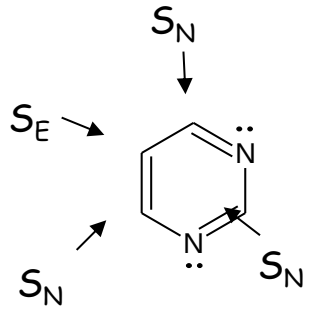
Magyarázat: a parciális töltések szuperponálódnak



pirazol



imidazol

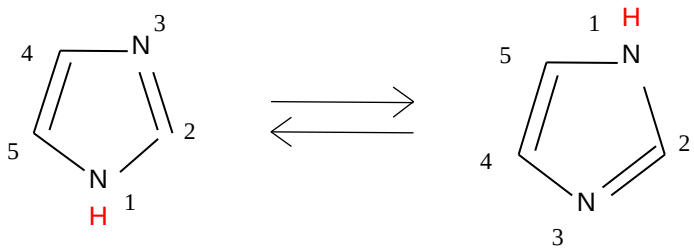


pirimidin

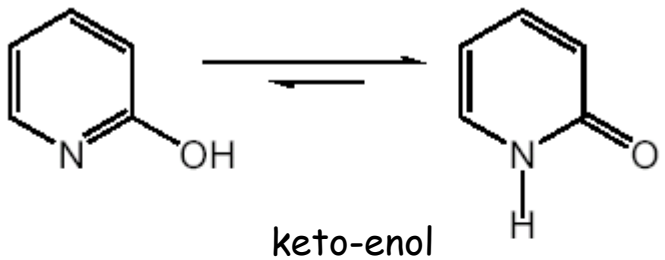
Tautoméria

egy kettős kötés és egy proton helyzetének megváltozása

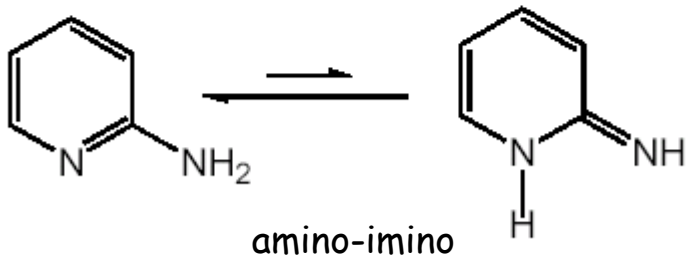
Imidazol



Piridin származékok

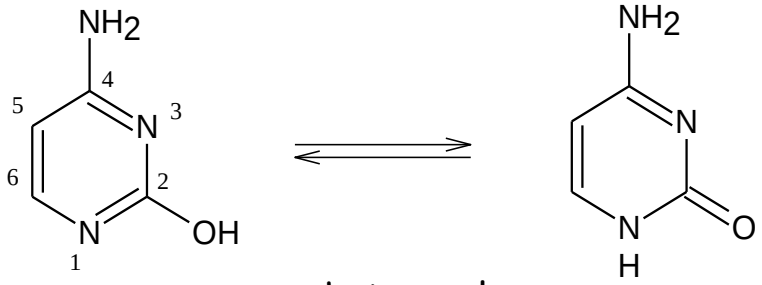


keto-enol



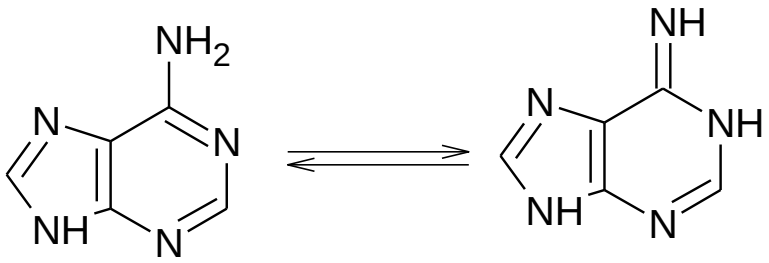
amino-imino

Pirimidin (citozin))



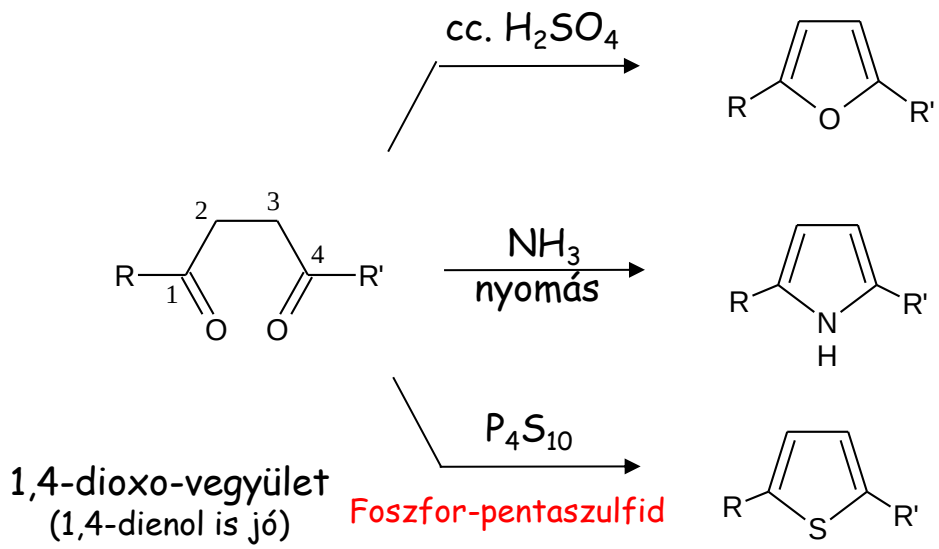
keto-enol

Purin (adenin)

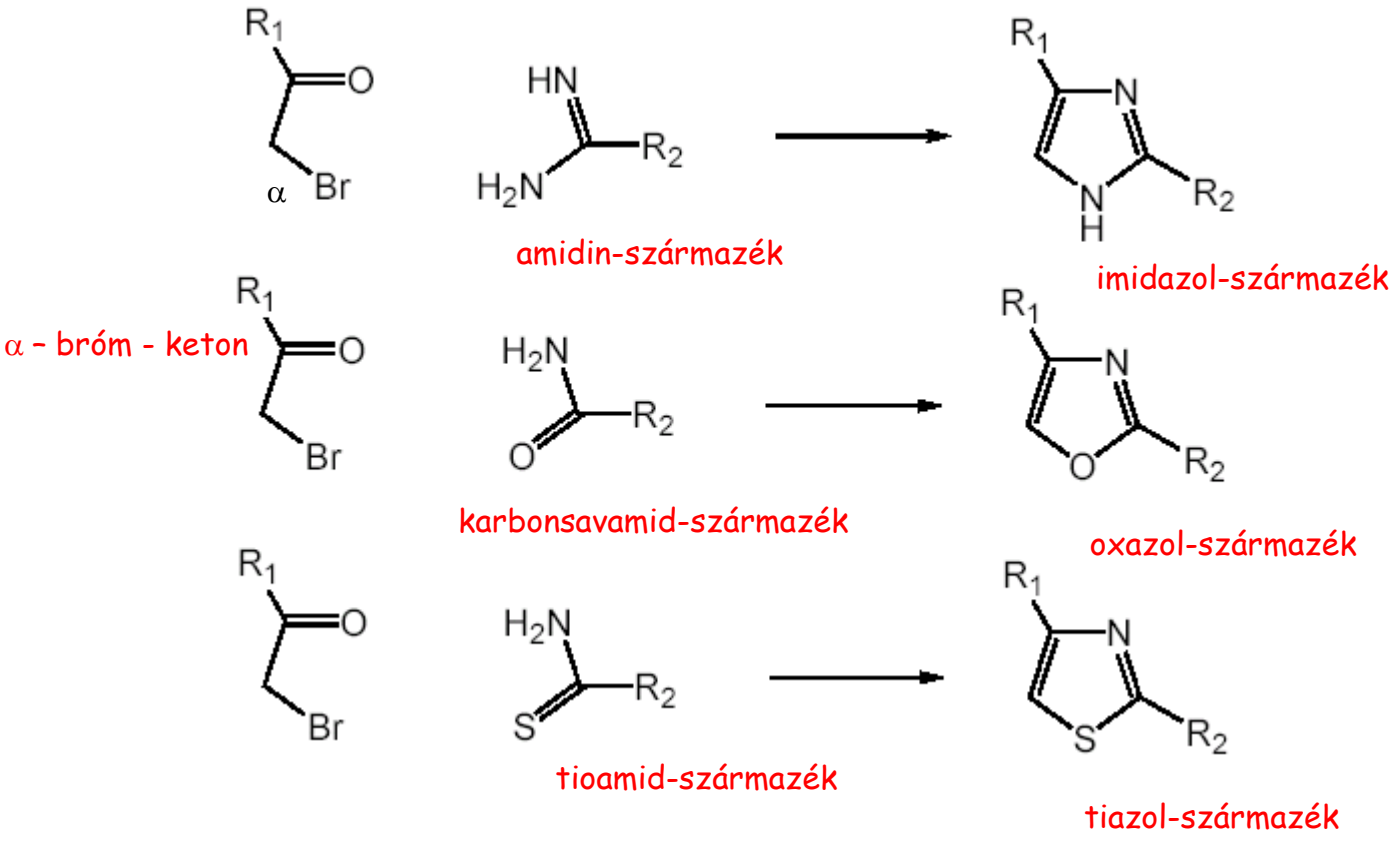


amino-imino

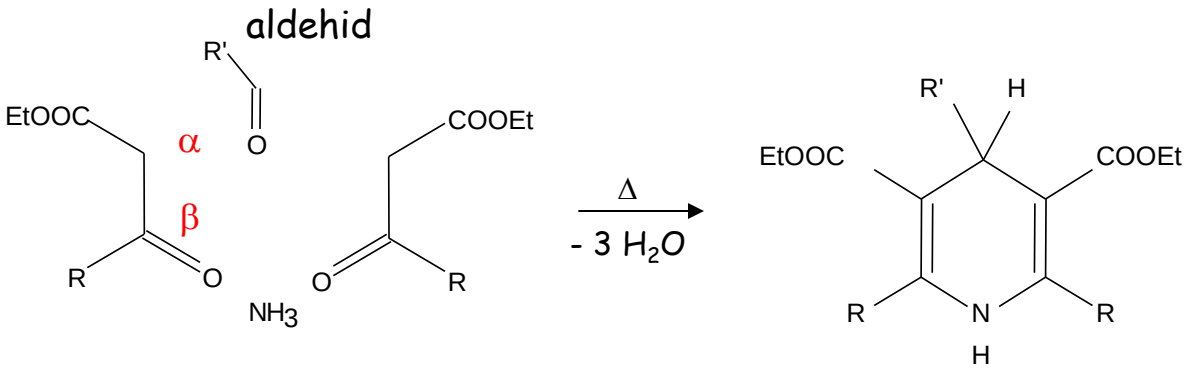
Furán, tiofén, pirrol vázas vegyületek szintézise (Paal-Knorr)



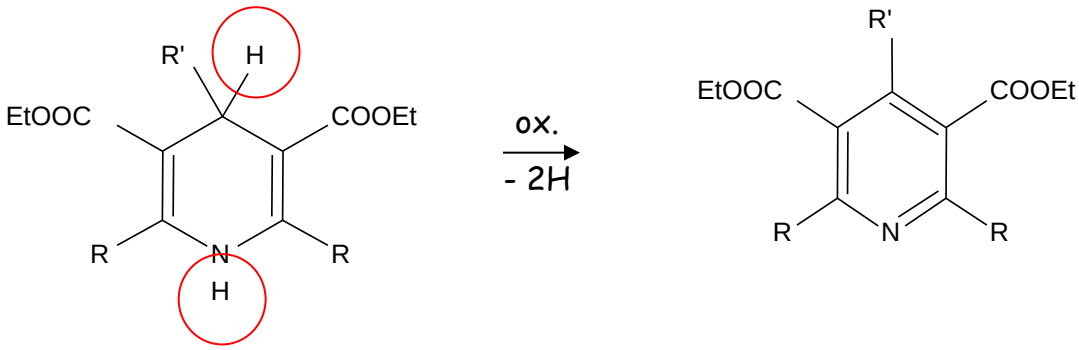
Példák



Piridin szintézis (Hantzsch)

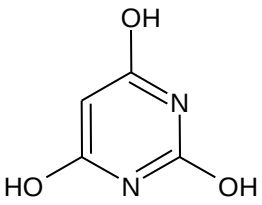


β - oxo karbonsav észter

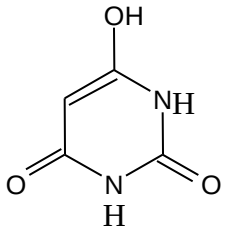


piridin-származék

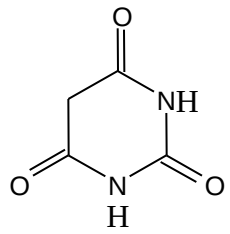
Purin szintézis



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

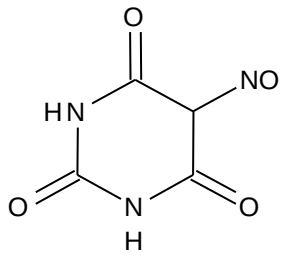


dilaktám-enol

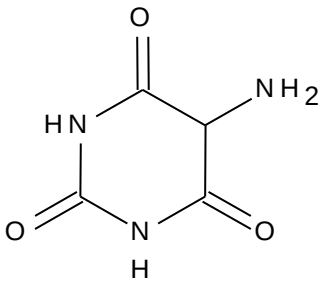


dilaktám-keto

HNO_2/HCl

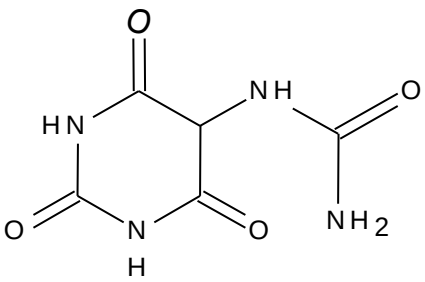


H_2/red



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

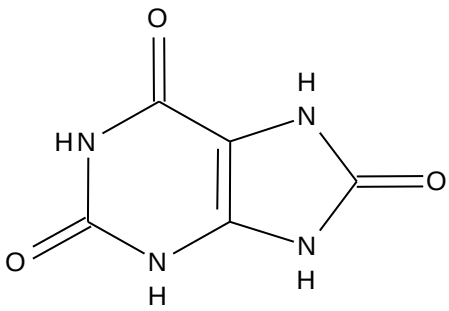
1. KOCN
2. Wöhler-
izomerizáció



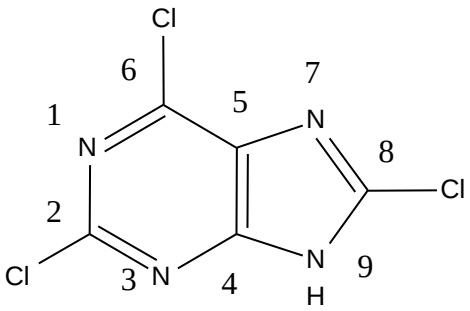
pszeudohúgysav

$-H_2O$

HCl
(20%)



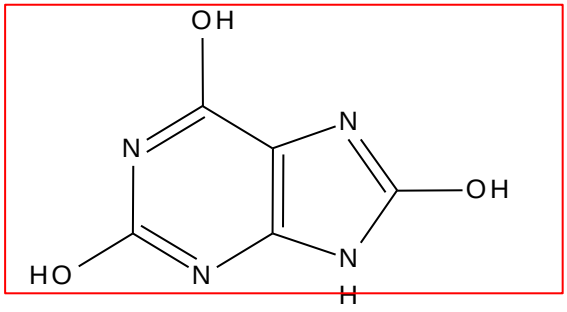
keto – enol
tautoméria



2,6,8-triklór-purin

$POCl_3$

140°C

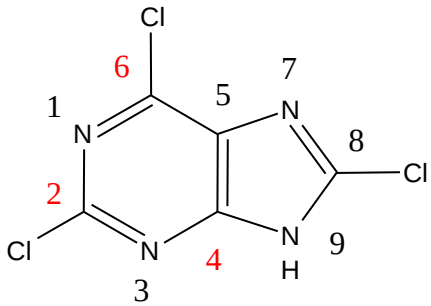


2,6,8-trihidroxi-purin (húgysav)

Purin szintézis (folytatás)

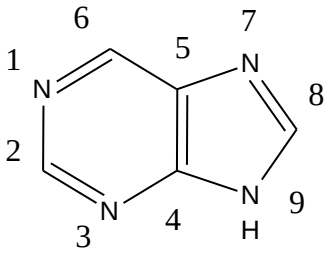
Reaktivitási sorrend

6 > 2 > 8



2,6,8-triklór-purin

Reduktív dehalogénezés

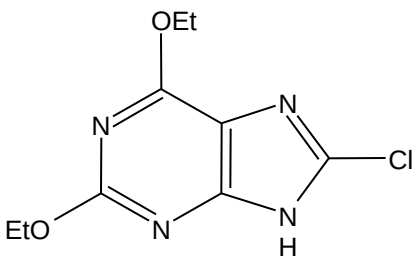


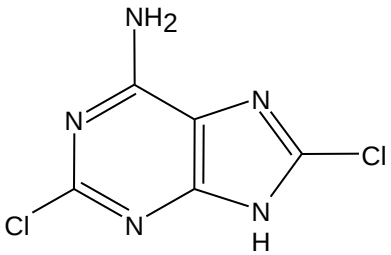
purin

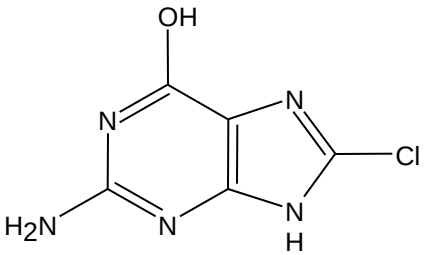
+ 2 Na^+EtO^-

+ NH_3

1. KOH
2. NH_3



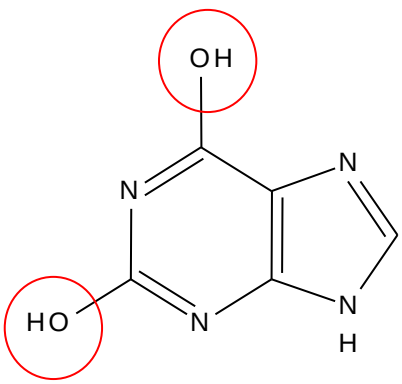


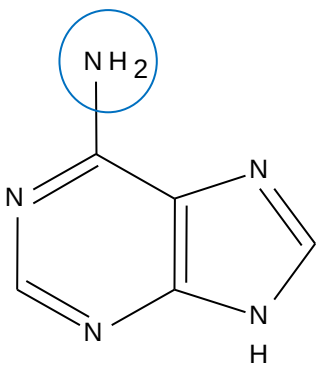


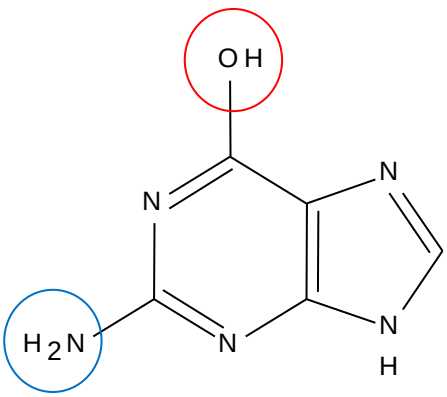
1. Elfőzés (cc. HCl)
2. red.dehalogénezés

red. dehal.

red. dehal.







xantin

6-aminopurin
(adenin)

guanin

Porfinvázas vegyületek

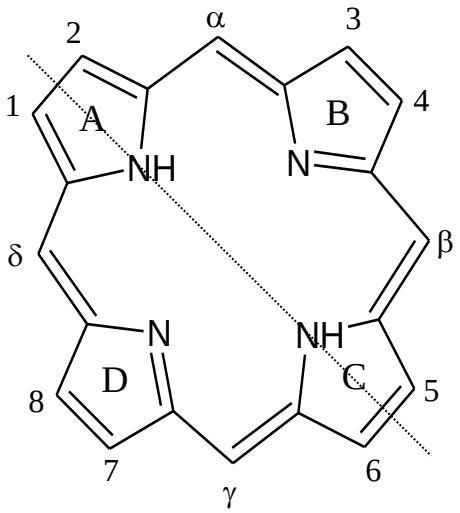
Makrociklus: ciklusba zárt molekula (nincs végcsoport)

vagy molekularészlet, amely

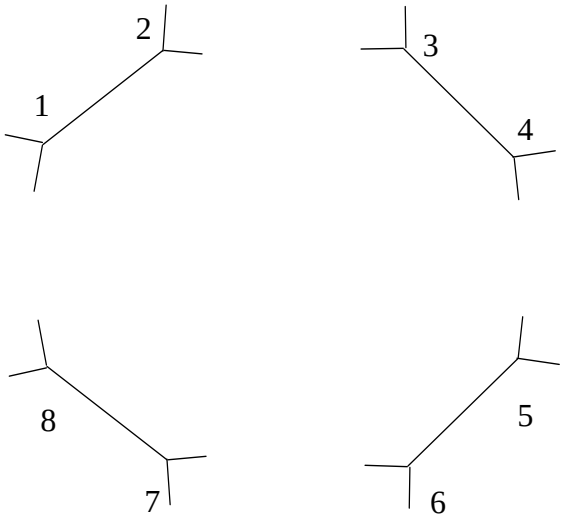
> 12 atomot tartalmaz

Porfinvázas vegyületek:

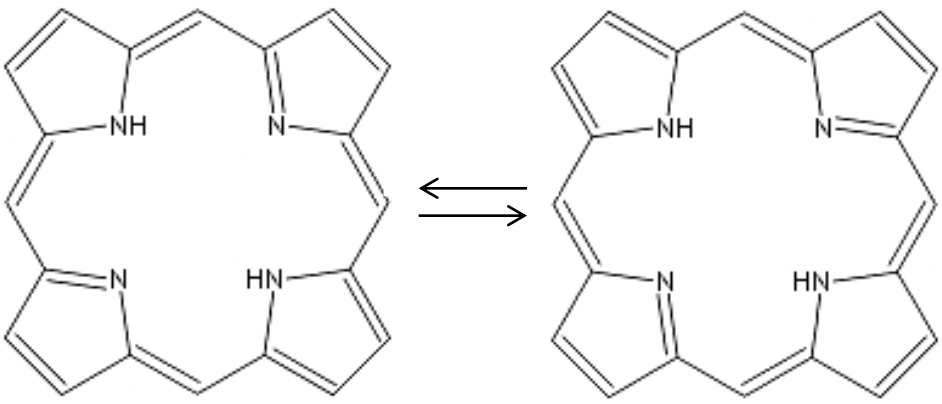
négy pirrol vagy részlegesen telitett pirrolgyűrűt



porfin – váz



Egyszerűsített jelölésmód



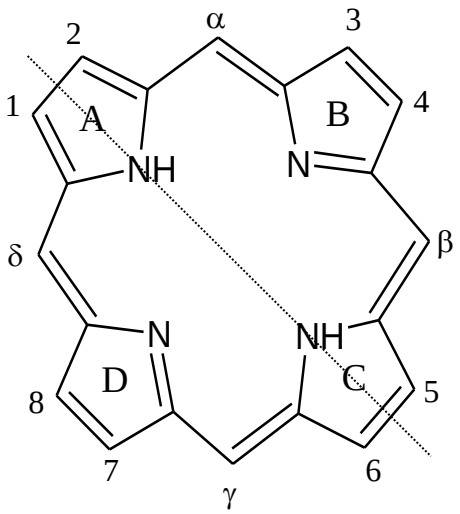
porfin izoporfin

Jellemzés:

1. síkalkat, 4n+2 elektron (26) → aromás makrociklus
2. amfoter jelleg a) NH → protonleadás

b) N: ← proton felvétel

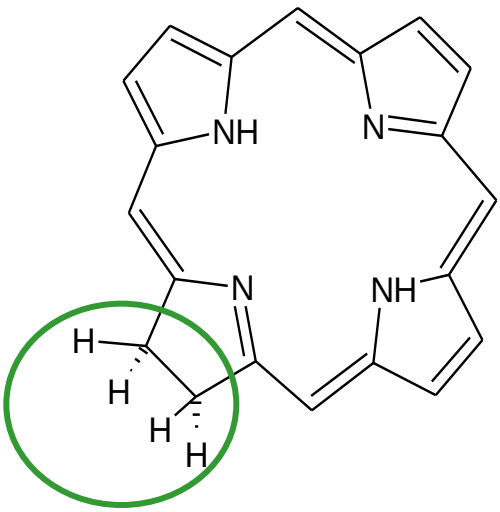
Porfinvázak



porfin – váz

(hem-proteinek)

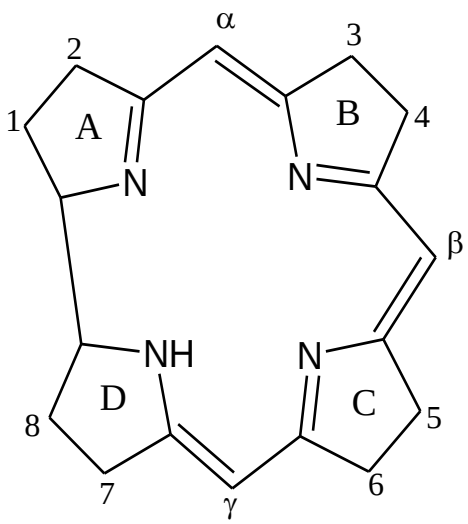
Fe^{2+} / Fe^{3+}



klorin (7,8-dihidro-porfin) – váz

(klorofill)

Mg^{2+}



korrin

(B_{12} vitamin)

Co^{3+}

Funkció: 1. 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, Fe^{3+})

1.5 Citokrómok (terminális oxidáció, $Fe^{2+} \rightarrow Fe^{3+}$)

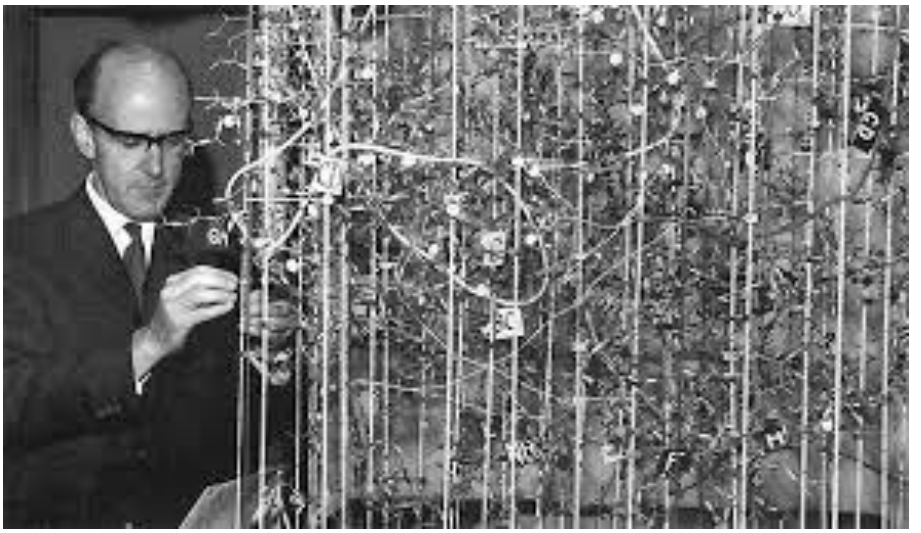
2. Klorofill (zöld növények)

3. Cianokobalamin (B12 vitamin)

1.1. Hemoglobin (1862, kristályos)

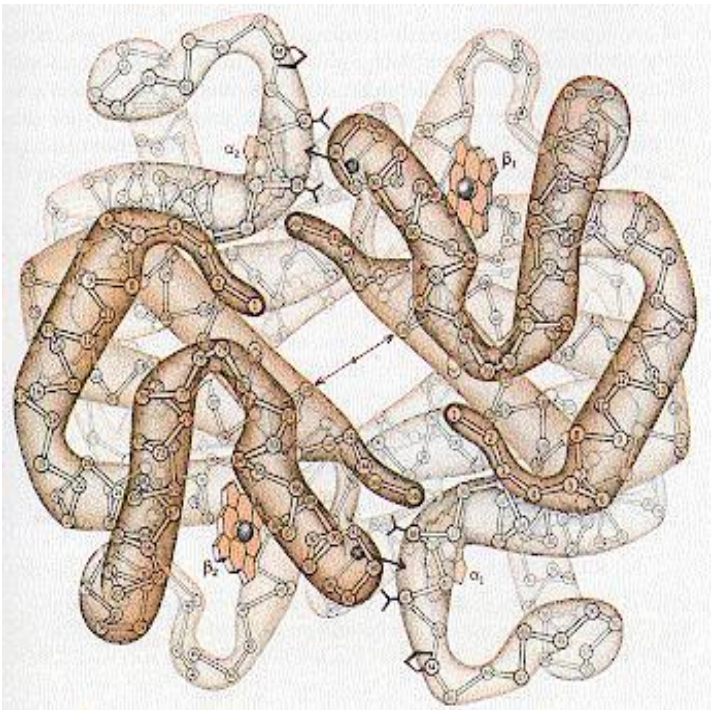
Prosztetikus csoport (vörös) +

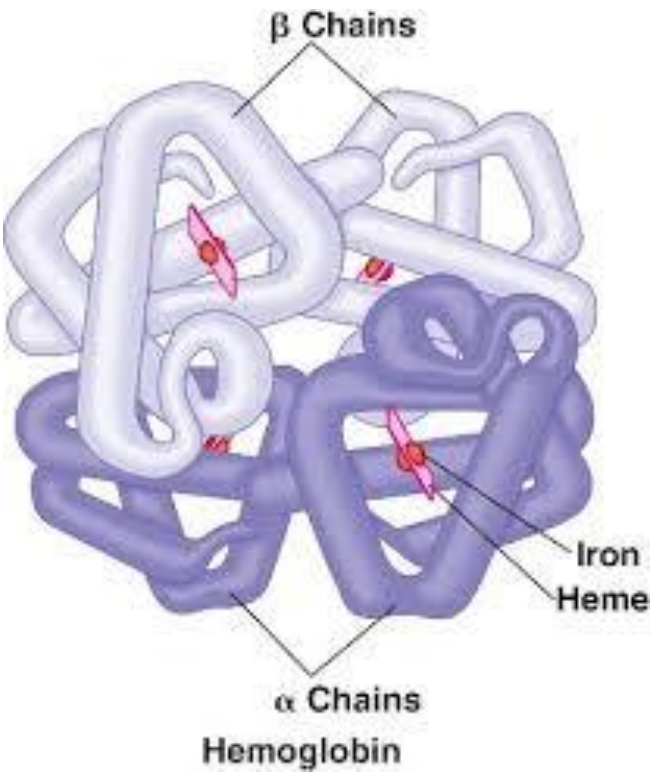
globin (4 polipeptid lánc, Mt: 17 000)



Max F. Perutz, 1960

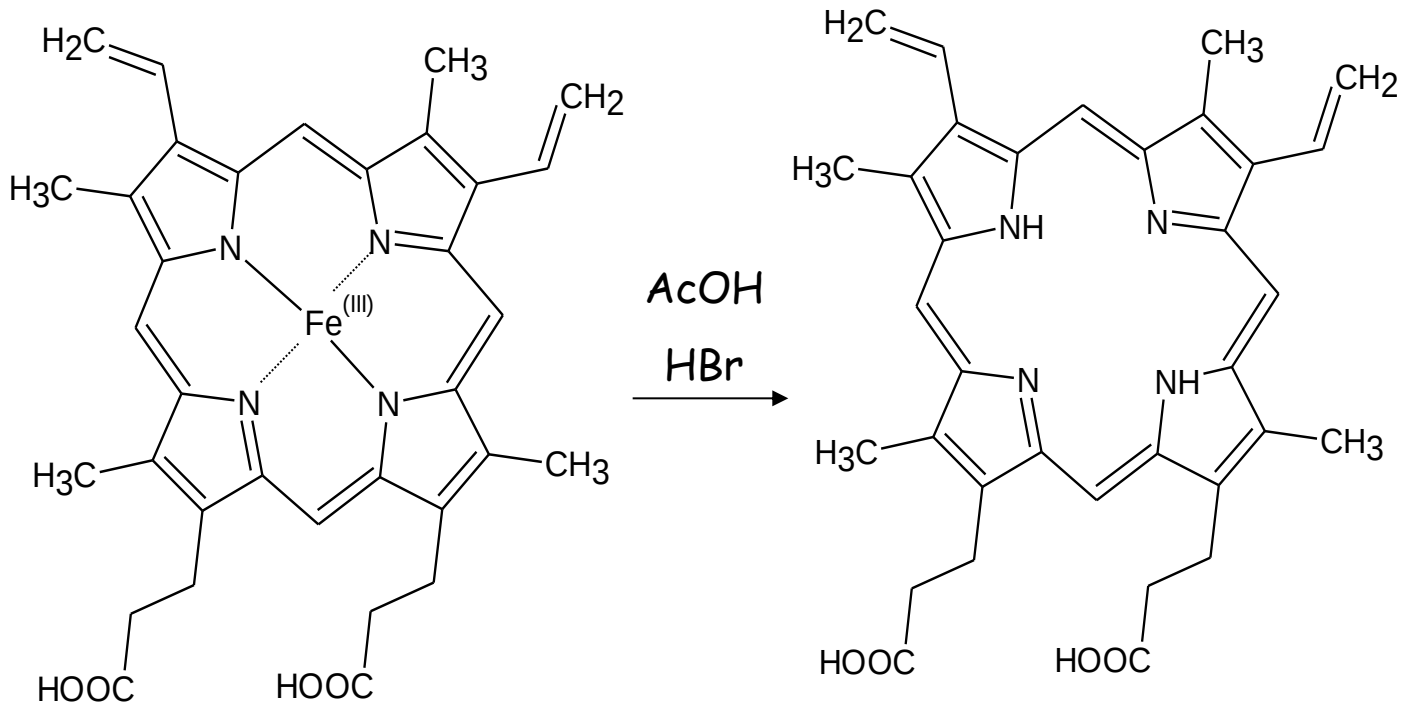
Nobel díj, (J. Kendrew) 1962 www.mfpl.ac.at





phm.utoronto.ca

Hem: Fe(III) só $\xrightarrow{\text{oxidáció}}$ Hemin: Fe(II) só

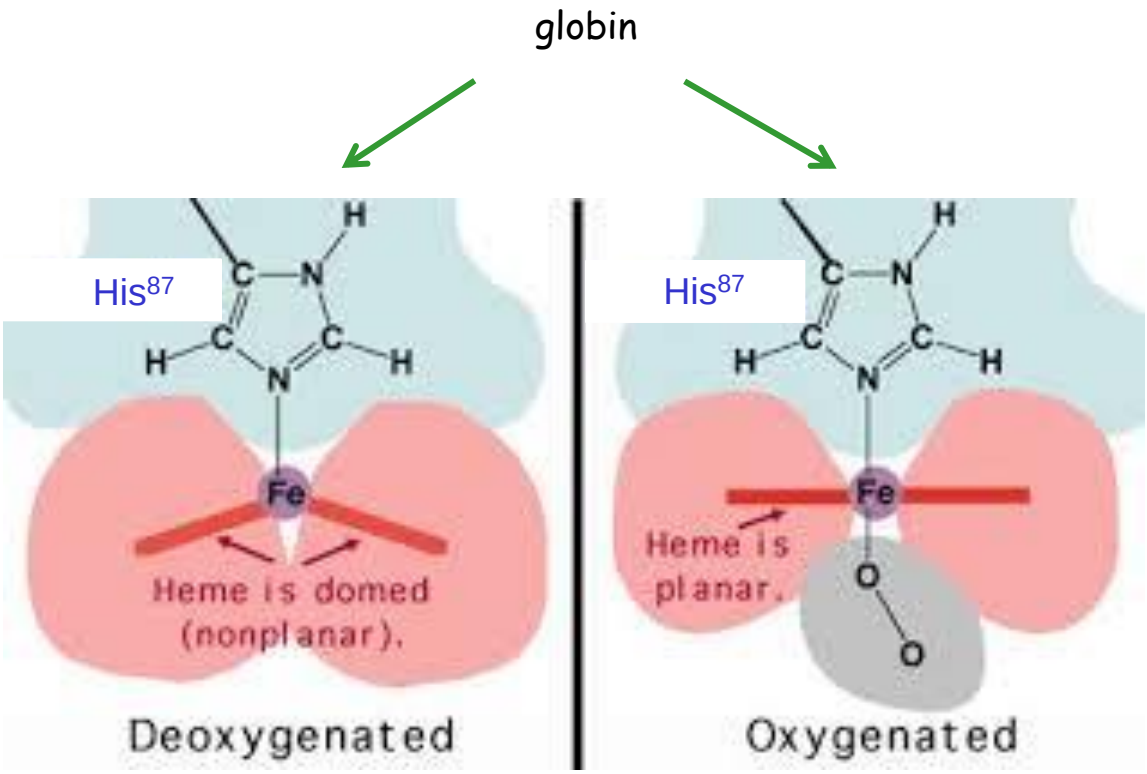


Protoporfirin

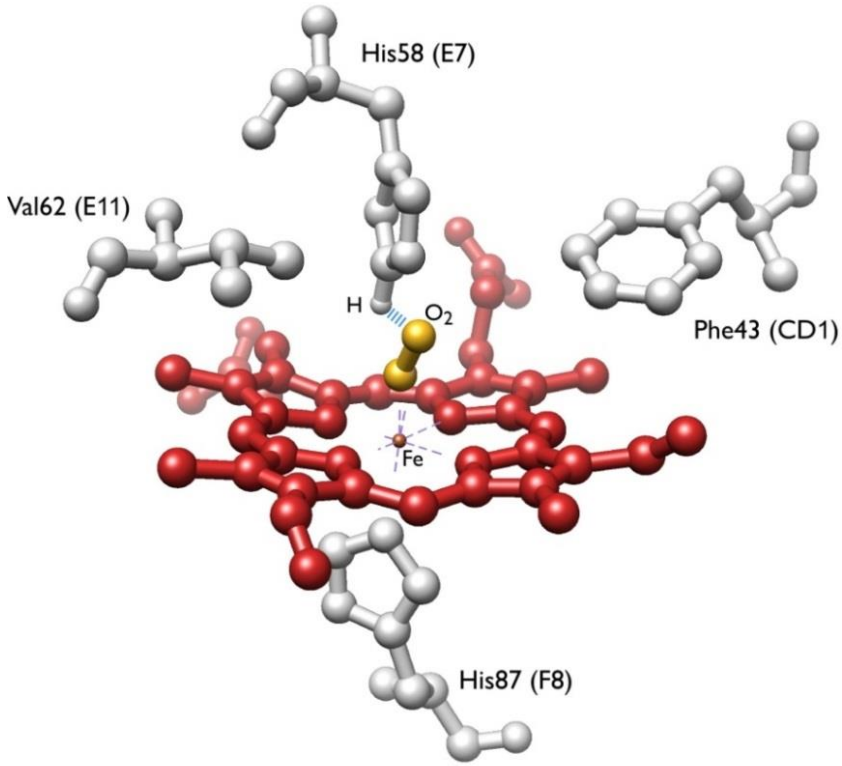
(vas mentes)

Jellemzés:

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



www.chemistry.wustl.edu



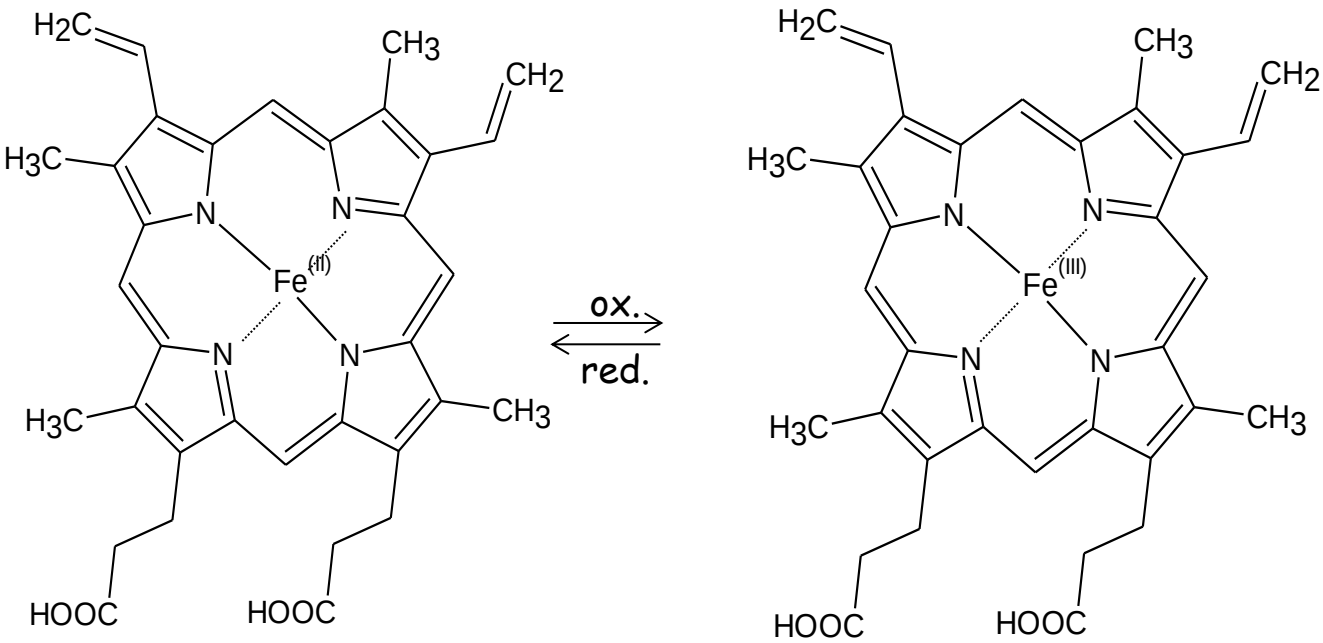
http://ttktamop.elte.hu/online-tananyagok/a_biokemia_es_molekularis_biologiai_alapjai/ch07s03.html

Paál. G. A fehérjeműködés paradigmája: mioglobin és hemoglobin

1.2. Mioglobin

Prosztetikus csoport (vörös) + globin (1 polipeptidlánc)

153 aminosav

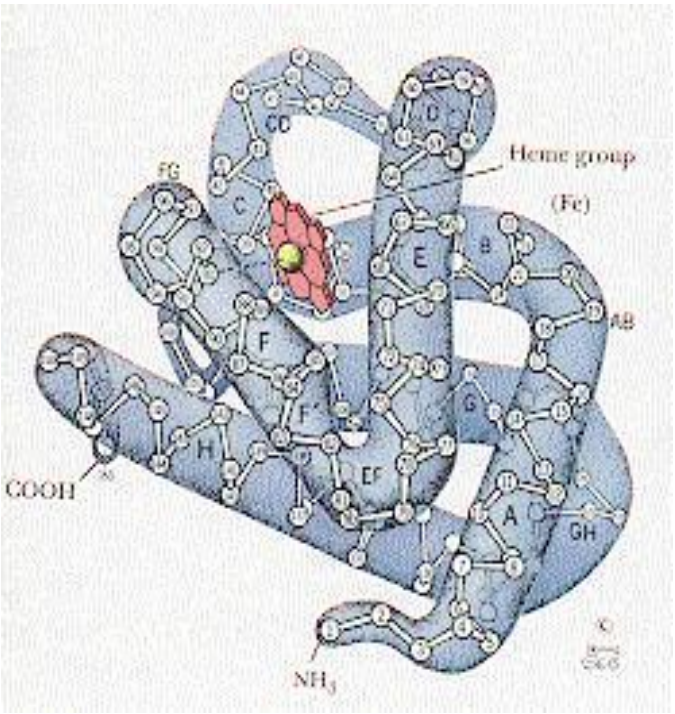


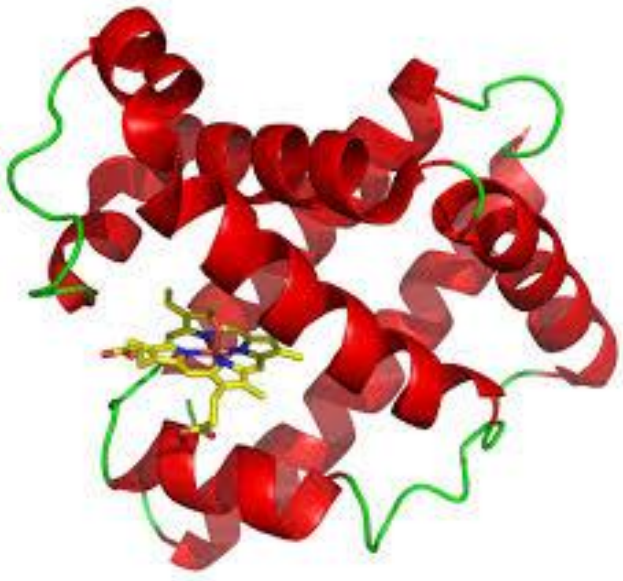
hemokromogén hemin

Jellemzés:

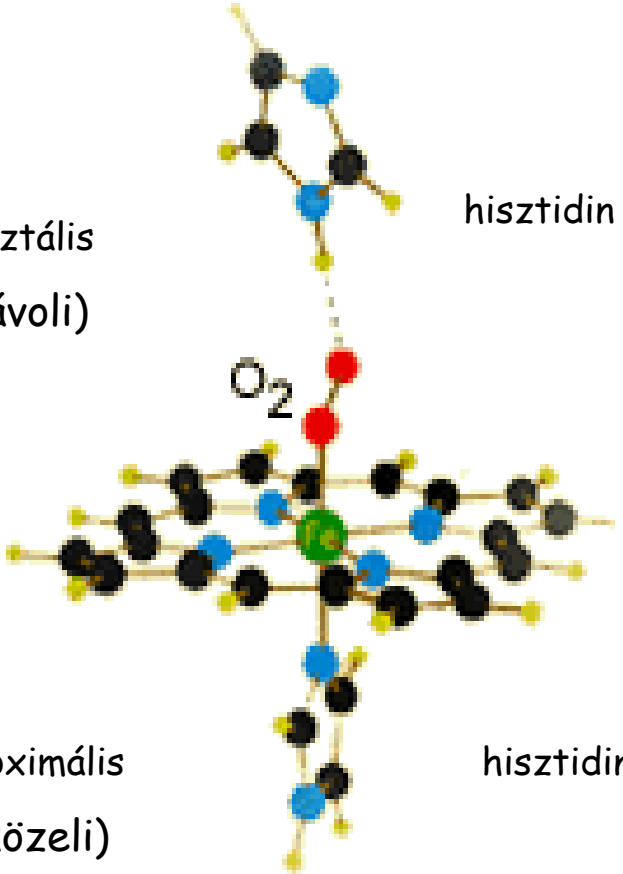
1. izomban fordul elő
2. O_2 megkötés (nagyobb, mint hemoglobin)
3. térszerkezet (J. Kendrew, Nobel díj)
   első fehérje, 1958
1. hem – protein zseb (His szerepe)

A mioglobin és O_2 kötőhelye





guweb2.gonzaga.edu



Disztális
(távoli)

hisztidin E7

hem

Proximális
(közeli)

hisztidin F8

Mioglobin, hemoglobin összegzés

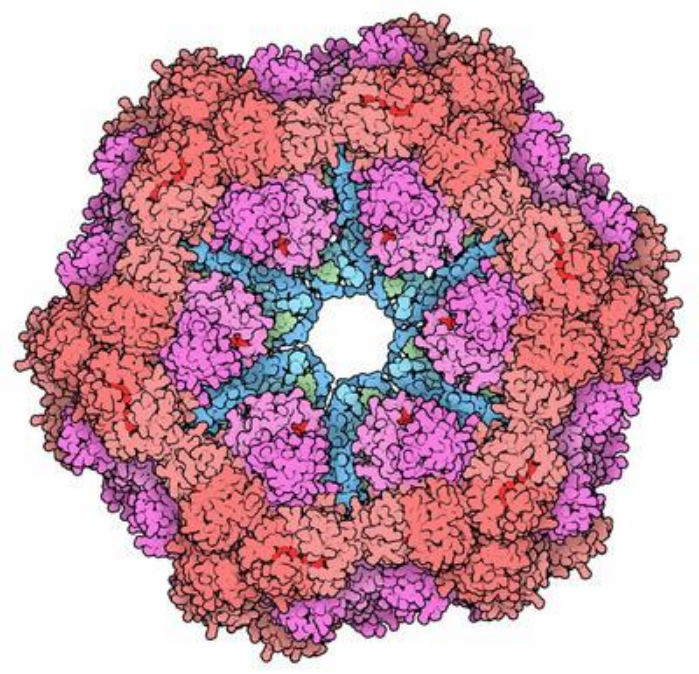
váz	fémion	prosztetikus csoport	protein	funkció
Proto-porfirin	Fe^{2+}	hem	ferrohemoglobin (hemoglobin)	O_2 kötés
	Fe^{3+}	hemin	ferrihemoglobin (hemiglobin)	H_2O
	Fe^{2+}	hem	oximioglobin	O_2 kötés
	Fe^{3+}	hemin	ferrimioglobin	H_2O
	Fe^{2+}	hem	dezoximioglobin	O_2 kötés

humán hemoglobin	F1	F2	F3	F4	F5	F6	F7	F8	F9
α lánc	Leu	Ser	Ala	Leu	Ser	Asp	Leu	His	Ala
β lánc	Phe	Ala	Thr	Leu	Ser	Glu	Leu	His	Cys
ámbráscet mioglobin	Leu	Lys	Pro	Leu	Ala	Gln	Ser	His	Ala

1.3. Eritrokruorin és klorokruorin

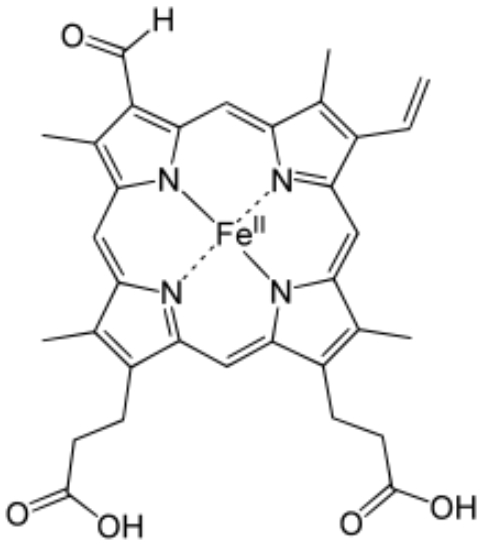
Oxigén szállító, hem-tartalmú fehérjék (Mt > 3,5 millió Da)

Gyűrűsférgek, soksertéjűek (Polychaeta)



Eritrokruorin (4 x 36 globin)

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

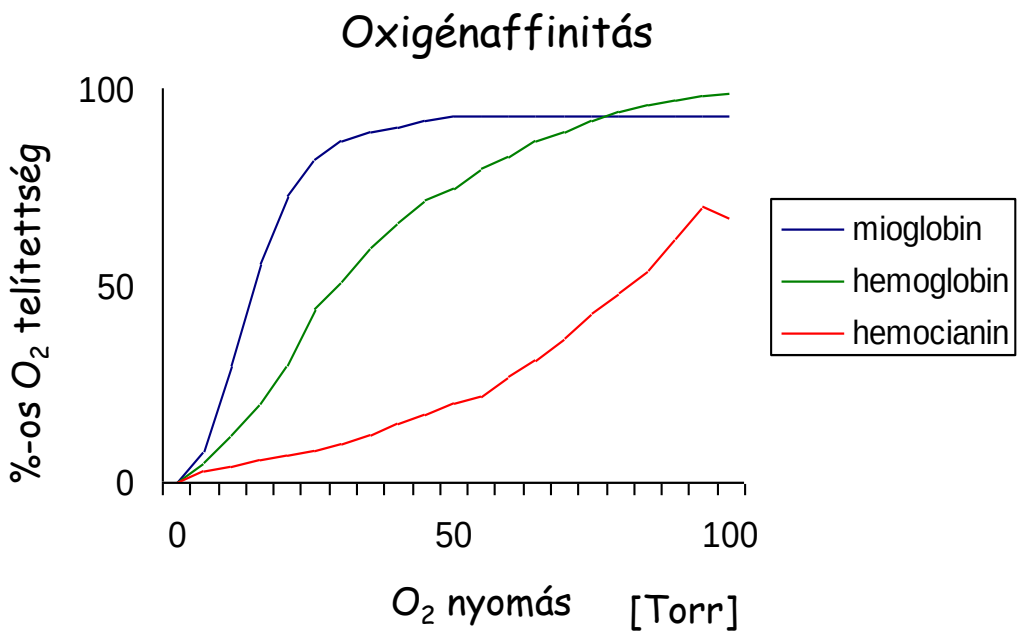


Prosztetikus csoport klorokruorin

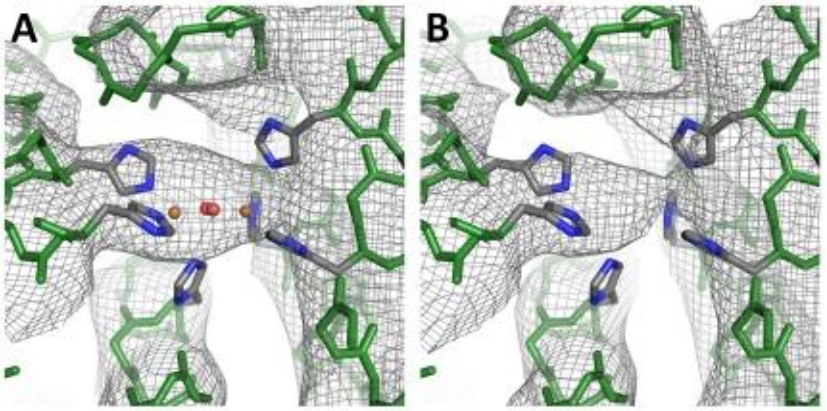
Légzési színezékek (kiegészítés)

O_2 diffúzió: 2 mm mélység ⇒ „szállítófolyadék"

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



Hemocianin
(metalloprotein)

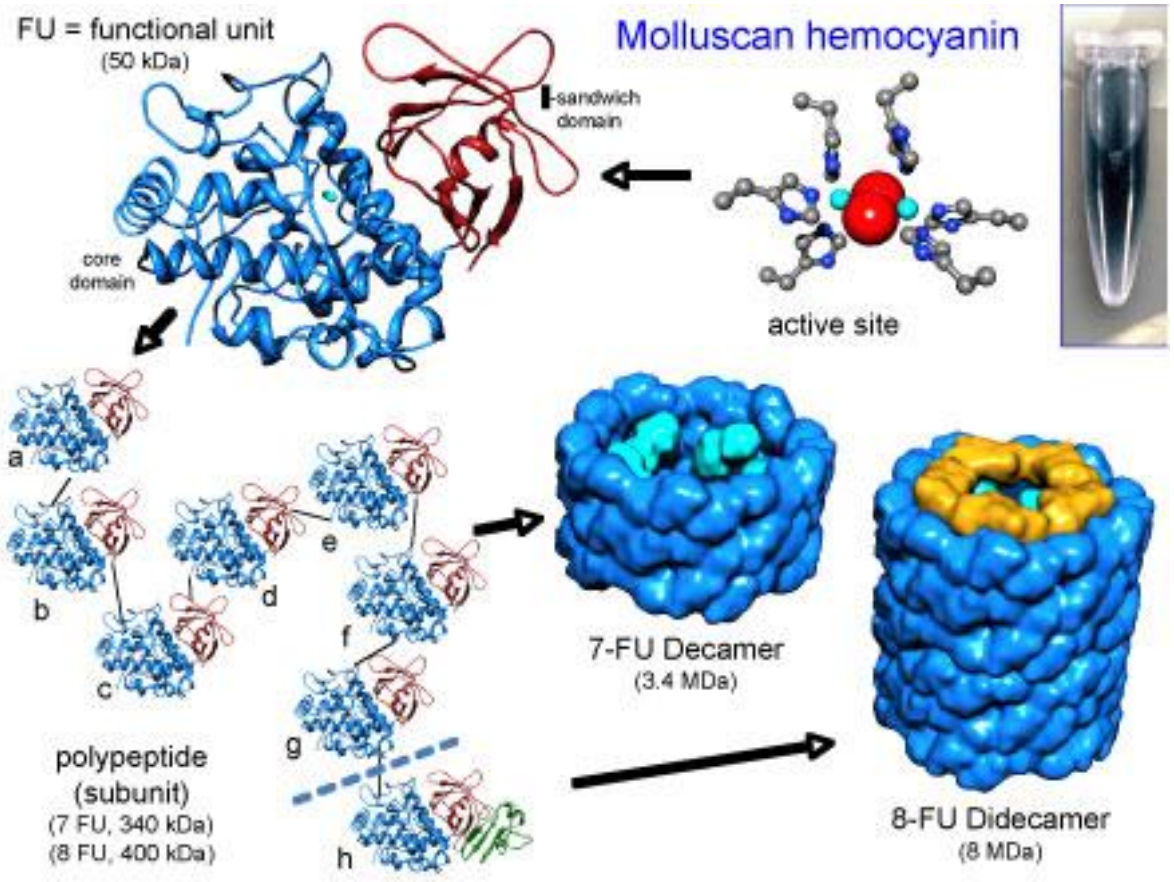


Cu = narancs, O = vörös

Hemocianin from *Pandinus imperator*
E. Jaenicke et al. PLoS One 2012, 7(3) e 32548

Megathura crenulata

(keyhole limpet)



http://www.biosyncorp.com/

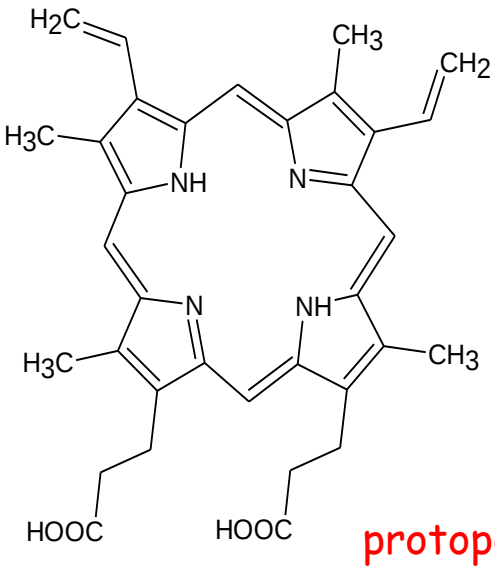
Epefestékek

hemoglobin hem részének bomlástermékei

A. biliverdin, zöld (máj)

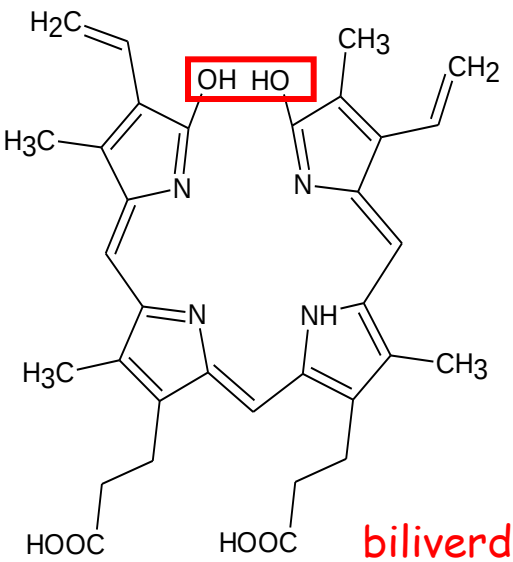
B. bilirubin, sárga (máj).

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



protoporfirin

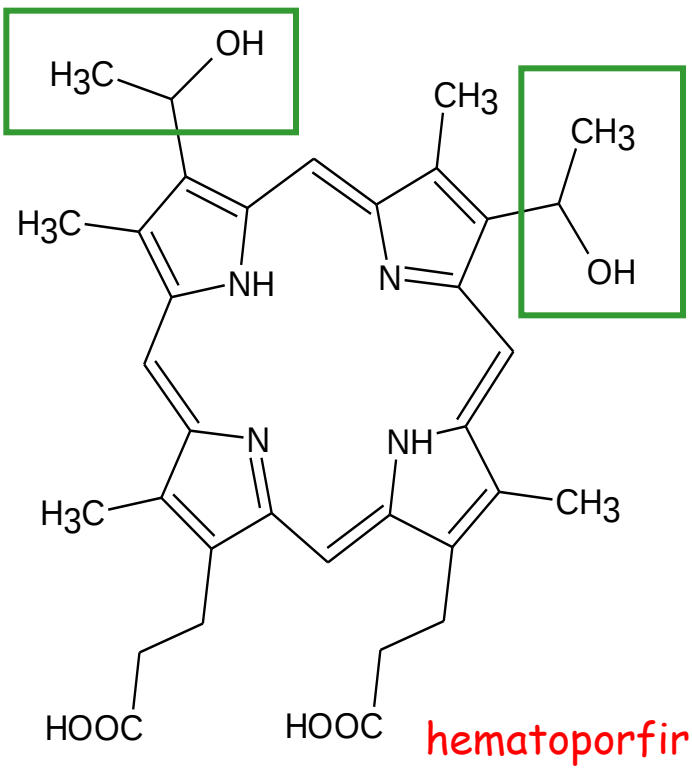
oxidáció



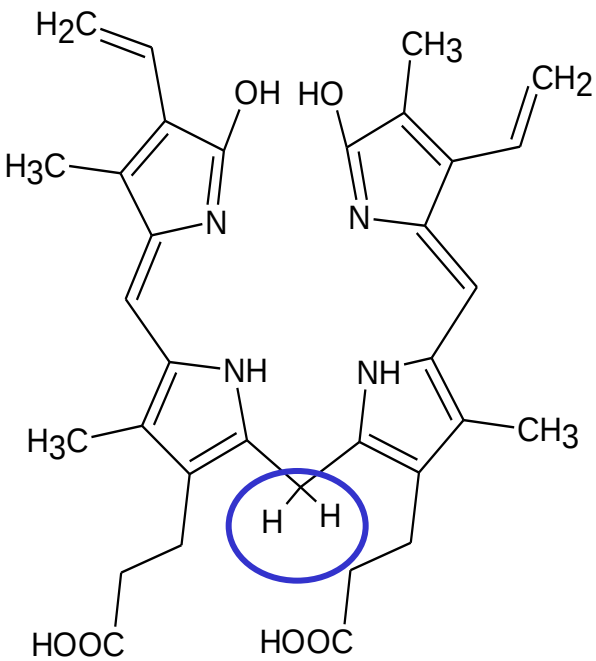
biliverdin

C_2H_5OH, lúg / Δ

redukció



hematoporfirin

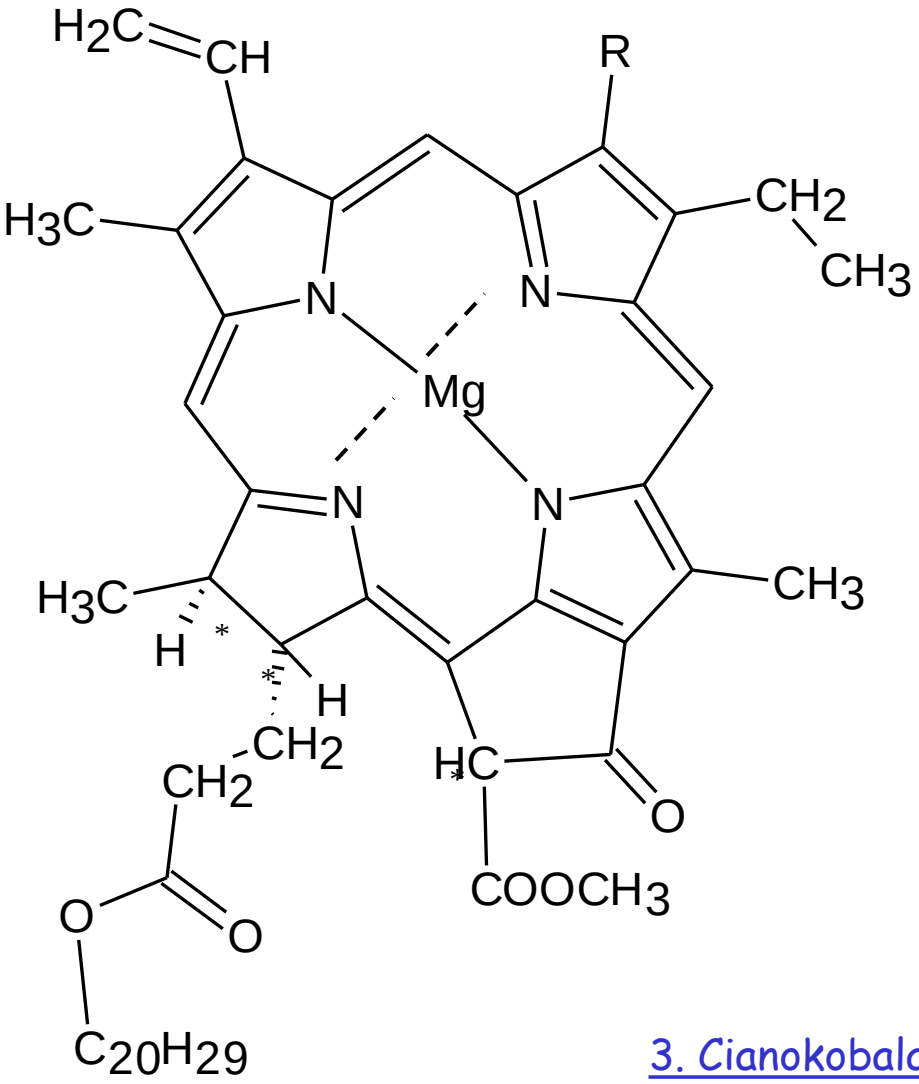


bilirubin

2. Klorofill

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

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



R = -CH_3 A
= -CHO B

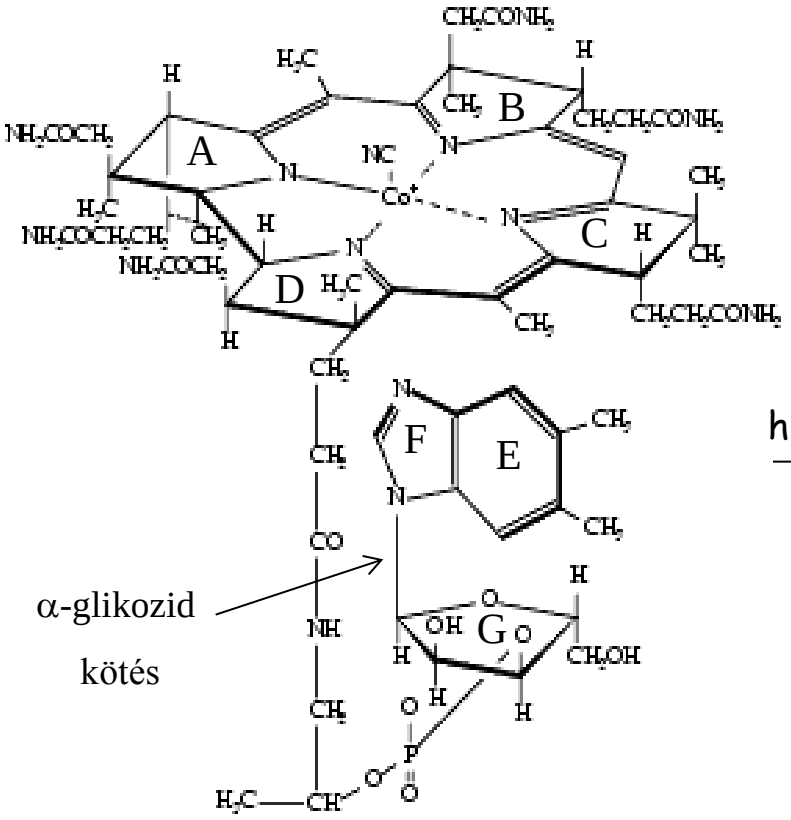
3. Cianokobalamin (B_{12})

Co^{3+}, 4,3% kobalt

$C_{68}H_{88}O_{14}N_{14}Co$

($C_{20}H_{29}$) fitol észter

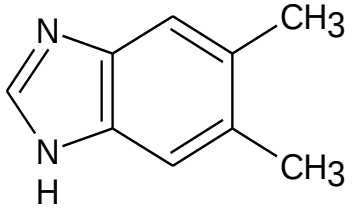
Cisz-7(R)-11 (R)-3,7,11,15-tetrametil-2-hexadecén-1-ol

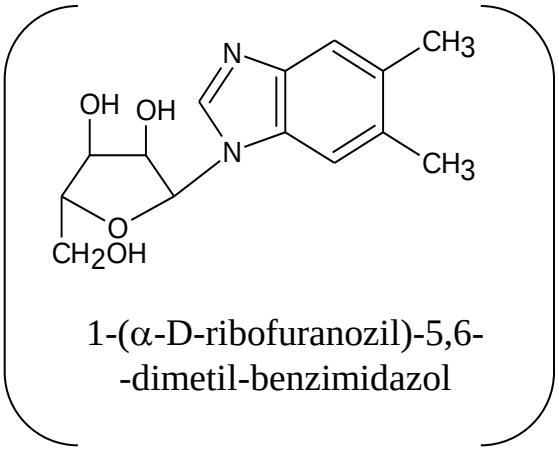


korrin-váz
(nem aromás!)

NH_2-$CH_2(CH_3)$-OH
(2-hidroxil-propilamin)
$+H_3PO_4$ + 6 NH_3 +
+ D-ribóz +

hidrolízis
H^+





1-(α-D-ribofuranozil)-5,6-
-dimetil-benzimidazol

Variációk: - CN B_{12}
- OH B_{12a}
- NO_2 B_{12c}

1926: májkivonat – vészes vérszegénység (Minot, Murphy)

1947: mikrobák növekedési faktora (Shoriz)

1948: izolálás tengeri algákból (Folkers, Smith)

1954-56: térszerkezet (Hodgkin)