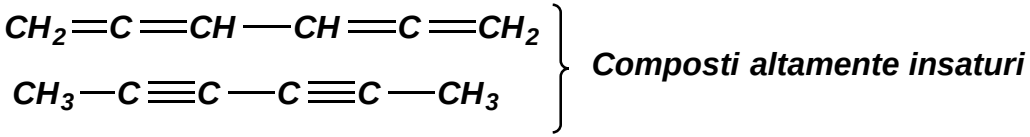
Aromaticità

Benzene ⟹ $(CH)_x$ ⟹ **(1825) Isolato per la prima volta da Faraday**

C_6H_6 ⟹ **(1834)**

Struttura? Sulla carta sono possibili diverse strutture di formula molecolare C_6H_6:



Composti altamente insaturi

Ma la REATTIVITA' del Benzene è molto diversa da quella di molecole con legami Carbonio-Carbonio doppi e tripli

Alchene

- Br_2 → **Reazione di addizione**
- H_2 / Pt → **Facile addizione di Idrogeno e trasformazione in Alcano**
- H_2O / H^+ → **Reazione di addizione per formare Alcoli**

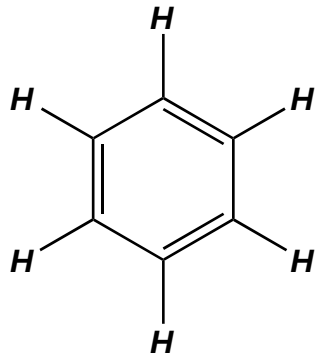
Benzene

- H_2O / H^+ → **Nessuna reazione**
- H_2 / Pt → **Reagisce molto lentamente ad a temperature e pressione di H_2 molto elevate**
- Br_2 → **Reazione solo in presenza di $FeBr_3$ dando reazioni di SOSTITUZIONE**

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3\ (Cat.)} C_6H_5Br + HBr$$

Esiste un solo C_6H_5Br (ovvero tutti gli atomi di idrogeno del Benzene sono equivalenti)

Kekulè (1865) ⇨

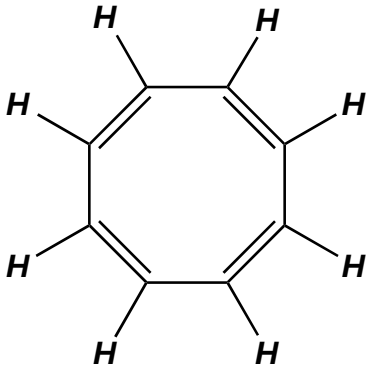


Anello con legami semplici e doppi alternati

⇨ ***Spiega perchè esiste un solo C_6H_5Br***

⇨ ***Non spiega perchè esiste un solo 1,2-$C_6H_4Br_2$***

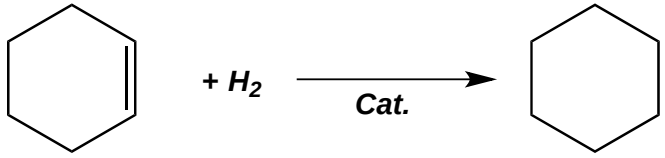
AROMATICITA' ⇨ ***Caratteristica che ha come conseguenza reazioni di SOSTITUZIONE piuttosto che reazioni di addizione.***



1,3,5,7-Cicloottatetraene (1911)

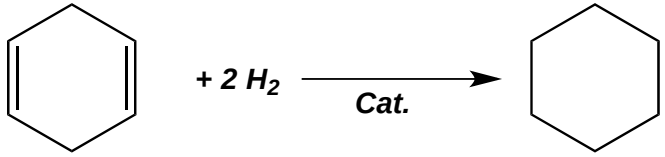
⇨ ***Addiziona Br_2***

⇨ ***Addizione H_2 facilmente***



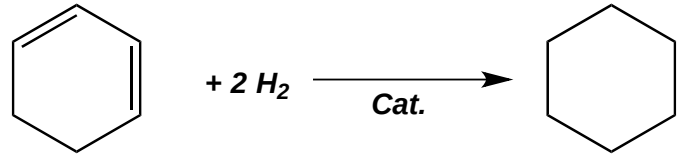
Cicloesene *Cicloesano*

ΔH = -28,6 Kcal/mole



1,4-Cicloesadiene *Cicloesano*

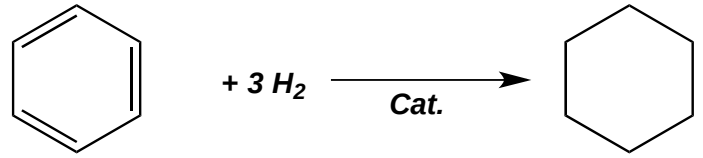
ΔH = -57,2 Kcal/mole (= 28,6 X 2)



1,3-Cicloesadiene *Cicloesano*

ΔH = -54,9 Kcal/mole

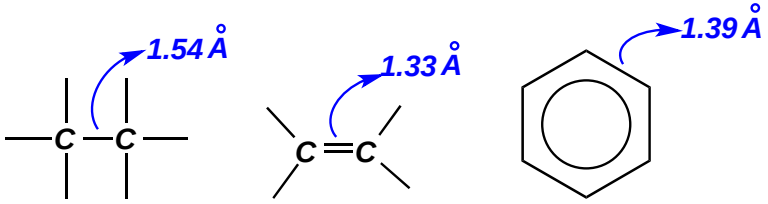
ΔH atteso per 3 doppi legami: -28,6 X 3 = -85.8 Kcal/mole

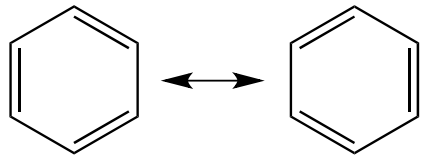


1,3,5 -Cicloesatriene *Cicloesano*

ΔH = -48,8 Kcal/mole

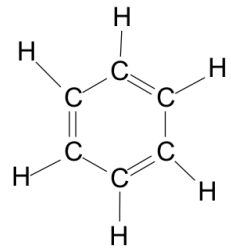
Il Benzene non si comporta come un triene, è più stabile di 36 Kcal/mol di quello che ci si aspetterebbe da un anello a sei termini con tre doppi legami alchenici

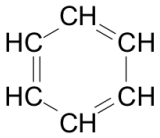


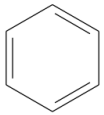


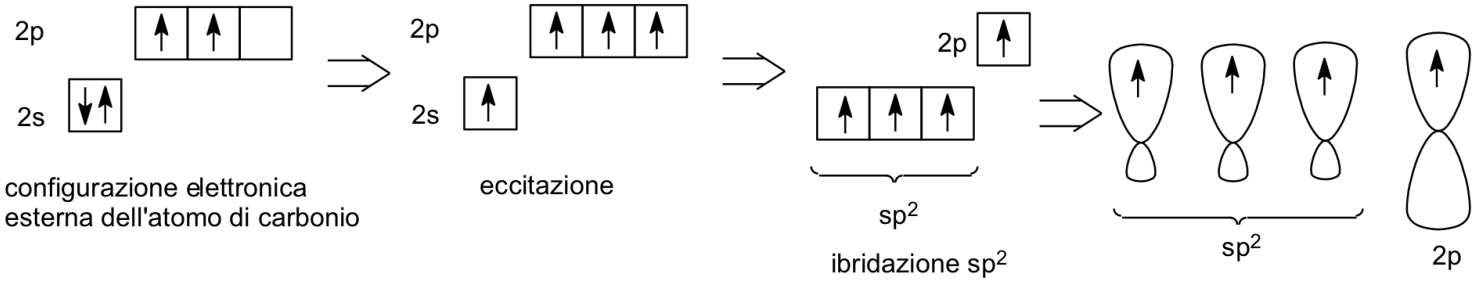
ENERGIA DI RISONANZA

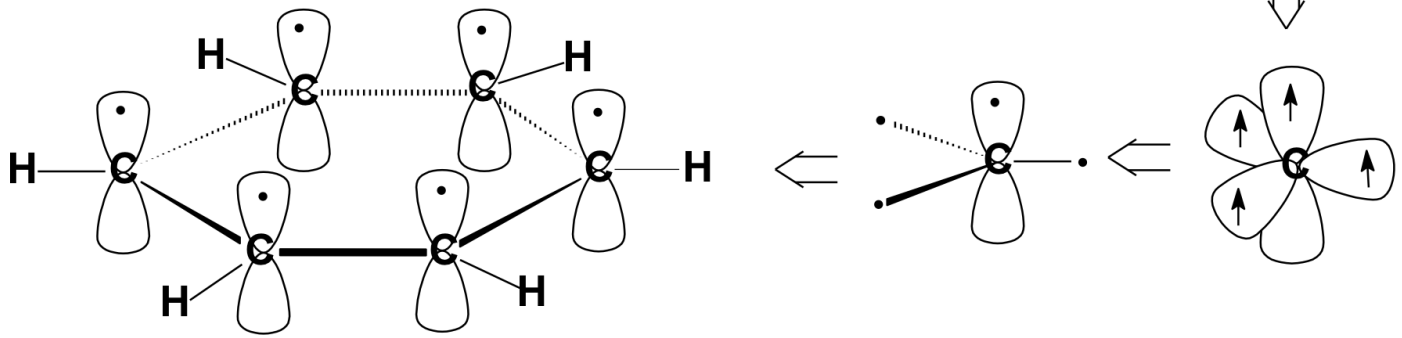
BENZENE

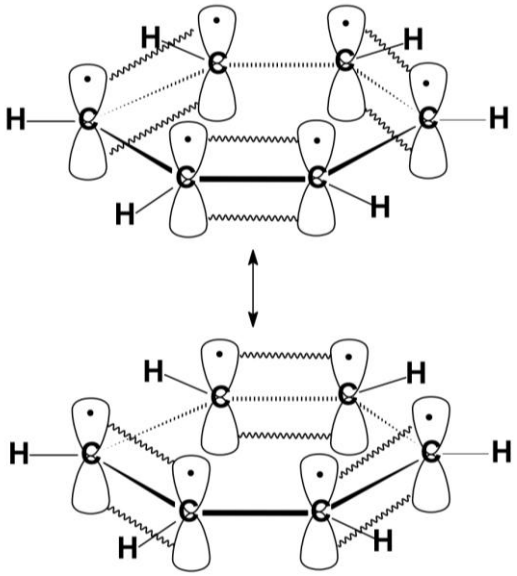


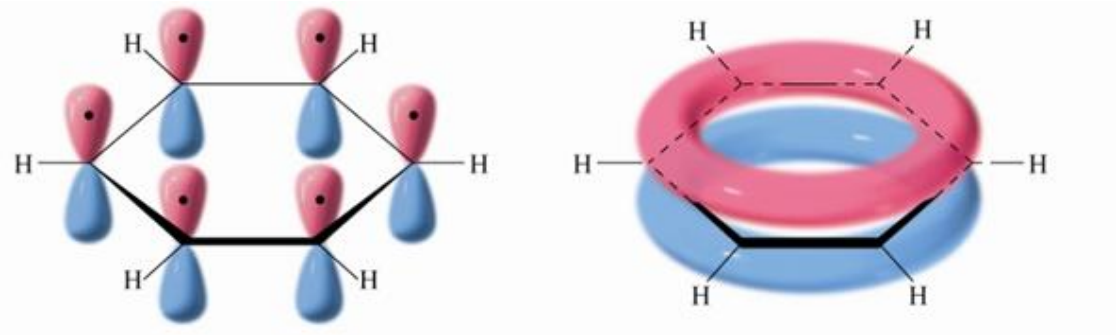

CH
HC
CH
HC
CH

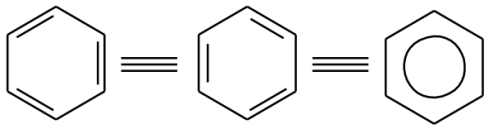



2p
2s
2p
2s
2p
sp2
sp2
2p
configurazione elettronica
esterna dell'atomo di carbonio
eccitazione
ibridazione sp2

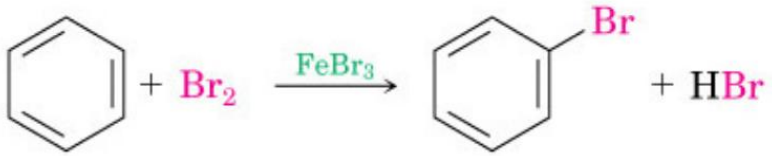






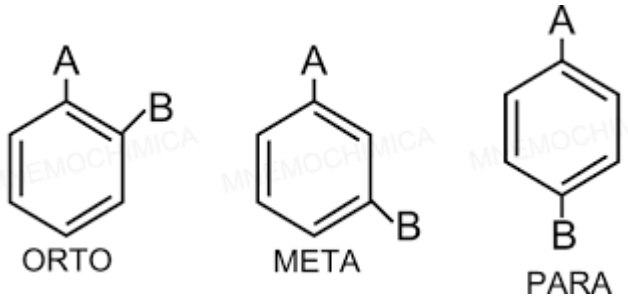


BENZENE



Reazione di Sostituzione elettrofila aromatica

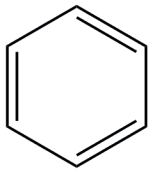
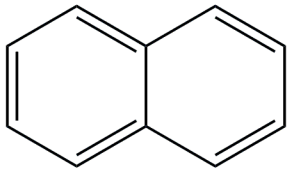
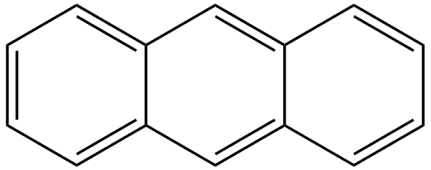
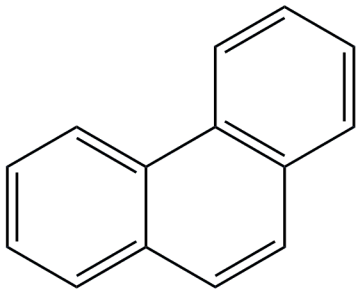
non si ha addizione perché si romperebbe l'aromaticità

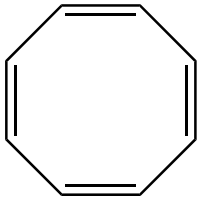


AROMATICITA'

Regola di Huckel**: sono aromatici tutti i sistemi ciclici di doppi legami coniugati che hanno un numero di **elettroni π** pari a: **4n + 2
per n = 1, 2, 3, 4, ...

*Ovvero: una specie è aromatica se ha **4n + 2 elettroni π coniugati in forma ciclica**.*

n=1	*4 x 1 + 2 = 6*	*Benzene*	
n=2	*4 x 2 + 2 = 10*	*Naftalene*	
n=3	*4 x 3 + 2 = 14*	*Antracene*	
n=3	*4 x 3 + 2 = 14*	*Fenantrene*	

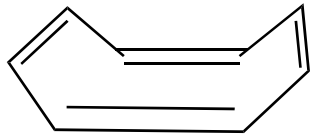


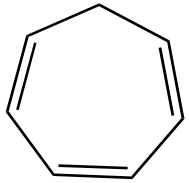
Cicloottatetraene

possiede 8 elettroni p ⇨ ***gli elettroni*** p ***sono coniugati in forma ciclica***

⇨ ***NON obbedisce alla regola di 4n + 2 elettroni*** p

⇨ ***NON è aromatico***

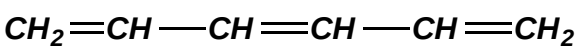




Cicloeptatriene

possiede 6 elettroni p ⇨ ***NON sono tutti coniugati***

⇨ ***NON è aromatico***



1,3,5-Esatriene

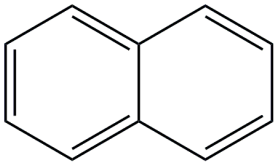
possiede 6 elettroni p ⇨ ***sono tutti coniugati***

⇨ ***NON è un sistema ciclico***

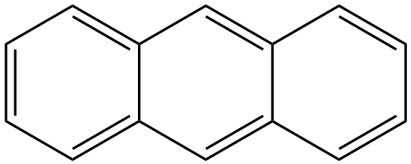
⇨ ***NON è aromatico***

IDROCARBURI AROMATICI POLINUCLEARI (POLICICLICI): sono caratterizzati dall'avere due o più anelli benzenici fusi assieme in modo che ciascuna coppia di anelli abbia in comune due carboni adiacenti.

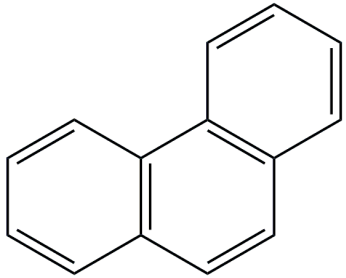
***IPA** (Idrocarburi Policiclici Aromatici)*
PAH, PAHs (Poly Aromatic Hydrocarbons)



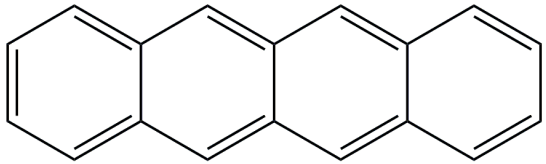
Naftalene



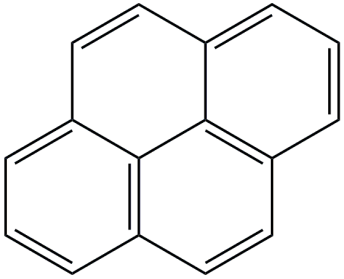
Antracene



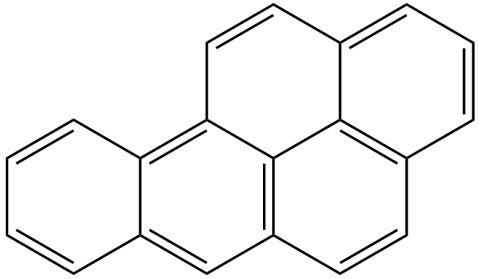
Fenantrene



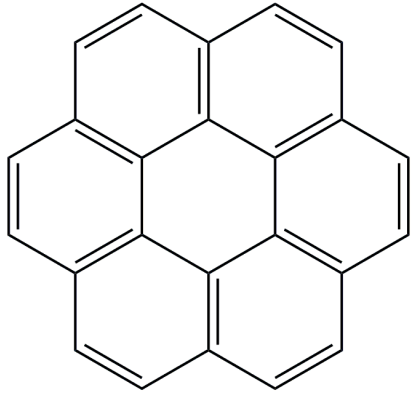
Tetracene



Pirene



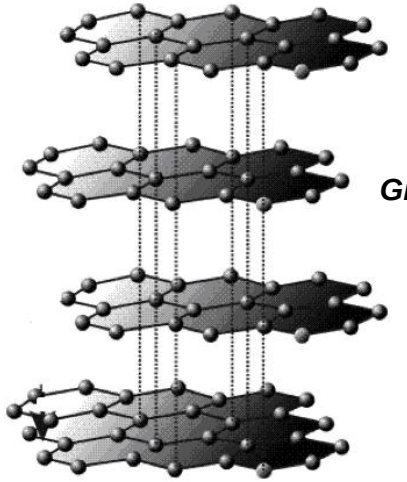
Benzopirene



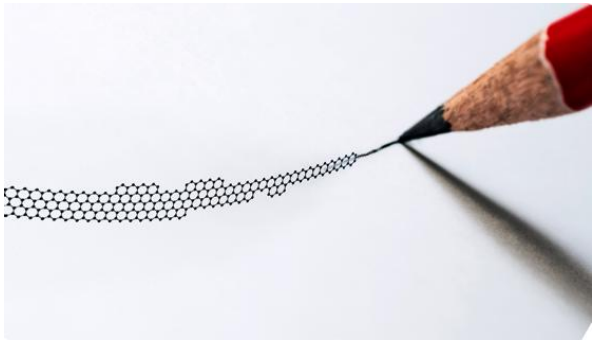
Coronene

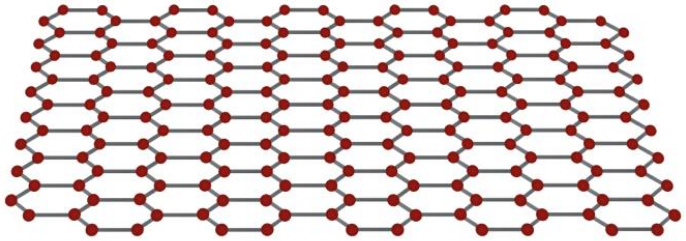
Gli IPA presenti nell'ambiente provengono da numerose fonti; traffico autoveicolare (dagli scarichi dei motori benzina e diesel e dall'usura di pneumatici), dal fumo delle sigarette, dalla superficie di alimenti affumicati (carni in particolare) o cucinati alla griglia e dai processi di combustione in generale in cui il carbonio non viene completamente convertito in CO e CO_2.
Molti di essi sono cancerogeni.

La grafite rappresenta la forma limite di IPA.
La grafite è formata da piani paralleli di anelli benzenici condensati, che formano strati di piani di atomi carbonio.
I piani di atomi carbonio condensati possono scorrere gli uni sugli altri, quindi la grafite ha proprietà lubrificanti.
Nella grafite non sono presenti atomi di idrogeno se non alla periferia degli strati.

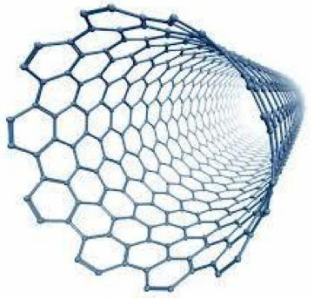


Grafite





Grafene

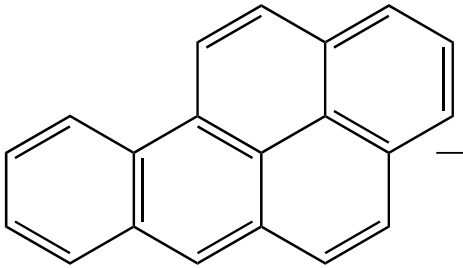


Nanotubi

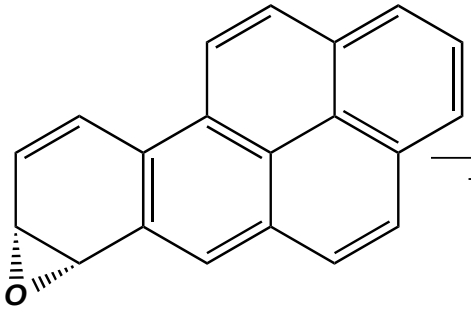
Fullerene

Gli IPA, in generale, non sono di per sé agenti cancerogeni, ma lo sono alcuni derivati in cui essi vengono convertiti dall'organismo nel tentativo di renderli idrosolubili, e quindi più facilmente eliminabili. Il benzo[a]pirene è una delle prime sostanze di cui si è accertata la cancerogenicità.

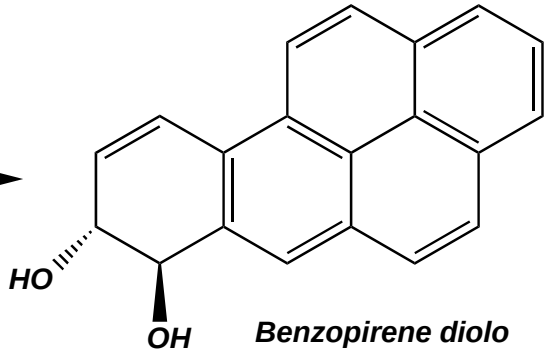
Di seguito viene illustrata la sequenza di reazioni metaboliche che subisce il benzo[a]pirene nell'organismo umano.



Benzopirene

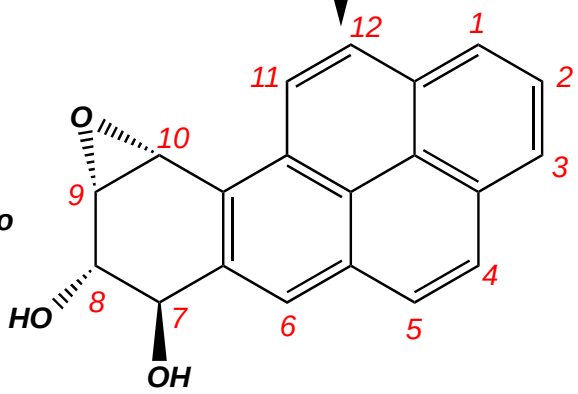


Benzopirene epossido

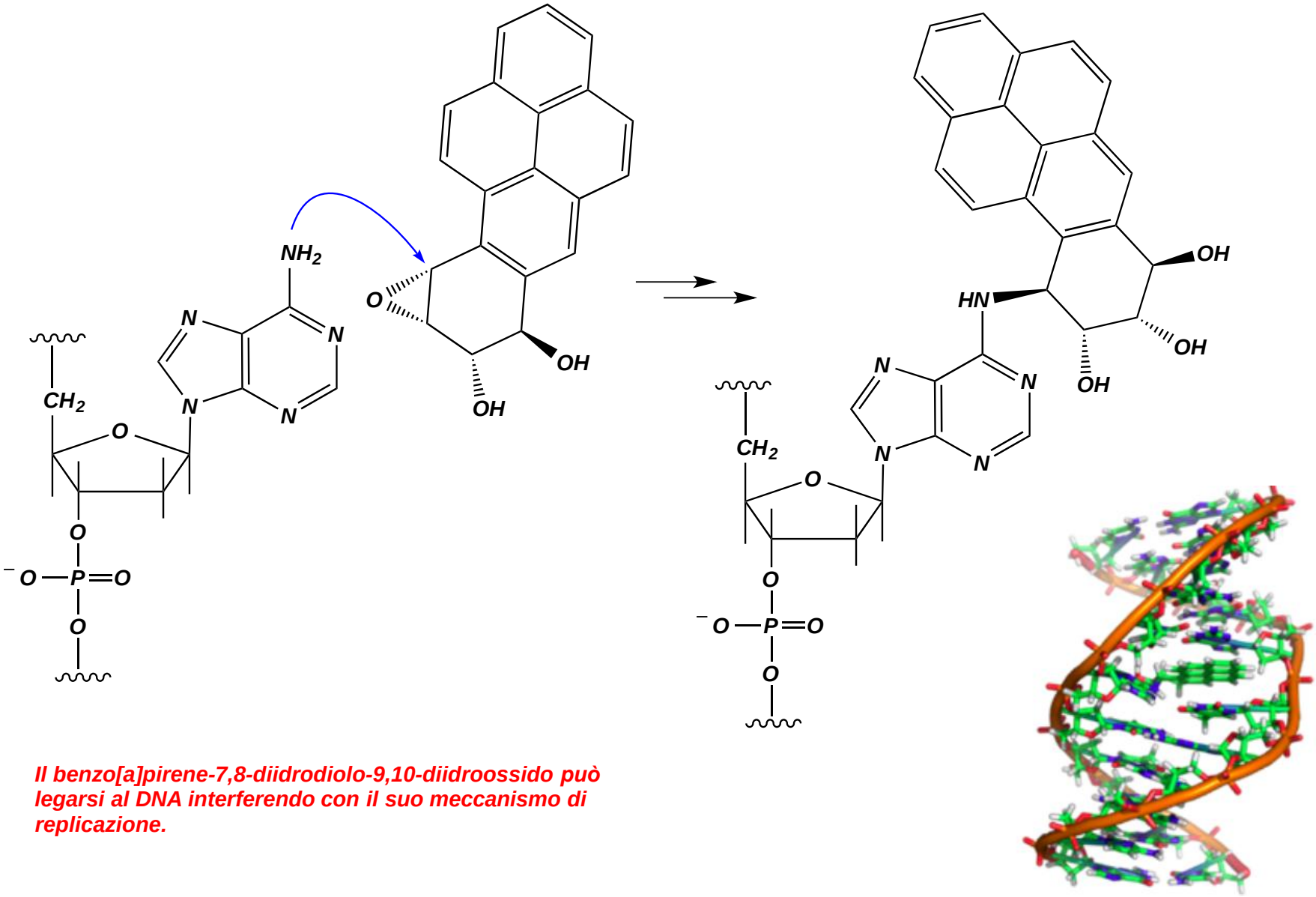


Benzopirene diolo

Benzopirene diolo epossido

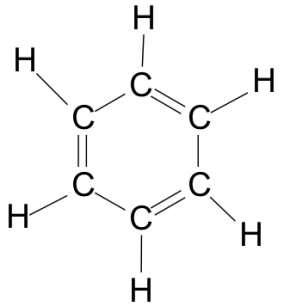


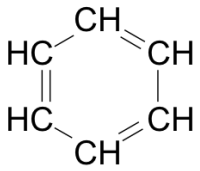
7,8-Diidrodiolo-9,10-epossibenzo[a]pirene

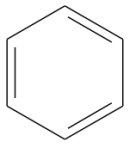


Il benzo[a]pirene-7,8-diidrodiolo-9,10-diidroossido può legarsi al DNA interferendo con il suo meccanismo di replicazione.

Composti eterociclici aromatici

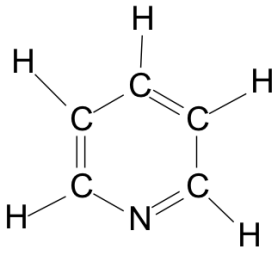


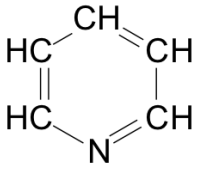


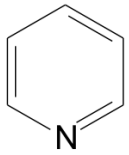


1,3,5-cicloesatriene

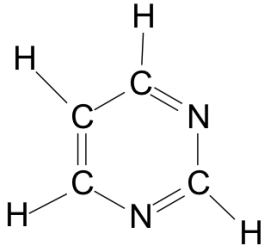
BENZENE

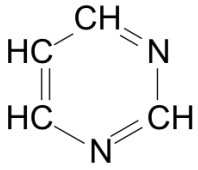


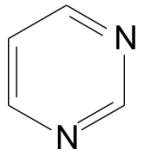




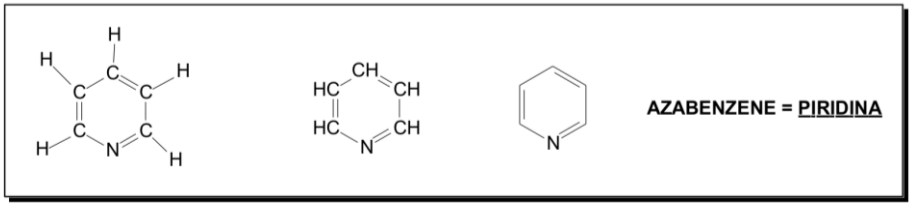
AZABENZENE = <u>PIRIDINA</u>

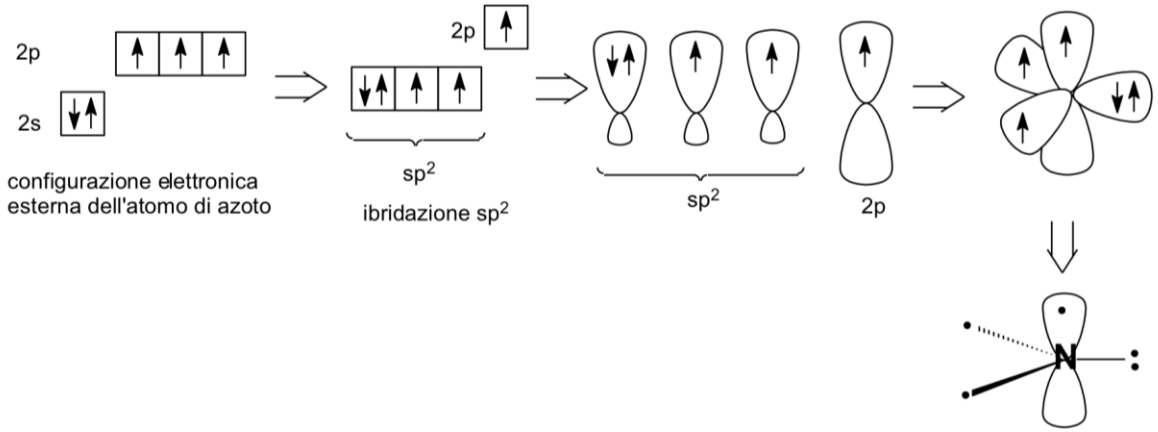


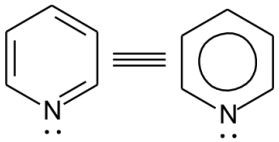




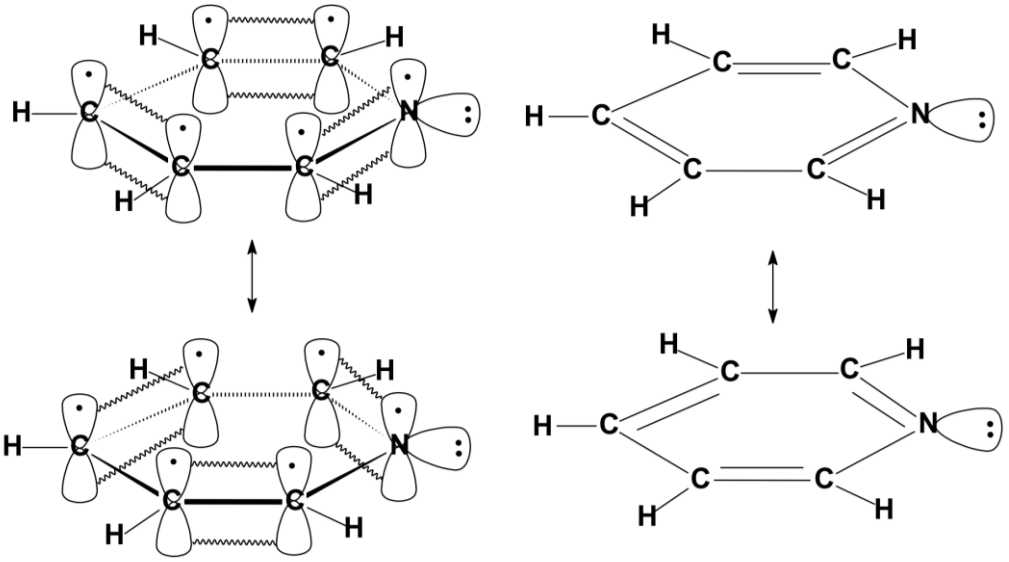
1,3-DIAZABENZENE = <u>PIRIMIDINA</u>



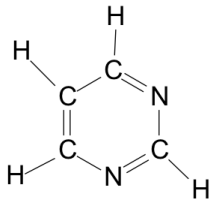


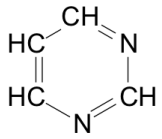


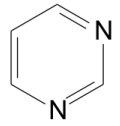
PIRIDINA



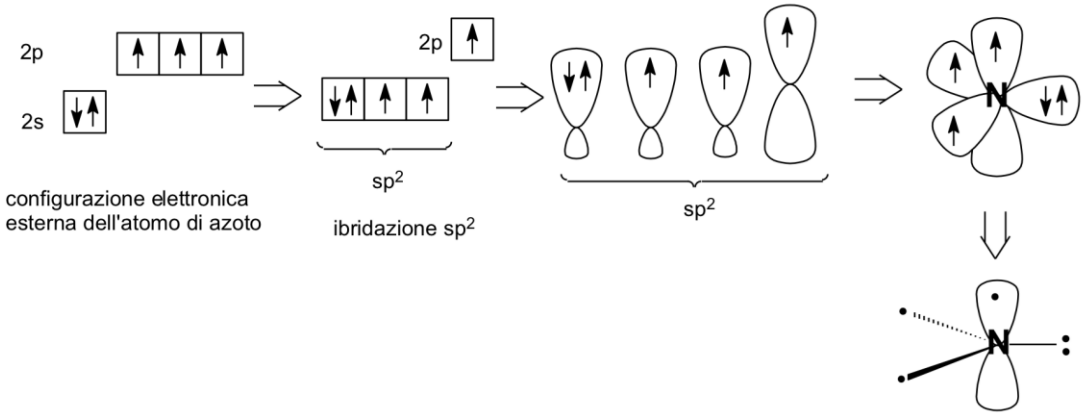
- ***La piridina è aromatica***
- ***È solubile in acqua (polarità e legame idrogeno)***
- ***È basica, ma meno delle ammine (N sp^2 più elettronegativo di N sp^3)***

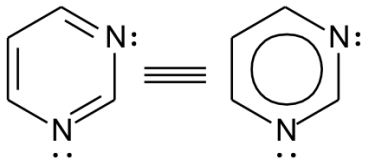




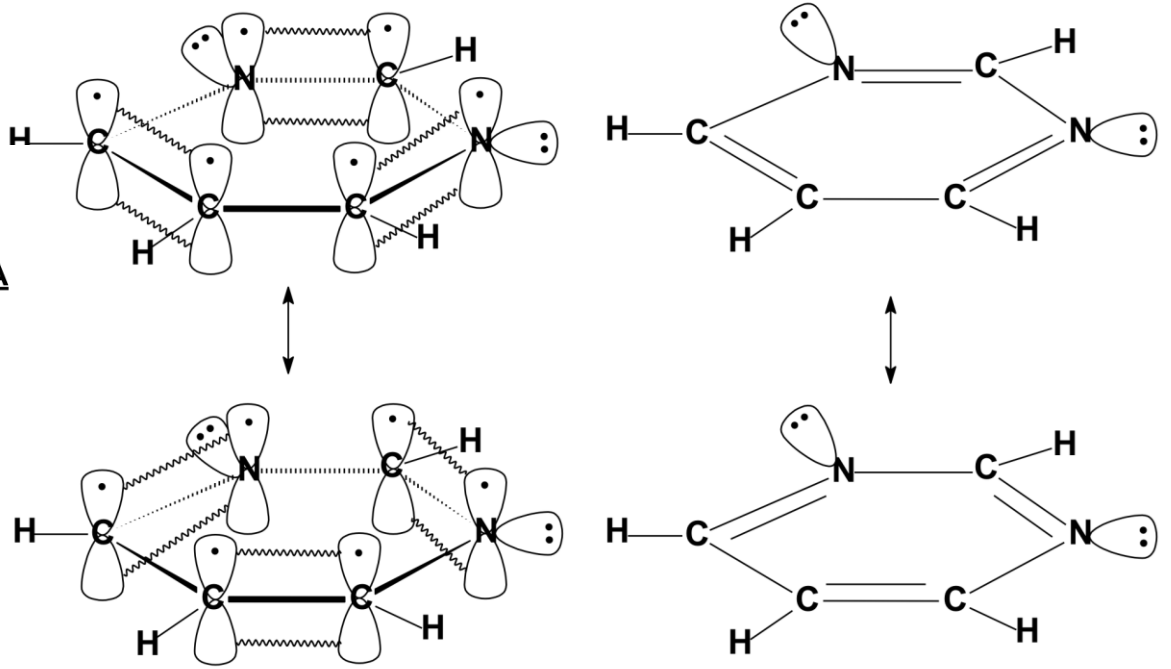


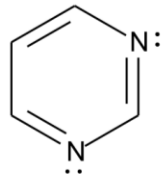
1,3-DIAZABENZENE = PIRIMIDINA



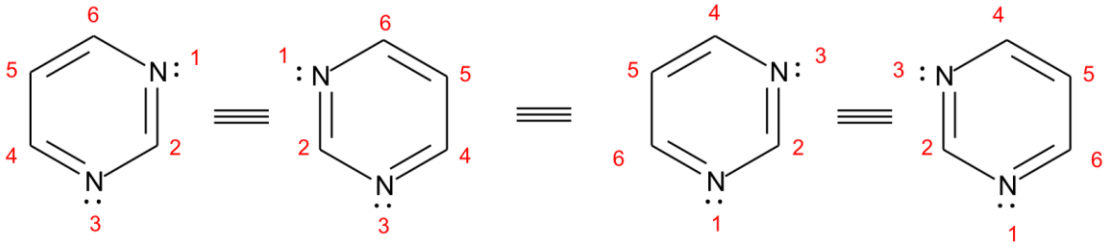


PIRIMIDINA

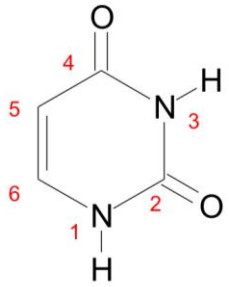




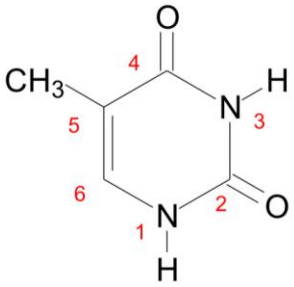
PIRIMIDINA



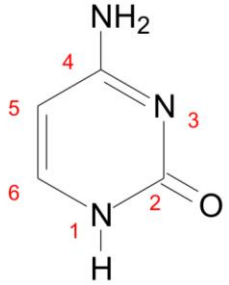
I derivati più importanti della pirimidina sono l'**URACILE**, la **TIMINA** e la **CITOSINA**. L'**URACILE** e la **CITOSINA** sono presenti nell'RNA, la **TIMINA** e la **CITOSINA** sono presenti nel DNA.



URACILE

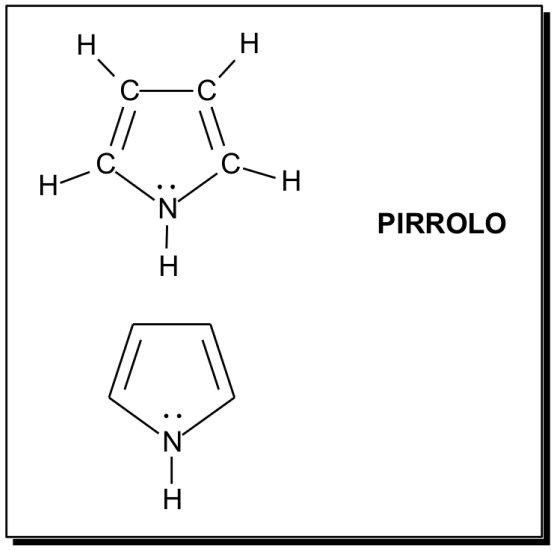


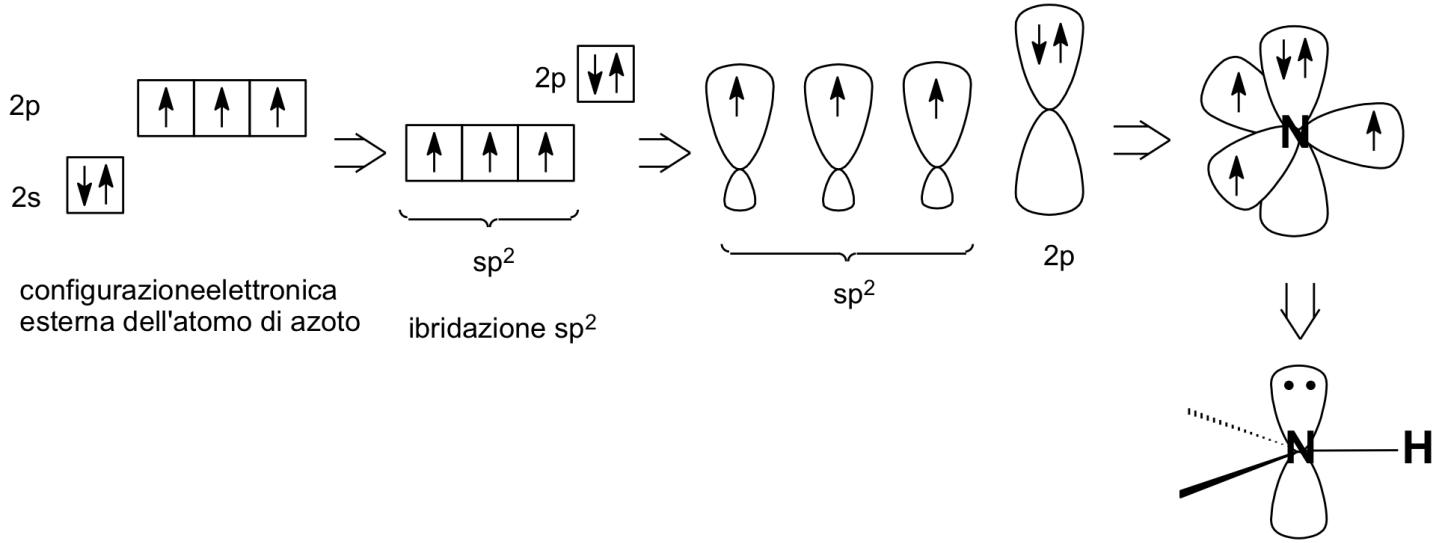
TIMINA



CITOSINA

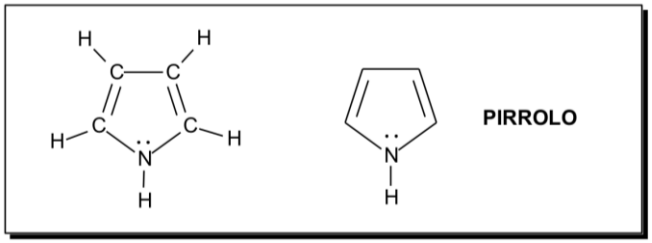
Essendo derivati della pirimidina l'**URACILE**, la **TIMINA** e la **CITOSINA** sono chiamate ***basi pirimidiniche***.

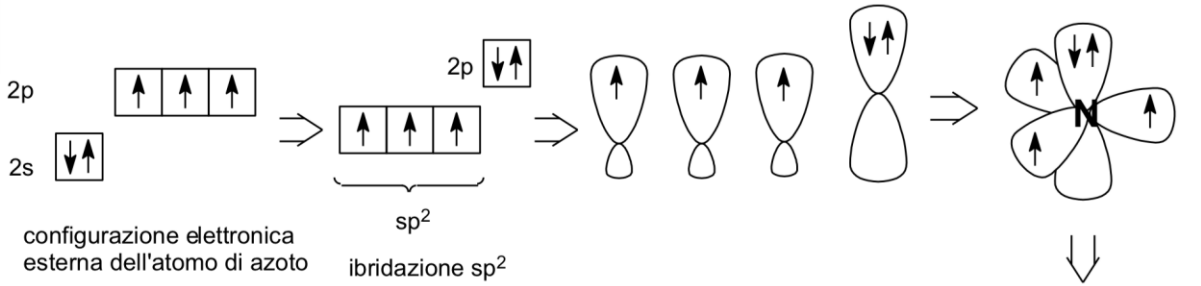


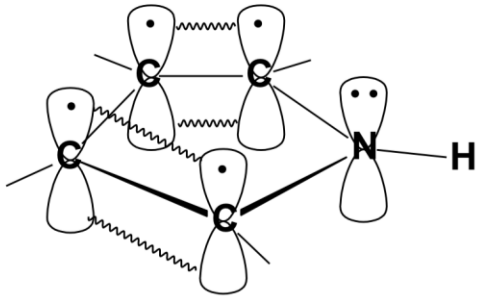


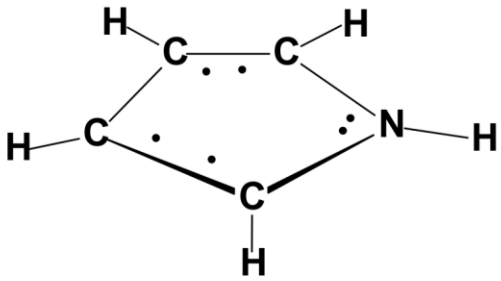
configurazioneelettronica
esterna dell'atomo di azoto

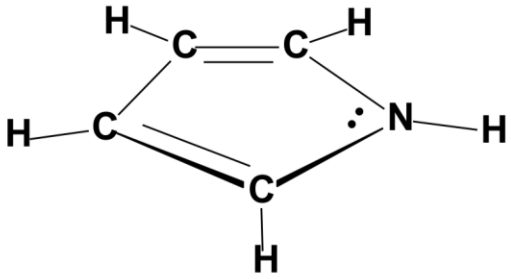
ibridazione sp^2



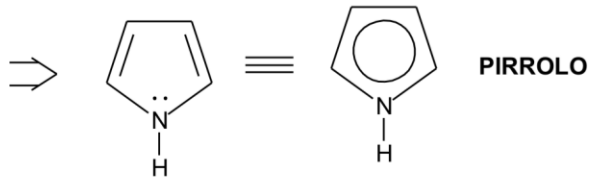


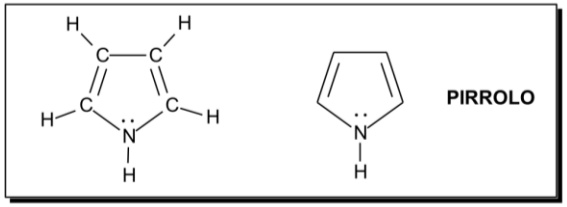


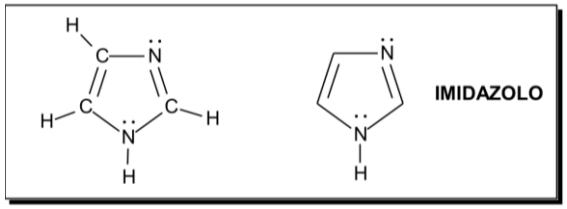


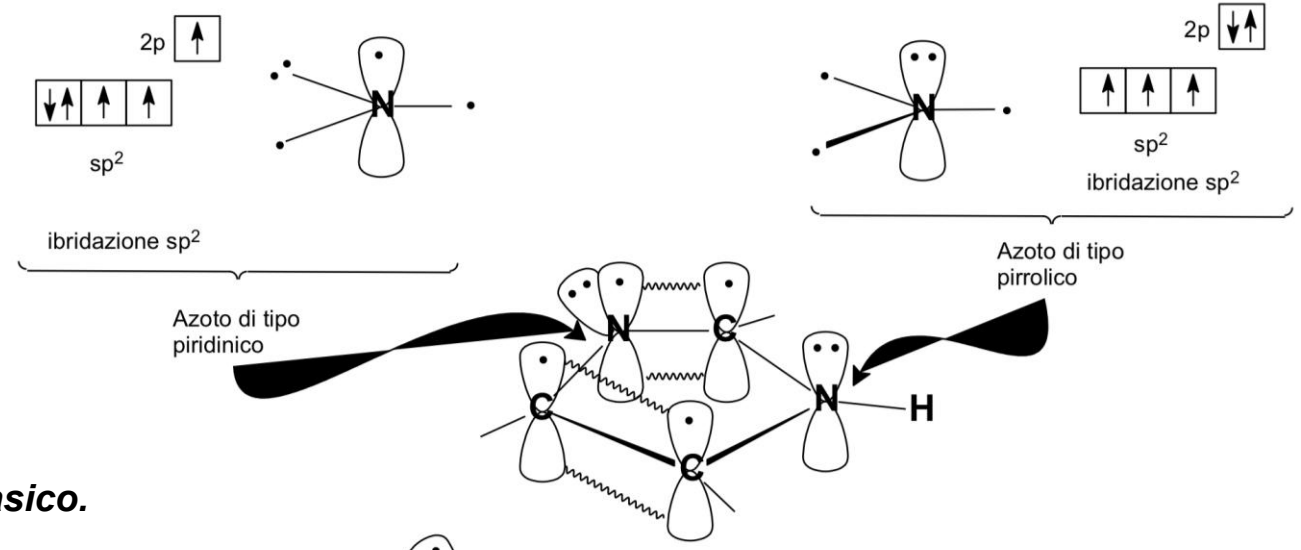


- ***Il pirrolo è aromatico***
- ***Non è solubile in acqua***
- ***Non è basico***



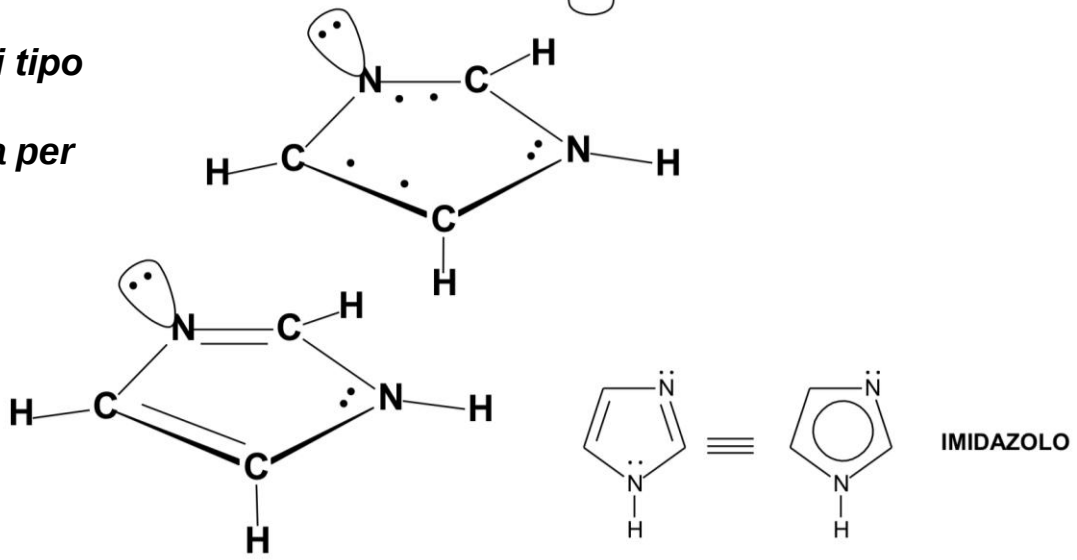


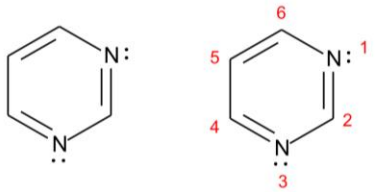




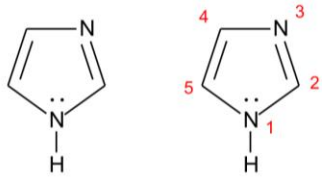
L'imidazolo è basico.

Si protona l'azoto 3 di tipo piridinico, e la forma protonata si stabilizza per risonanza

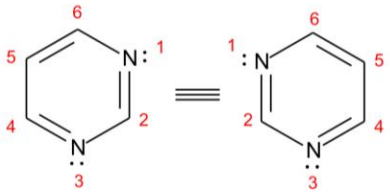


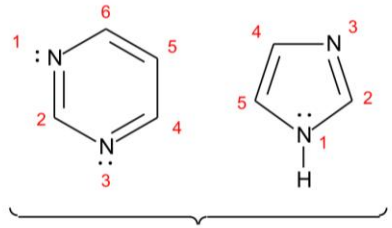


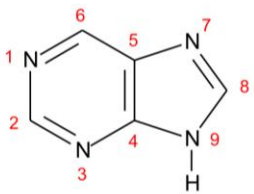
PIRIMIDINA



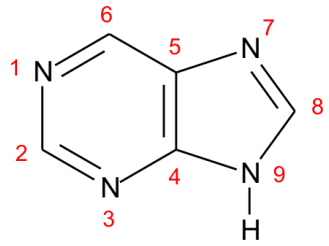
IMIDAZOLO





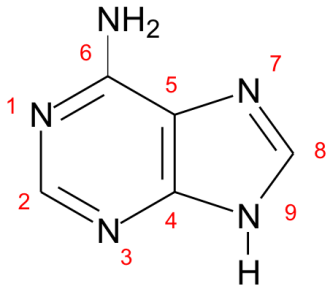


PURINA

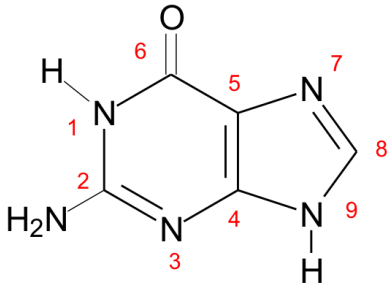


PURINA

I derivati più importanti della purina sono l'**ADENINA** e la **GUANINA** presenti nel DNA.

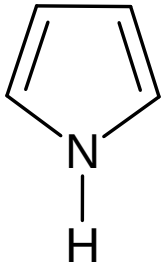


ADENINA

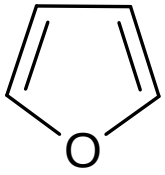


GUANINA

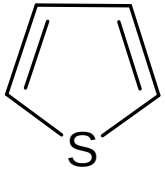
Essendo derivati della purina l'**ADENINA** e la **GUANINA** sono chiamate ***basi puriniche***.



PIRROLO

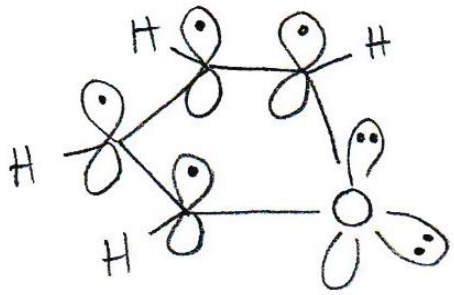


FURANO



TIOFENE

Sono AROMATICI perché una coppia di elettroni dell'eteroatomo contribuisce al sestetto di elettroni π



furano e tiofene

O o S sp^2