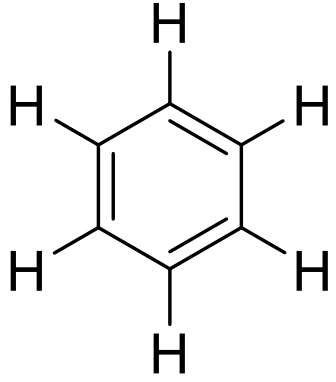
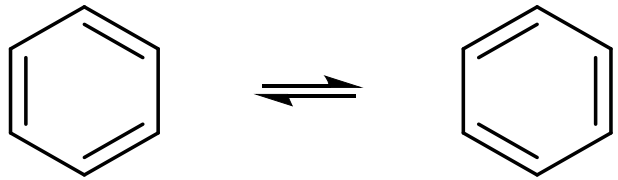
Benzene e Derivati

Benzene

- Il benzene (C_6H_6) è il più semplice tra gli IDROCARBURI AROMATICI (o areni)
- Ha 4 gradi di insaturazione
- È planare
- Tutti i legami C-C hanno la stessa lunghezza

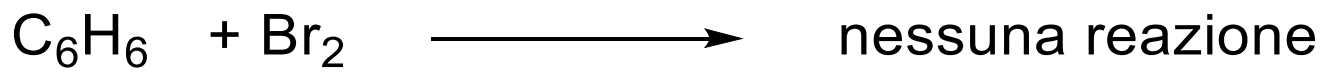


Kekulè nel 1865 descrisse la sua struttura come un equilibrio tra due forme

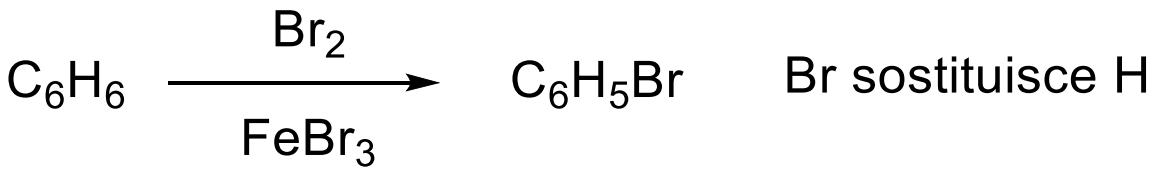


Benzene

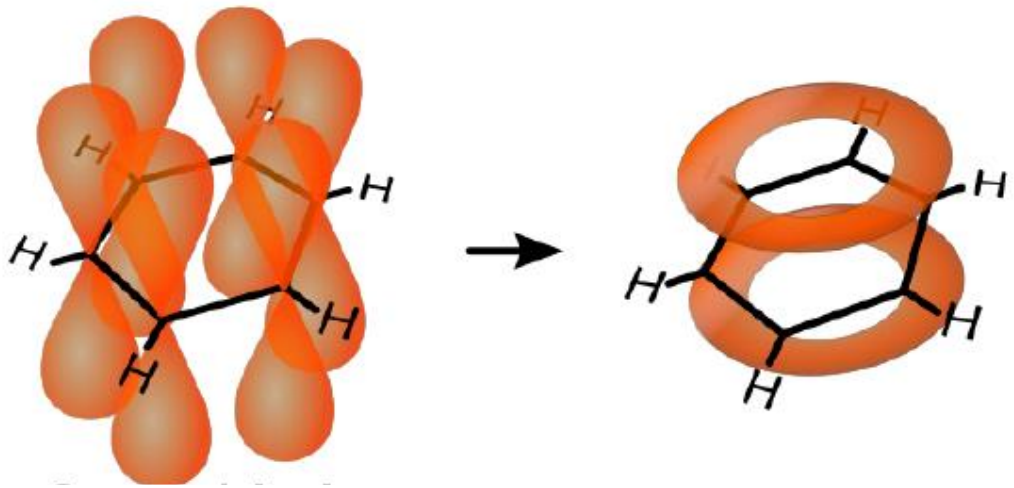
- Mentre gli idrocarburi insaturi (alcheni e alchini) danno facile reazione di addizione, il benzene NO!



- Il benzene è molto stabile e reagisce con bromo solo il presenza di un catalizzatore, $FeBr_3$ (un acido di Lewis)
- La reazione è una sostituzione non una addizione



Legami delocalizzati



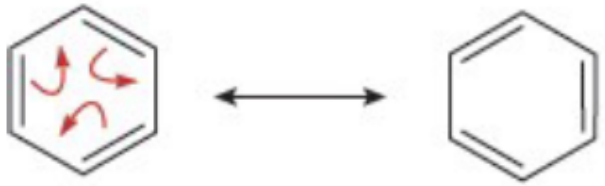
Sei orbitali 2p
con 1 elettrone ciascuno

Nuvola elettronica con 6 elettroni
delocalizzati su tutta la molecola

Risonanza

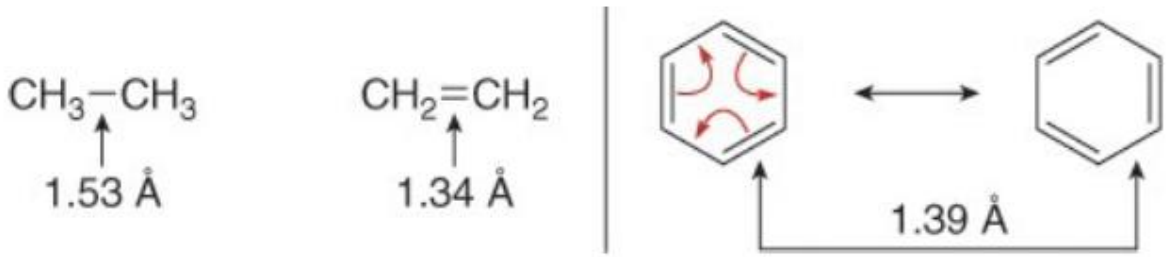
- Le strutture di risonanza (forme limite di risonanza) non sono reali
- Nessuna singola struttura di risonanza può adeguatamente rappresentare la reale struttura di una specie con elettroni delocalizzati
- Le strutture di risonanza NON sono isomeri, differiscono solo per la distribuzione degli elettroni (π o doppietti non condivisi), non dei nuclei
- Le strutture di risonanza NON sono in equilibrio

Risonanza

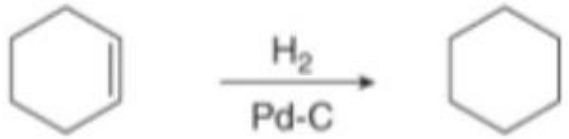
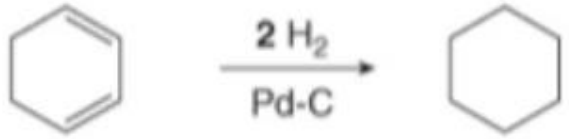
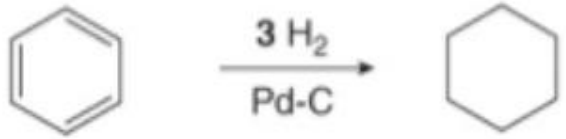


Forme limite di risonanza

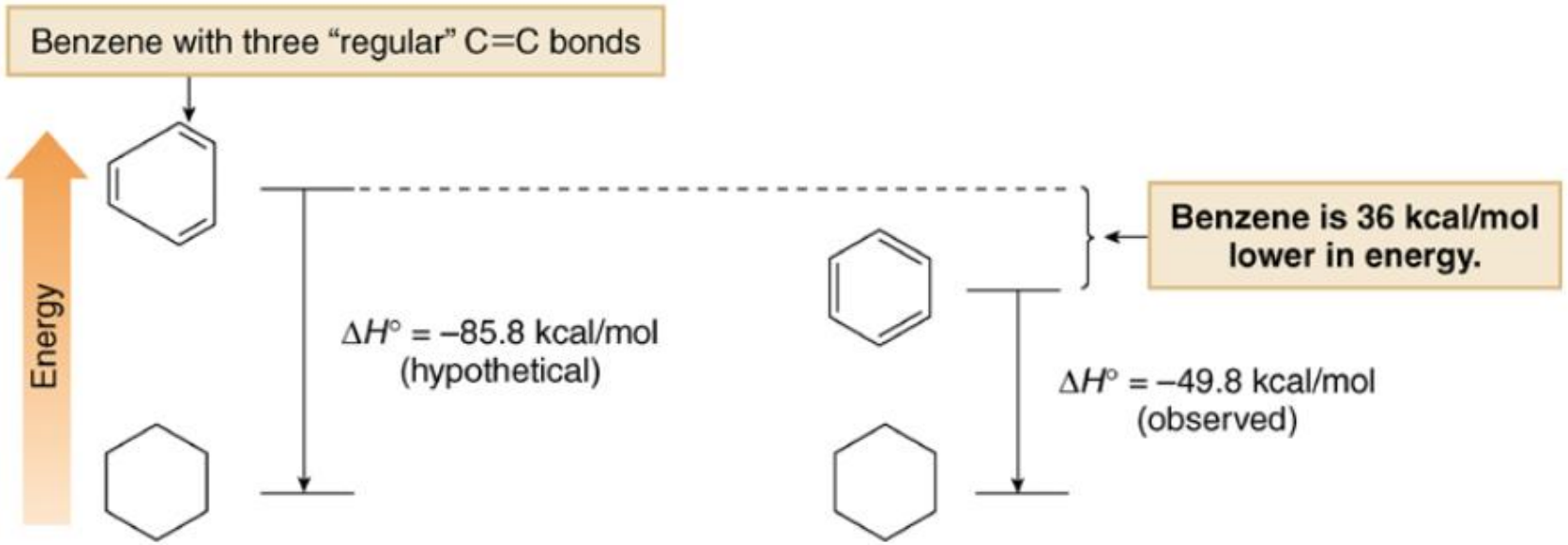
Ibrido di risonanza



Aromaticità, energia di risonanza

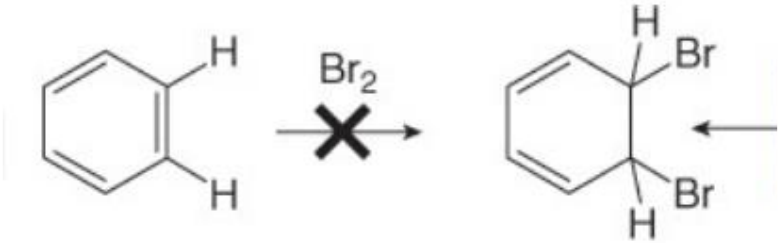
		ΔH_{found} (Kcal/mol)	$\Delta H_{expected}$ (Kcal/mol)	$\Delta H_{found-exp}$ (Kcal/mol)
[1]	 cyclohexene	-28.6		
[2]	 1,3-cyclohexadiene	-55.4	-57.2	1.8
[3]	 benzene	-49.8	-85.8	**36**

Aromaticità, energia di risonanza



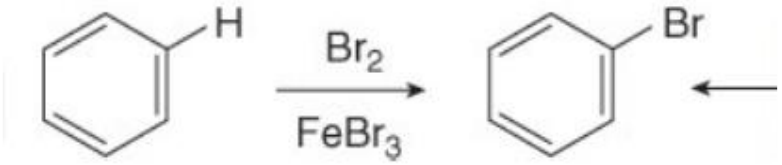
Stabilità del benzene aromaticità

La reazione di addizione non avviene



Verrebbe persa l'aromaticità

Avviene la reazione di sostituzione

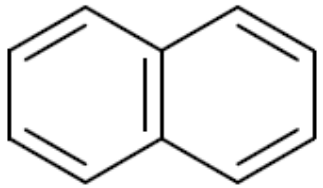


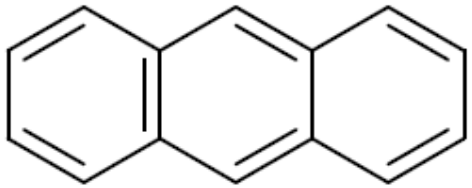
Il prodotto di sostituzione mantiene l'anello aromatico

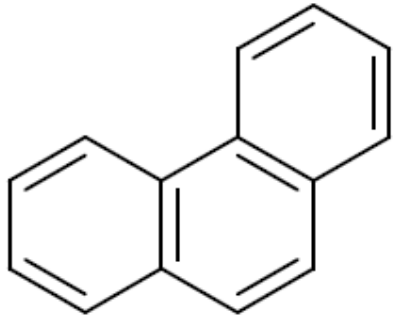
Criteri di aromaticità

- La molecola deve essere ciclica
- Tutti gli atomi devono essere ibridati sp^2
- La molecola deve essere planare
- La molecola deve avere 2, 6, 10, 14, ….(4n+2) elettroni π
  - Regola di Hückel

Idrocarburi policiclici aromatici (IPA)







(4n+2) elettroni π
n = 2

10 π

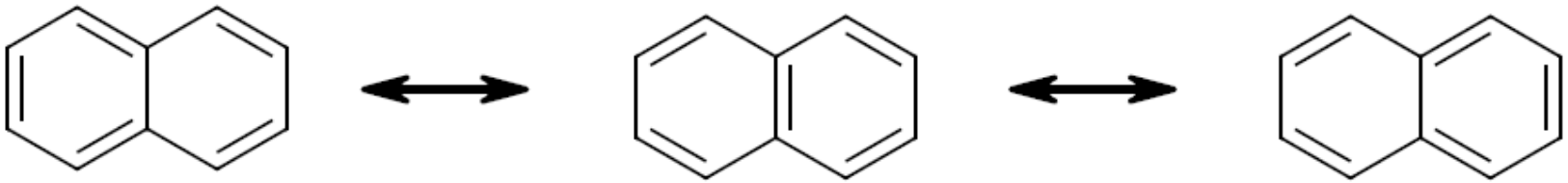
14 π

(4n+2) elettroni π
n = 3

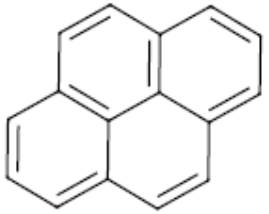
naftalene

antracene

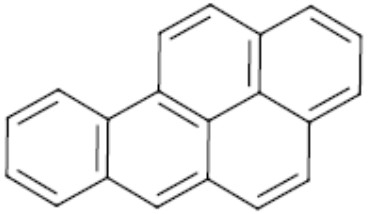
fenantrene



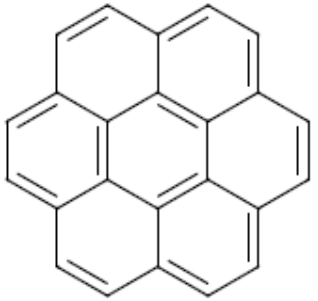
Idrocarburi policiclici aromatici (IPA)



pyrene
16 π

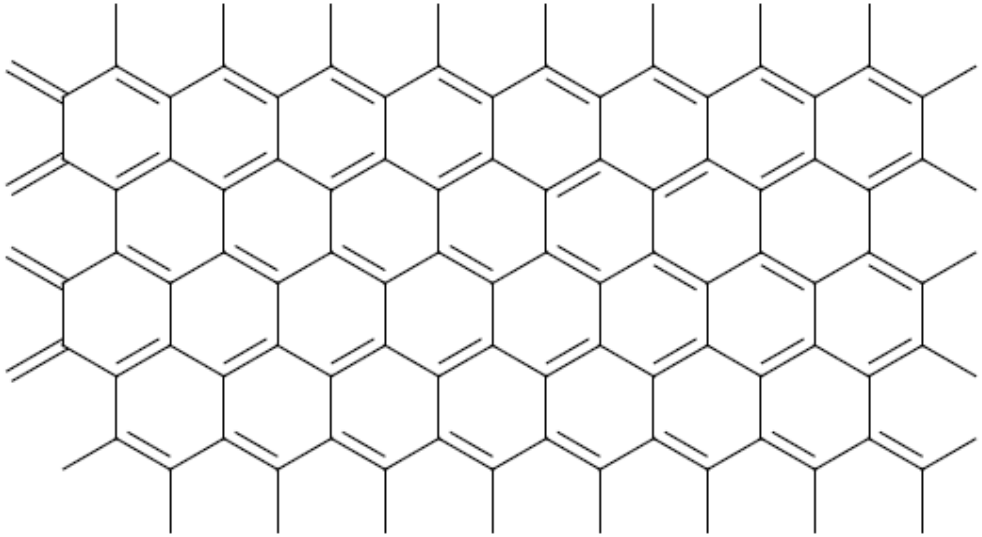


benzopyrene
20 π



coronene
24 π

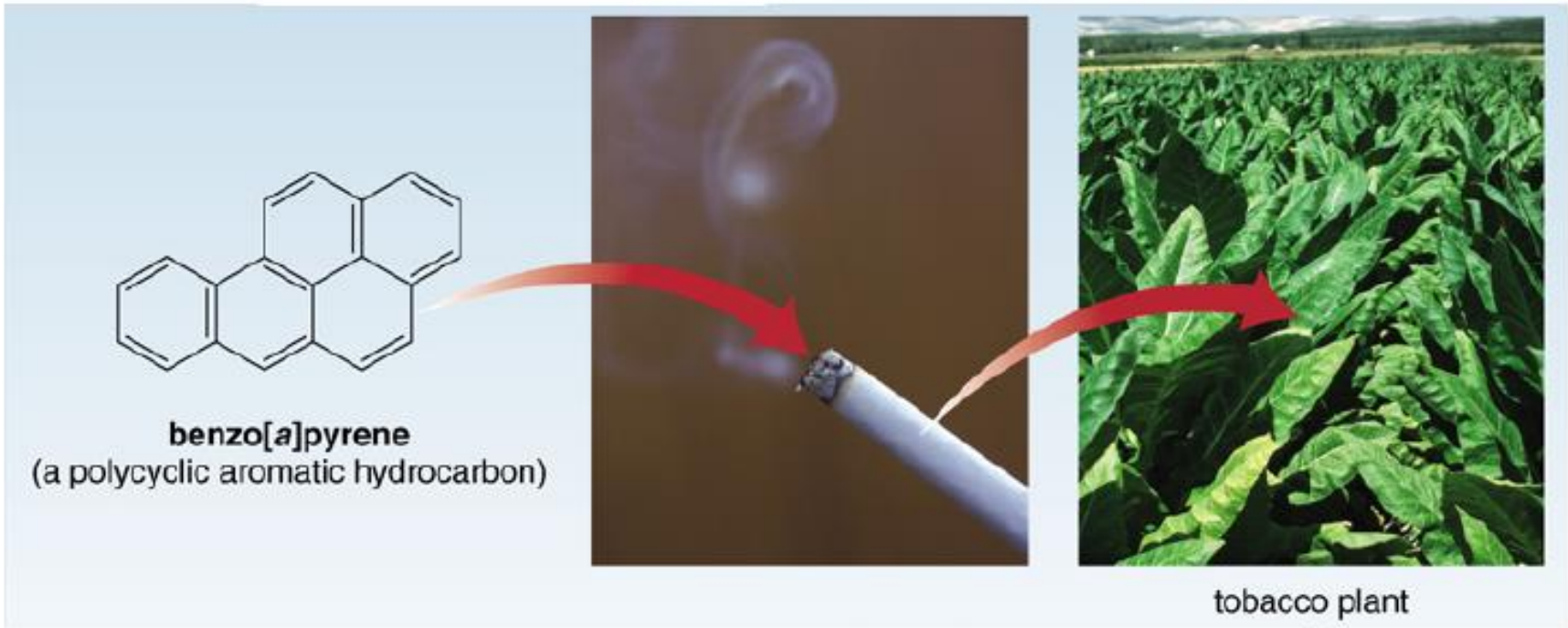
La regola di Hückel non si applica a sistemi grandi: tutti i sistemi policiclici insaturi con più di 3 anelli sono aromatici.



graphene

Interesting Aromatic Compounds

- Benzo[*a*]pyrene, produced by the incomplete oxidation of organic compounds in tobacco, is found in cigarette smoke.

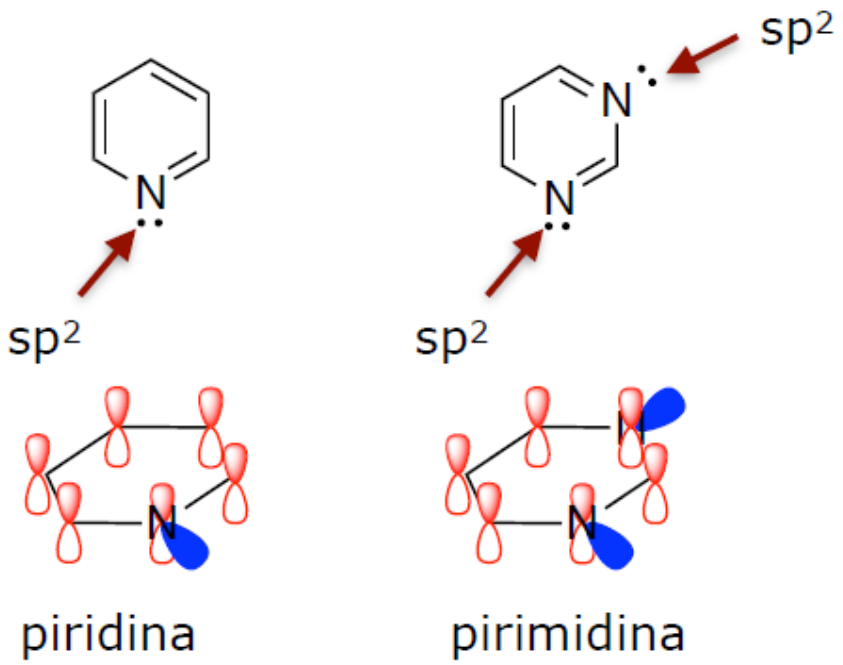


benzo[*a*]pyrene
(a polycyclic aromatic hydrocarbon)

tobacco plant

- When ingested or inhaled, benzo[a]pyrene and other similar PAHs are oxidized to carcinogenic products.

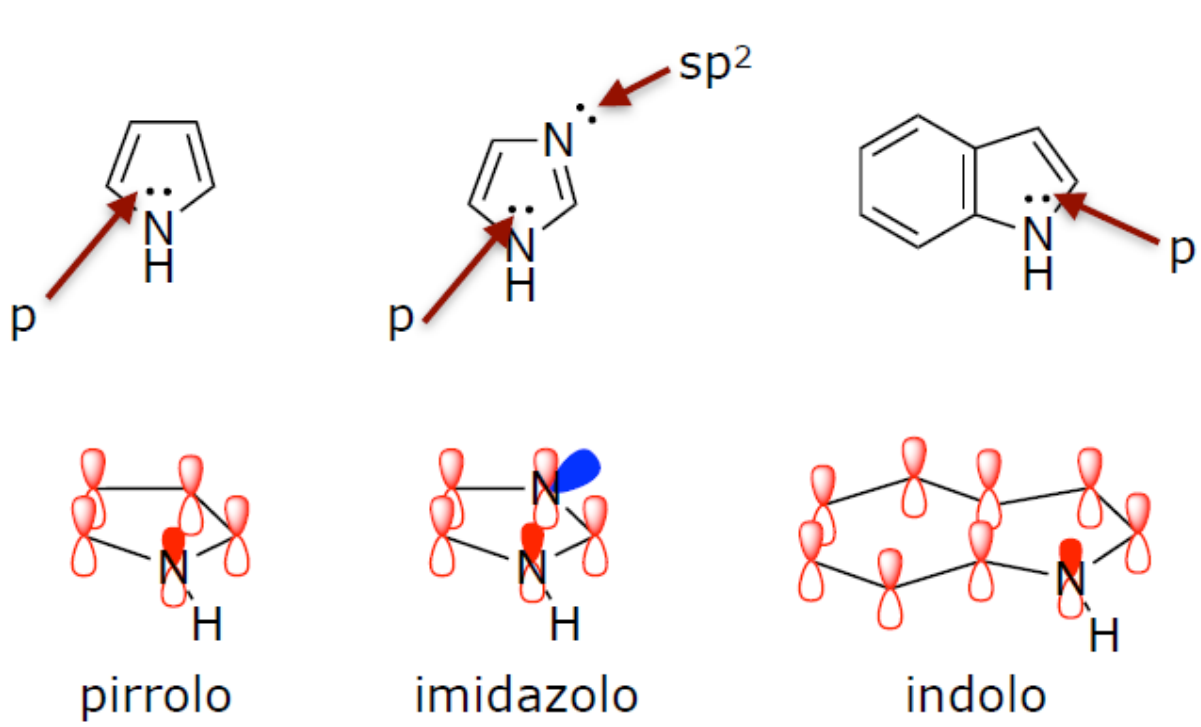
Composti Eterociclici Aromatici

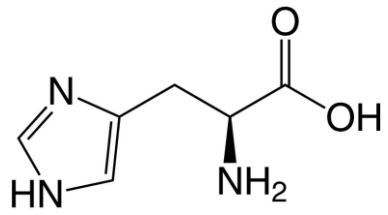


Il doppietto dell'azoto è in un orbitale sp^2

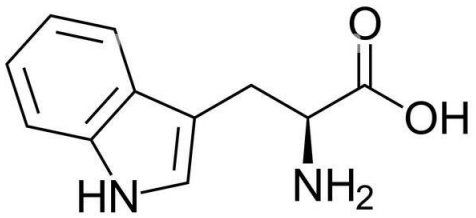
Piridina e pirimidina sono sostanze basiche e debolmente nucleofile

Composti Eterociclici Aromatici





Istidina

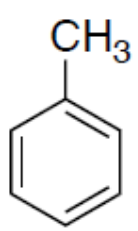


Triptofano

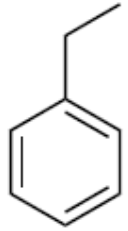
Il doppietto dell'azoto è nell'orbitale 2p e fa parte degli elettroni π delocalizzati, contribuisce all'aromaticità del sistema

Pirrolo e indolo non sono sostanze basiche

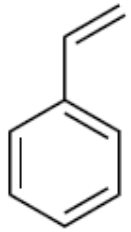
Nomenclatura del benzene monosostituito



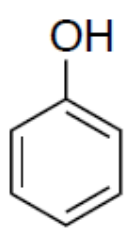
metilbenzene
toluene



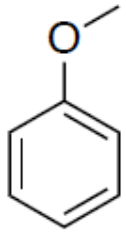
etilbenzene



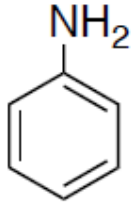
vinilbenzene
stirene



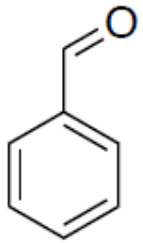
idrossibenzene
fenolo



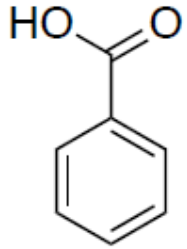
metossibenzene
fenilmetiletere
anisolo



amminobenzene
anilina



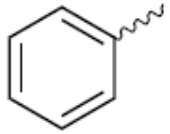
benzaldeide



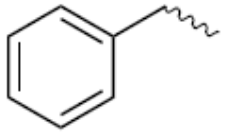
acido benzoico

Nomenclatura del benzene monosostituito

C_6H_5-
Ph

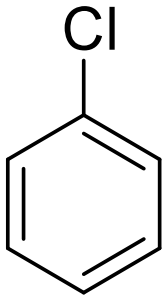


gruppo
fenile

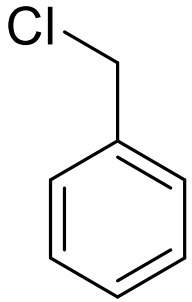


gruppo
benzile

$C_6H_5CH_2$-



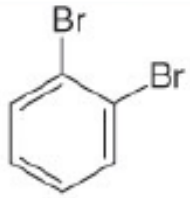
Clorobenzene



Benzil cloruro

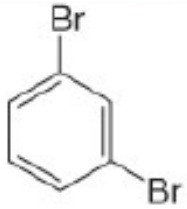
Nomenclatura del benzene disostituito

Benzene 1,2-disostituito:
Isomero ***orto***



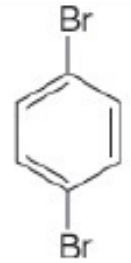
1,2-dibromobenzene
o-dibromobenzene

Benzene 1,3-disostituito:
Isomero ***meta***

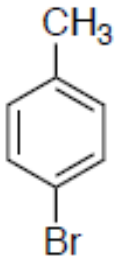


1,3-dibromobenzene
m-dibromobenzene

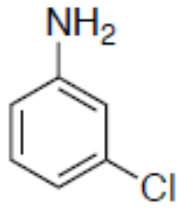
Benzene 1,4-disostiruito:
Isomero ***para***



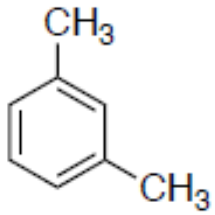
1,4-dibromobenzene
p-dibromobenzene



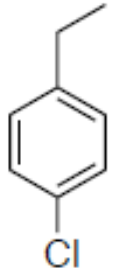
4-bromotoluene
p-bromotoluene



3-cloroanilina
m-cloroanilina

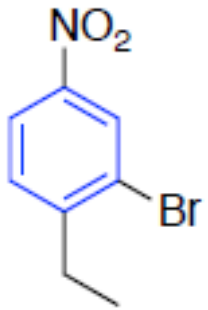


1,3-dimetilbenzene
m-xilene

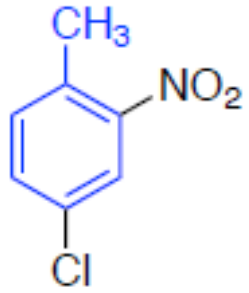


1-cloro-4-etilbenzene
p-cloroetilbenzene

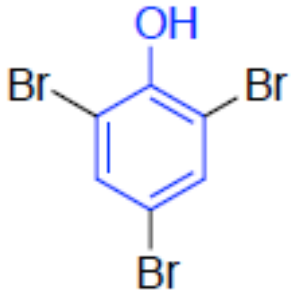
Nomenclatura: 3 o Più Sostituenti



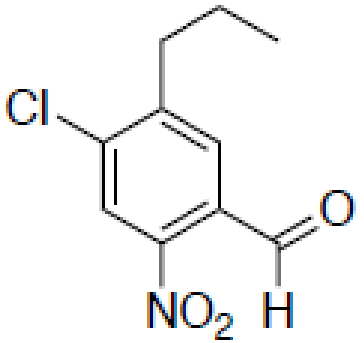
2-bromo-1-etil-4-nitrobenzene



4-cloro-2-nitro-toluene



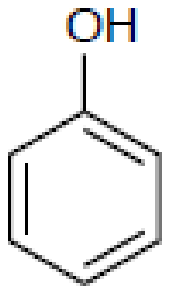
2,4,6-tribromofenolo



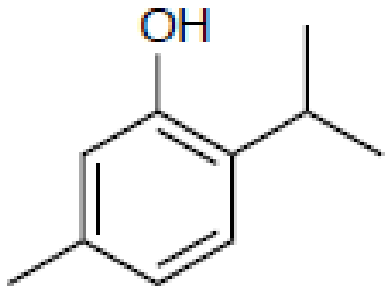
4-cloro-2-nitro-5-propilbenzaldeide

Sostituzione elettrofila aromatica

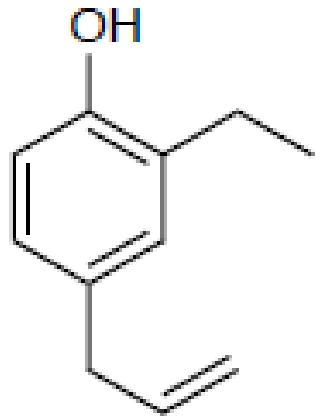
Fenoli (Alcoli Aromatici)



fenolo

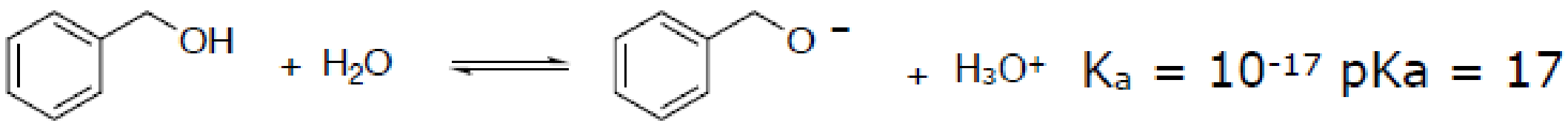


timolo
(timo)

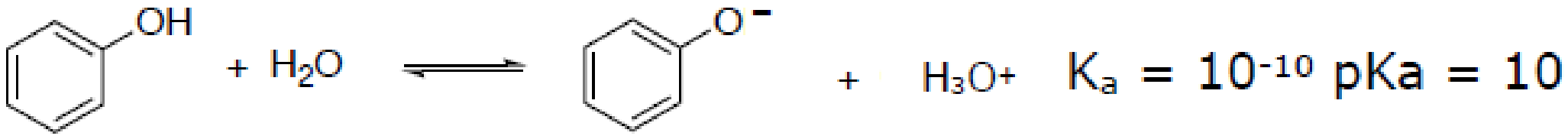


eugenolo
(chiodo di garofano)

Acidità dei Fenoli



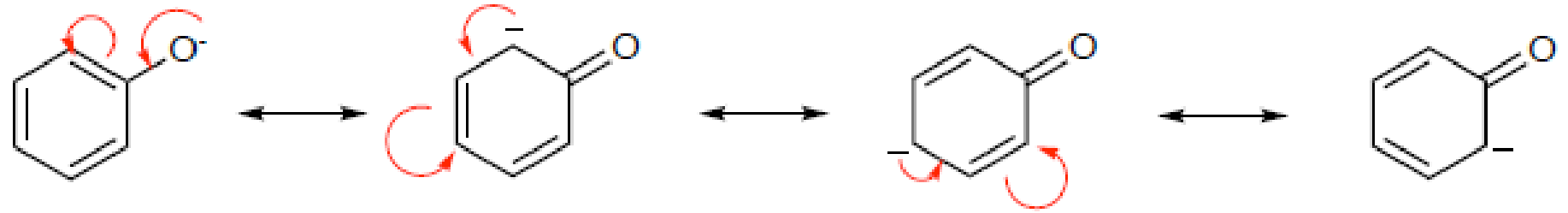
Alcol benzilico



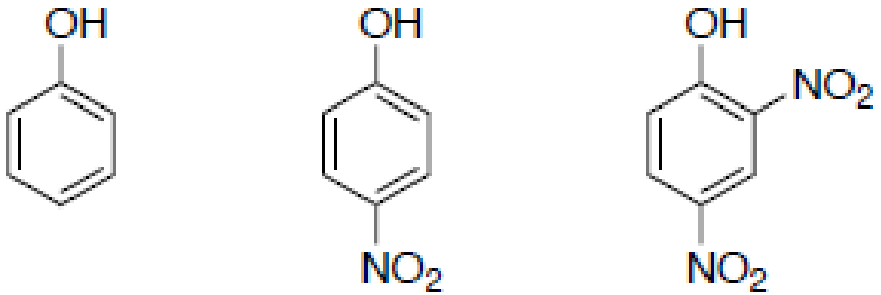
Fenolo

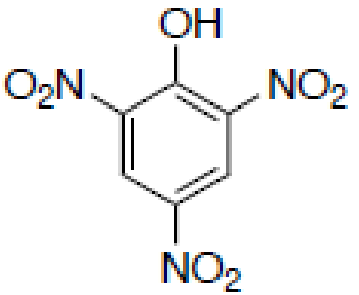
Acidità dei Fenoli

L'anione fenato é stabilizzato dalla delocalizzazione della carica sull'anello aromatico



Sostituenti elettron attrattori aumentano l'acidità del fenolo perché favoriscono la delocalizzazione





acido picrico

pKa	10	7.2	4	0.4