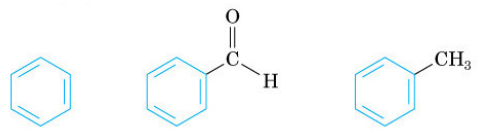
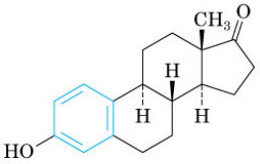
Benzene e aromaticità

Benzene e composti aromatici



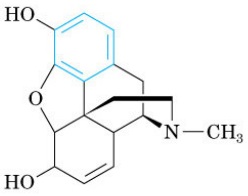
Benzene	Benzaldeide	Toluene
dal carbone	da ciliegie pesche mandorle	dal balsamo di Tolu

Benzene e composti aromatici



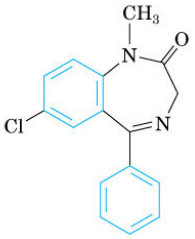
Estrone

ormone steroideo
naturale



Morfina

analgesico
naturale



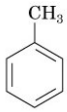
Diazepam (Valium)

tranquillante
sintetico

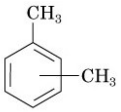
Benzene e composti aromatici

Alcuni idrocarburi aromatici presenti nel catrame di carbone

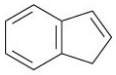
Benzene
(p.e. 80°C)



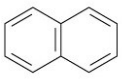
Toluene
(p.e. 111°C)



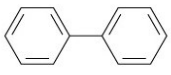
Xilene
(p.e. orto, 144°C;
meta, 139°C; para, 138°C)



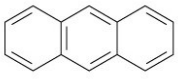
Indene
(p.e. 182°C)



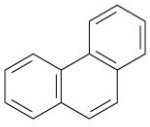
Naftalene
(p.f. 80°C)



Bifenile
(p.f. 71°C)



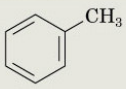
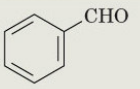
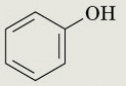
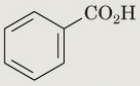
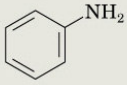
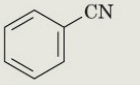
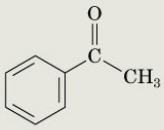
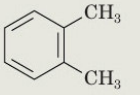
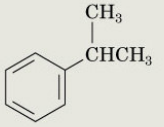
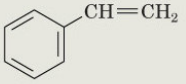
Antracene
(p.f. 216°C)



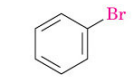
Fenantrene
(p.f. 101°C)

Benzene e composti aromatici

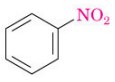
Nomi comuni di alcuni composti aromatici

Formula	Nome	Formula	Nome
	Toluene (p.e. 111°C)		Benzaldeide (p.e. 178°C)
	Fenolo (p.f. 43°C)		Acido benzoico (p.f. 122°C)
	Anilina (p.e. 184°C)		Benzonitrile (p.e. 191°C)
	Acetofenone (p.f. 21°C)		*orto*-Xilene (p.e. 144°C)
	Cumene (p.e. 152°C)		Stirene (p.e. 145°C)

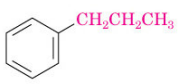
Composti aromatici: nomenclatura



Bromobenzene

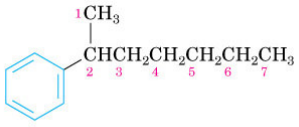


Nitrobenzene

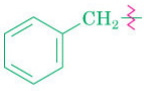


Propilbenzene

Gruppo fenilico

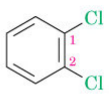


2-Fenileptano

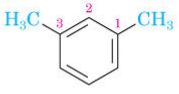


Gruppo benzilico

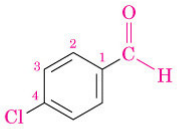
I benzeni disostituiti vengono denominati usando i prefissi ***orto- (o***
eta- (m), o ***para- (p)***. Un benzene orto-disostituito porta i due sostituen
ıll'anello in posizione 1,2, un benzene meta-disostituito ha i due sostituen
posizione 1,3, e un benzene para-disostituito presenta i sostituenti in p
zione 1,4.



***orto*-Diclorobenzene**
1,2 disostituito

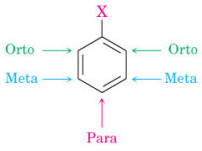


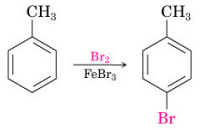
***meta*-Xilene**
1,3 disostituito



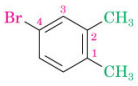
***para*-Clorobenzaldeide**
1,4 disostituito

Composti aromatici: nomenclatura

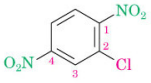




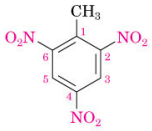
Toluene **p-Bromotoluene**



4-Bromo-1,2-dimetilbenzene

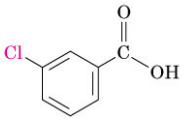


2-Cloro-1,4-dinitrobenzene



2,4,6-Trinitrotoluene (TNT)

2,6-Dibromo*fenolo*



Acido m-clorobenzoico

Aromaticità

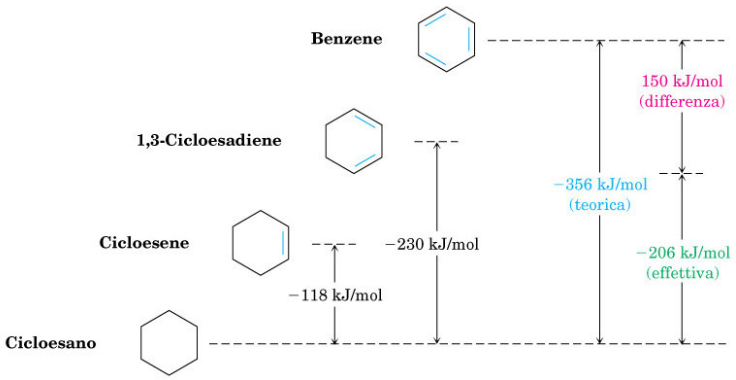
Benzene meno reattivo degli alcheni

Benzene **Bromobenzene (prodotto di sostituzione)** **(Prodotto di addizione)** ***NON si forma***

Il prodotto di sostituzione mantiene la coniugazione ciclica

Aromaticità

Confronto dei calori di idrogenazione per il cicloesene, l'1,3-cicloesadiene e il benzene. Il benzene risulta di 150 kJ/mole (36 kcal/ mol) più stabile di quanto ci si potrebbe aspettare per il "cicloesatriene".



Più stabile degli alcheni

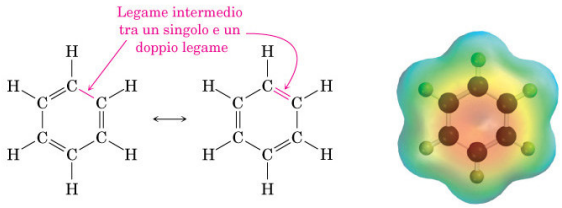
Aromaticità

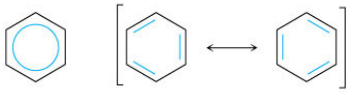
Tutti i legami hanno la stessa lunghezza di 139 pm, intermedia tra un legame singolo di 154 pm e uno doppio di 134 pm

Tutti gli angoli sono di 120°

La molecola è planare!

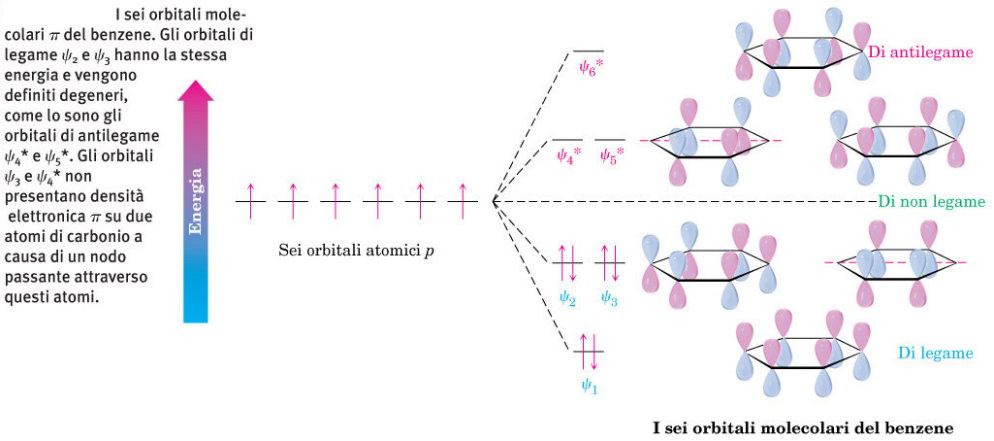
Tutti gli atomi di C sono ibridizzati sp^2





Rappresentazioni alternative del benzene. La rappresentazione con il cerchio deve essere usata con attenzione dal momento che non indica in numero degli elettroni π nell'anello.

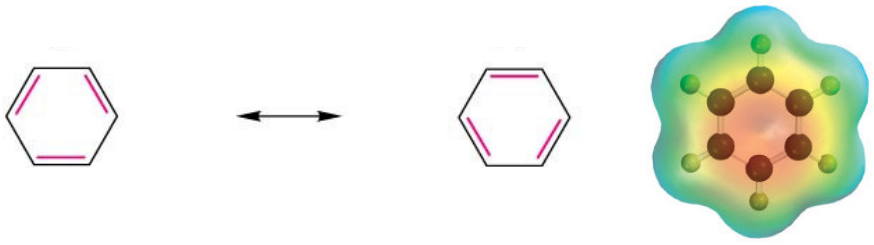
Aromaticità



I sei orbitali molecolari del benzene

regola di Hückel: una molecola è aromatica se possiede un sistema planare coniugato con un numero totale di **4n+2** elettroni π, con n=1,2,3,…

Aromaticità



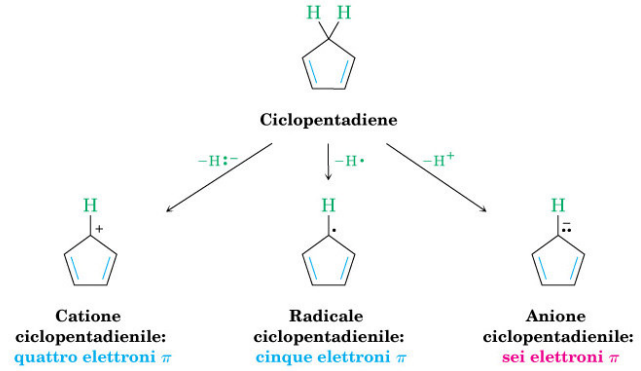
Le molecole sono aromatiche se sono soddisfatte le seguenti condizioni:

- La molecola è ciclica
- La molecola è interamente coniugata
- La molecola è planare (atomi di carbonio con ibridazione sp^2)
- regola di Hückel: la molecola contiene $(4n + 2)$ elettroni π

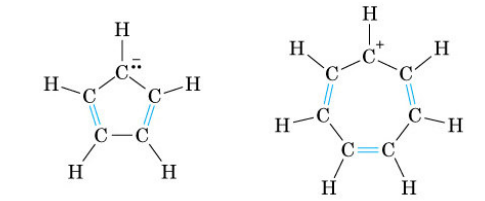
Aromaticità

Molecole aromatiche non neutre

Formazione del catione, radicale e anione ciclopentadienile per estrazione di un atomo di idrogeno dal ciclopentadiene.



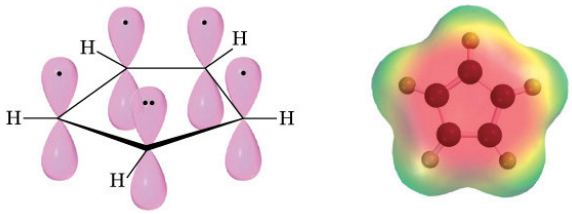
Aromaticità



Ioni aromatici a sei elettroni π

Aromaticità

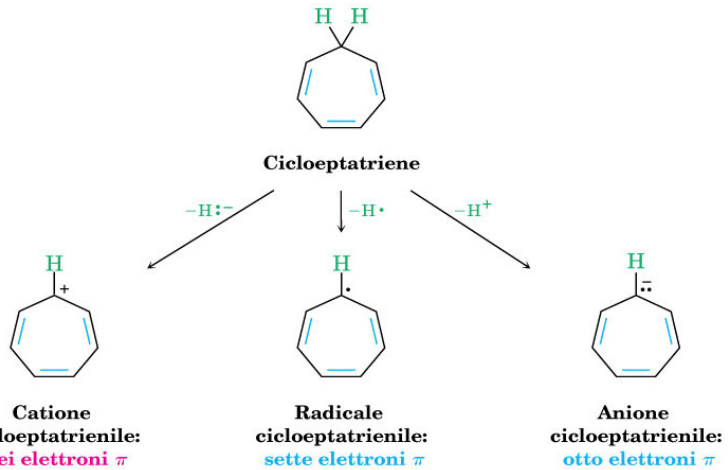
Rappresentazione degli orbitali dell'anione ciclopentadienile che dimostra la coniugazione ciclica dei sei elettroni p nei cinque orbitali p. La mappa di potenziale elettrostatico indica che lo ione risulta simmetrico, e che tutti i cinque atomi di carbonio sono elettronricchi (rosso).



L'anione aromatico ciclopentadienile, con sei elettroni π

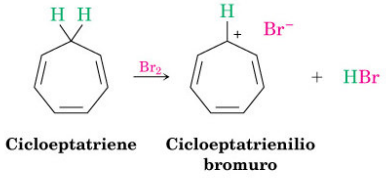
Aromaticità

Formazione del catione, radicale e anione cicloeptatrienile.
Soltanto il catione a sei elettroni π risulta aromatico.

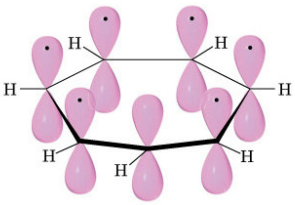


Aromaticità

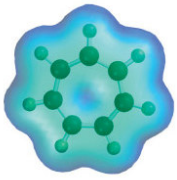
La reazione del cicloeptatriene con bromo porta al cicloeptatrienilio bromuro, un composto ionico contenente il catione cicloeptatrienile. La mappa di potenziale elettrostatico indica che tutti i sette atomi di carbonio hanno la stessa quantità di carica e sono elettronpoveri (blu).



Cicloeptatriene **Cicloeptatrienilio bromuro**



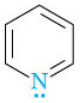
Catione cicloeptatrienile
sei elettroni π

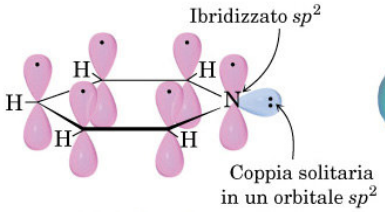


Aromaticità

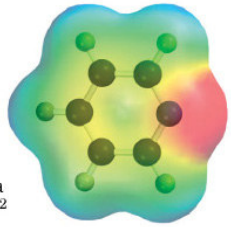
Aromaticità in composti eterociclici

La piridina, un eterociclo aromatico, ha una disposizione degli elettroni p molto simile a quella del benzene.



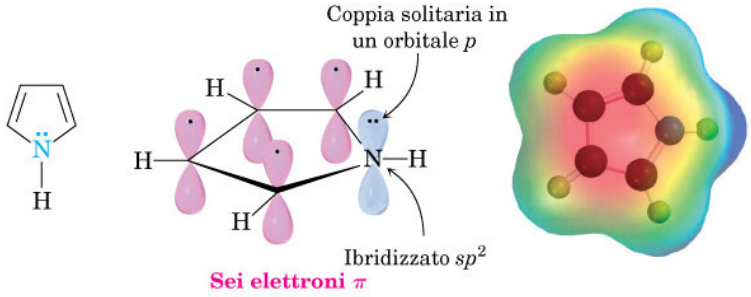


Sei elettroni π

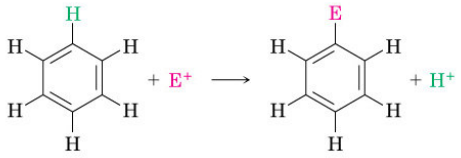


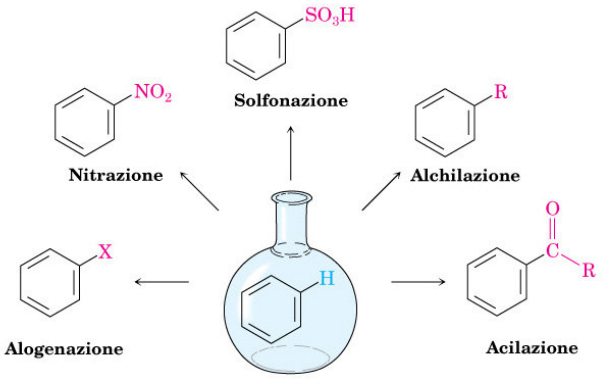
Aromaticità

Il pirrolo, un eterociclo aromatico a cinque termini, ha una disposizione degli elettroni p molto simile a quella dell'anione ciclopentadienile.



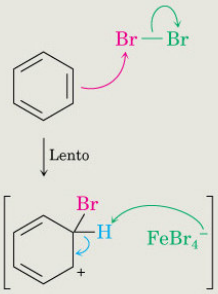
Sostituzione elettrofila aromatica





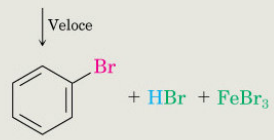
Sostituzione elettrofila aromatica

Una coppia di elettroni dell'anello benzenico attacca Br_2 formando un nuovo legame C—Br e lasciando un intermedio carbocationico non aromatico.



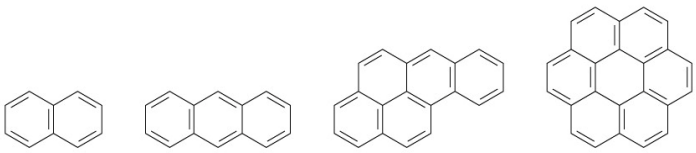
Carbocatione non aromatico

L'intermedio carbocationico perde H^+, e si forma il prodotto di sostituzione neutro, mentre i due elettroni del legame si spostano per rigenerare l'anello aromatico.

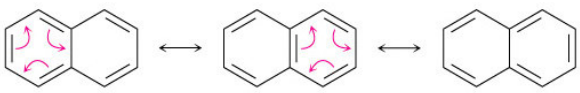


Aromatici policiclici

Policiclici aromatici

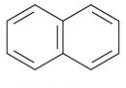


Naftalene **Antracene** **Benzo[a]pirene** **Coronene**

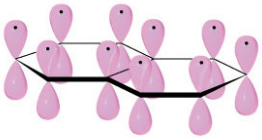


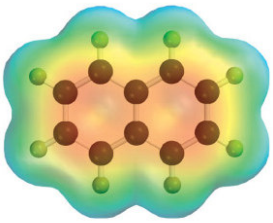
Aromatici policiclici

Il disegno degli orbitali e la mappa di potenziale elettrostatico del naftalene mostrano che i dieci elettroni π sono completamente delocalizzati su entrambi gli anelli.



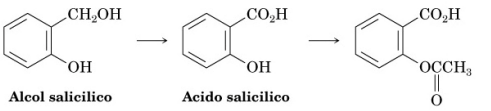
Naftalene



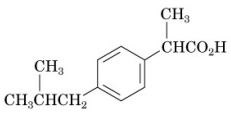


Anti-infiammatori

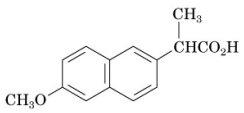
Anti-infiammatori non steroidei (≠ cortisone e derivati)



Alcol salicilico — Acido salicilico — Acido acetilsalicilico (Aspirina)



Ibuprofene



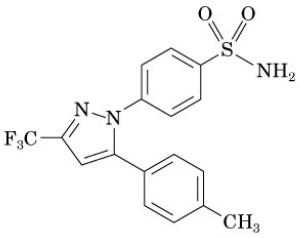
Naprossene

Molti atleti sotto sforzo fanno uso di farmaci anti-infiammatori non steroidei per alleviare il dolore e la fatica.

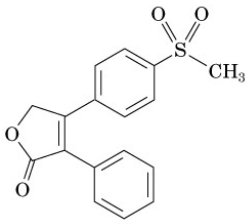
Rimane attivo più a lungo

Agiscono indistintamente sulle cicloossigenasi COX-1 e COX-2 producendo effetti collaterali

Anti-infiammatori



Celecoxib



Rofecoxib

agiscono selettivamente sulle cicloossigenasi COX-2 eliminando effetti collaterali

usati nel trattamento di artriti e altre patologie