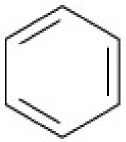
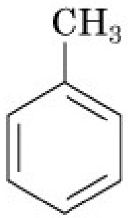
Composti aromatici

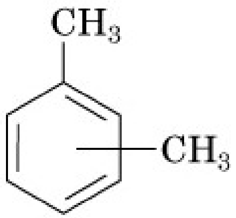
Alcuni idrocarburi aromatici presenti nel catrame di carbone.



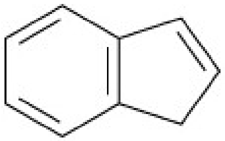
Benzene
(p.e. 80°C)



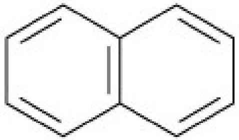
Toluene
(p.e. 111°C)



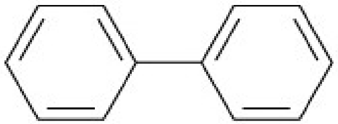
Xilene
(p.e. orto, 144°C;
meta, 139°C; para, 138°C)



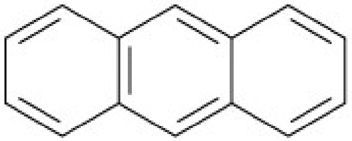
Indene
(p.e. 182°C)



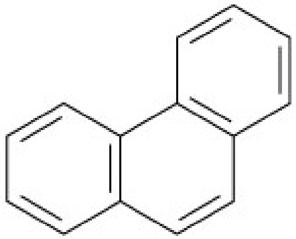
Naftalene
(p.f. 80°C)



Bifenile
(p.f. 71°C)

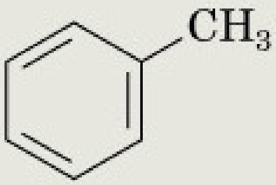
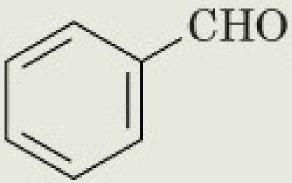
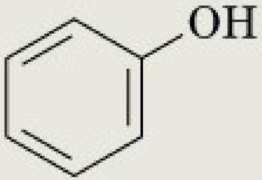
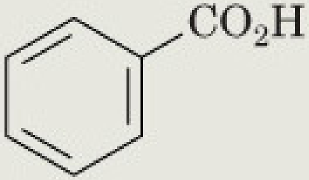
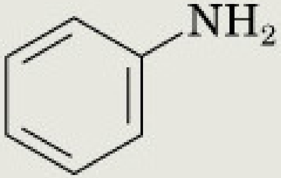
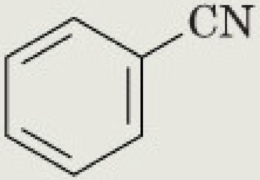
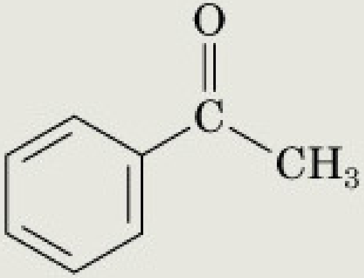
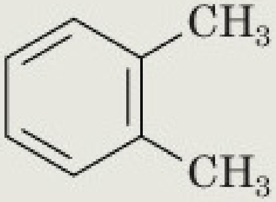
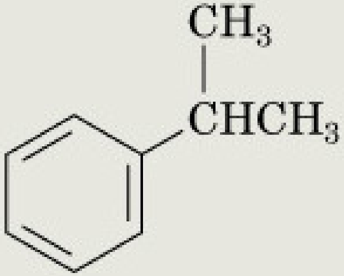
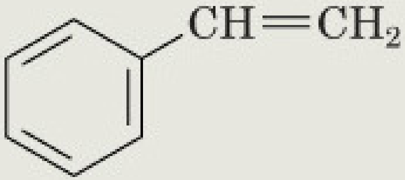


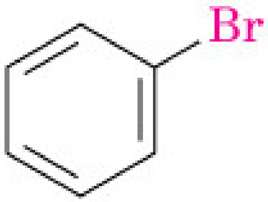
Antracene
(p.f. 216°C)



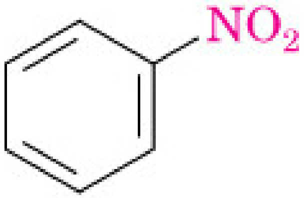
Fenantrene
(p.f. 101°C)

Tabella 15.1 Nomi comuni di alcuni composti aromatici

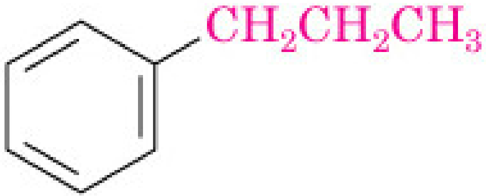
Formula	Nome	Formula	Nome
	Toluene (p.e. 111°C)		Benzaldeide (p.e. 178°C)
	Fenolo (p.f. 43°C)		Acido benzoico (p.f. 122°C)
	Anilina (p.e. 184°C)		Benzonitrile (p.e. 191°C)
	Acetofenone (p.f. 21°C)		*orto*-Xilene (p.e. 144°C)
	Cumene (p.e. 152°C)		Stirene (p.e. 145°C)



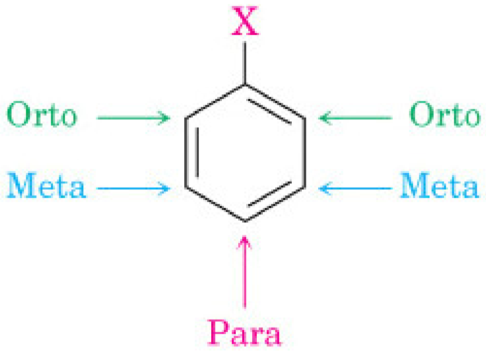
Bromobenzene

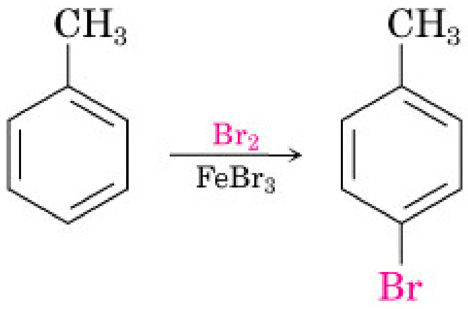


Nitrobenzene

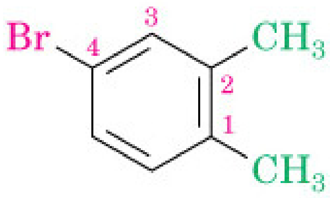


Propilbenzene

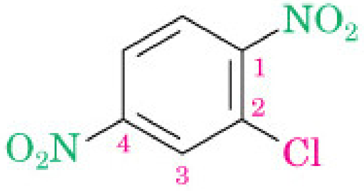




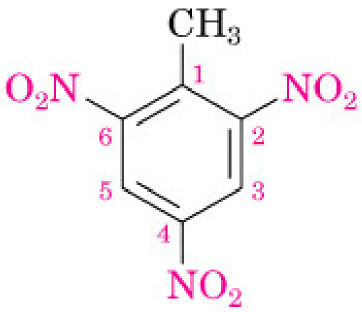
Toluene **_p_-Bromotoluene**



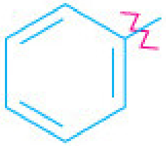
4-Bromo-1,2-dimetilbenzene



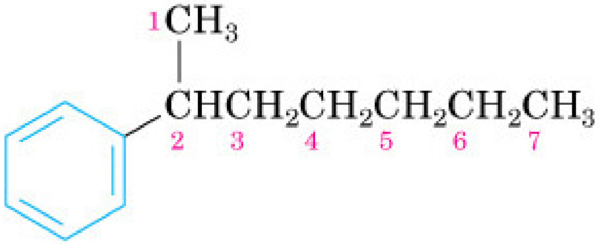
2-Cloro-1,4-dinitrobenzene



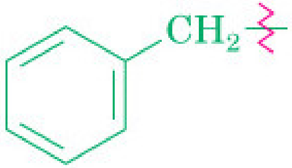
2,4,6-Trinitrotoluene (TNT)



Gruppo fenilico

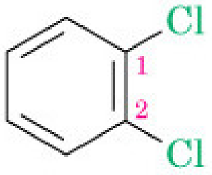


2-Fenileptano

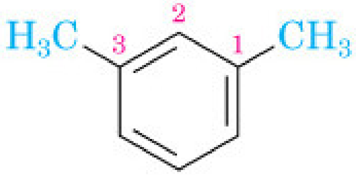


Gruppo benzilico

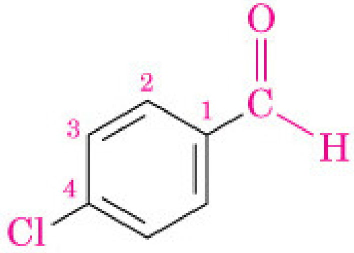
I benzeni disostituiti vengono denominati usando i prefissi ***orto- (o***
eta- (m), o ***para- (p)***. Un benzene orto-disostituito porta i due sostituen
ıll'anello in posizione 1,2, un benzene meta-disostituito ha i due sostituen
posizione 1,3, e un benzene para-disostituito presenta i sostituenti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



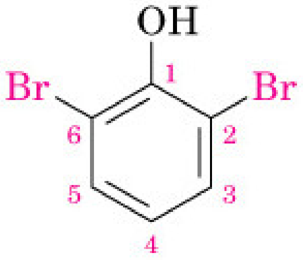
***orto*-Diclorobenzene**
1,2 disostituto



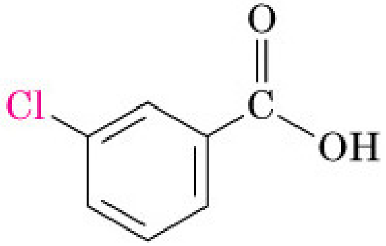
***meta*-Xilene**
1,3 disostituito



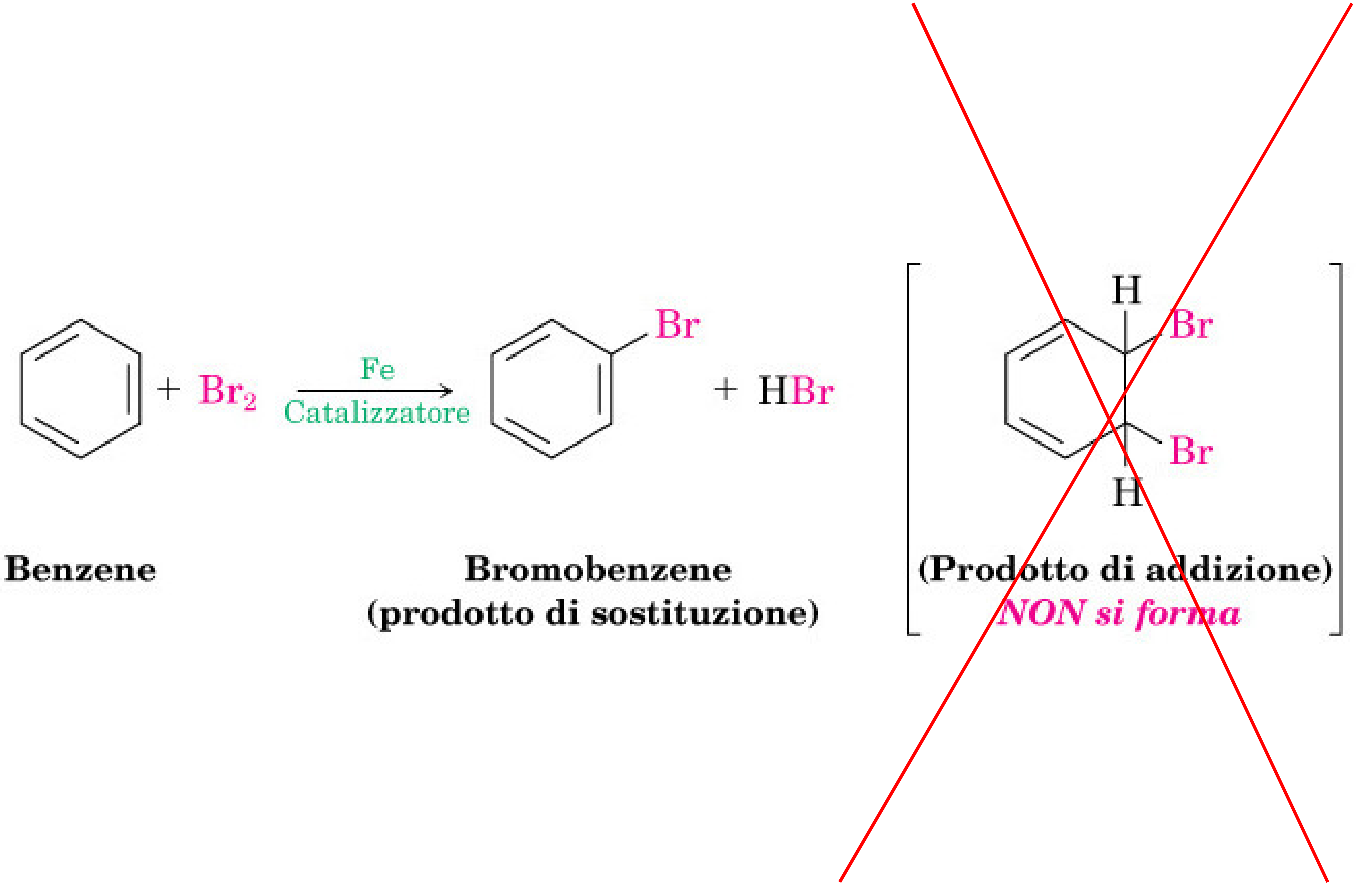
***para*-Clorobenzaldeide**
1,4 disostituto



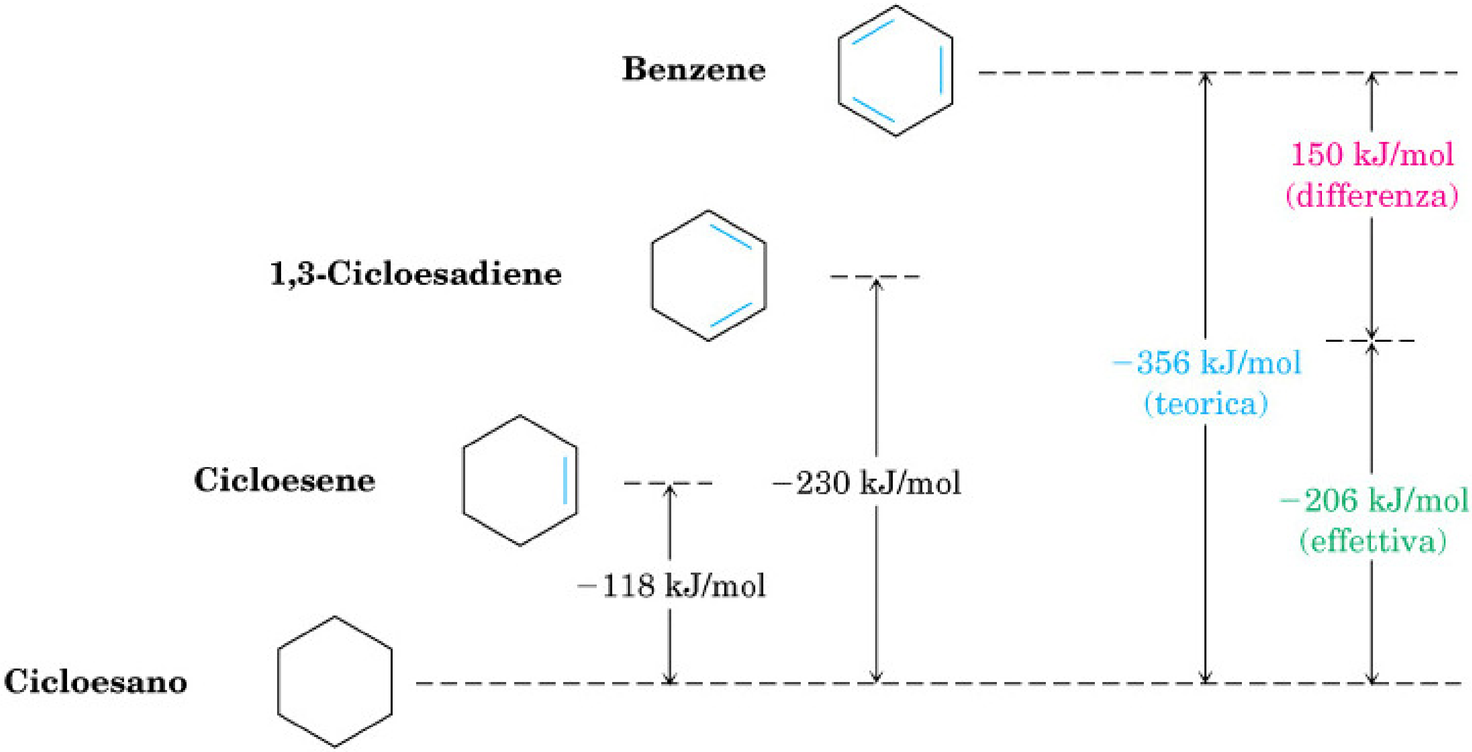
2,6-Dibromo*fenolo*

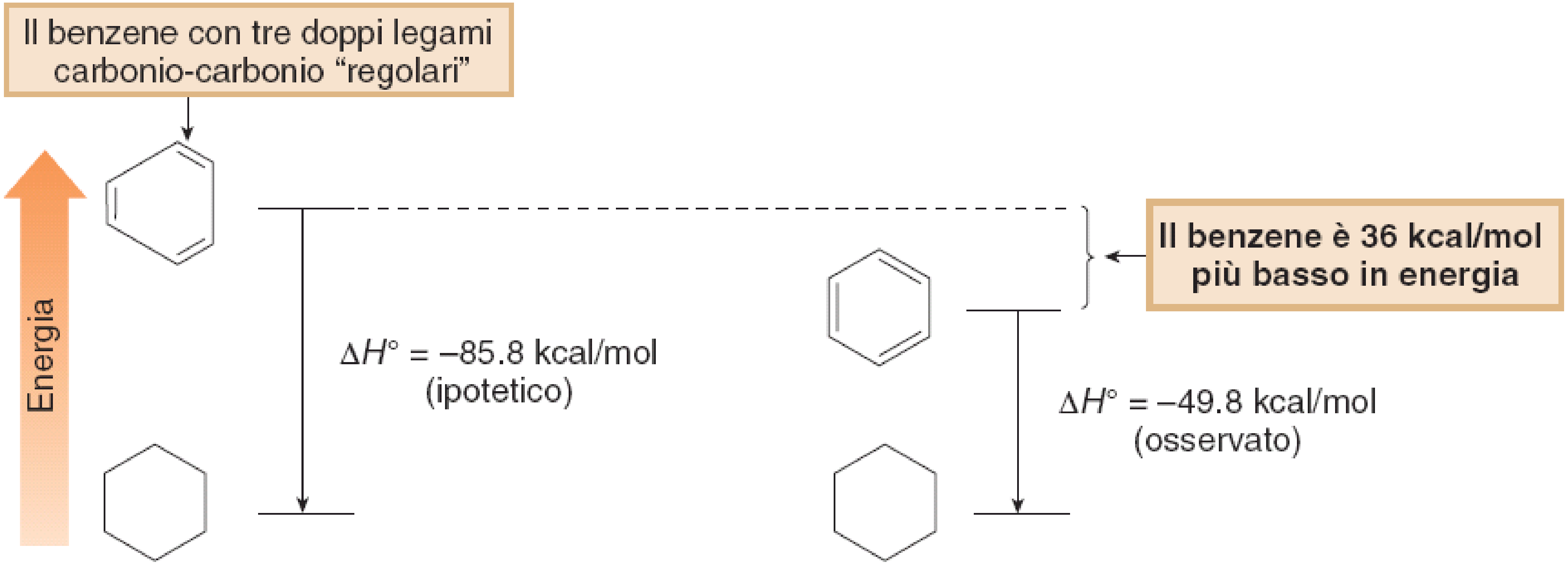


Acido m-cloro_benzoico_


Br$_2$
Fe
Catalizzatore
Br
HBr
H
Br
Br
H
Benzene
Bromobenzene
(prodotto di sostituzione)
(Prodotto di addizione)
NON si forma

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



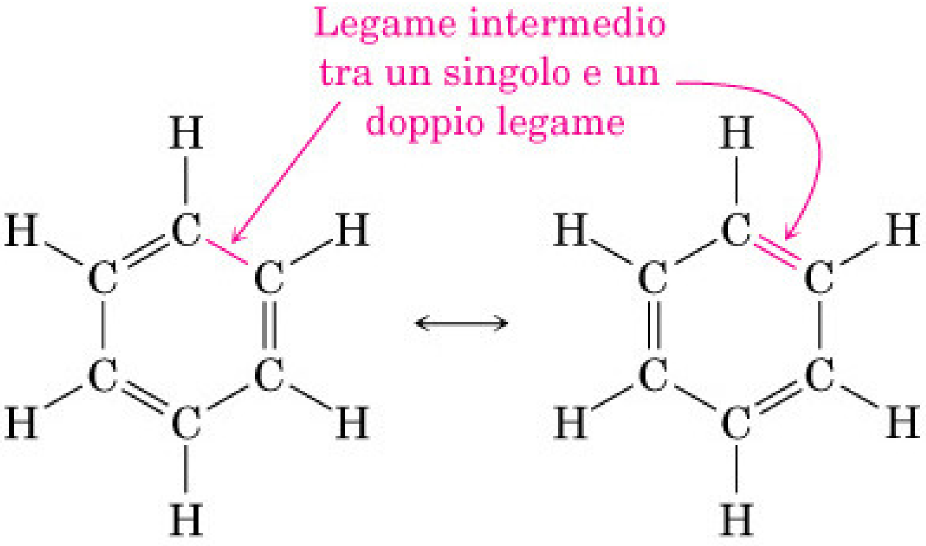


Il benzene con tre doppi legami carbonio-carbonio “regolari”

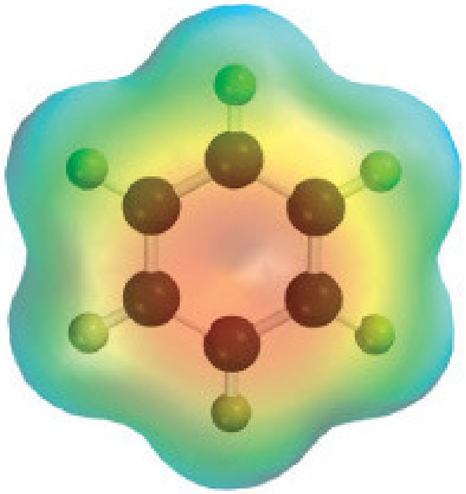
Il benzene è 36 kcal/mol più basso in energia

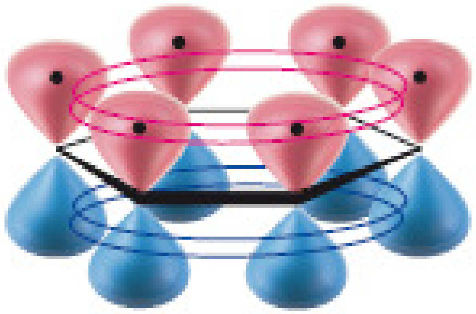
$\Delta H^\circ = -85.8$ kcal/mol
(ipotetico)

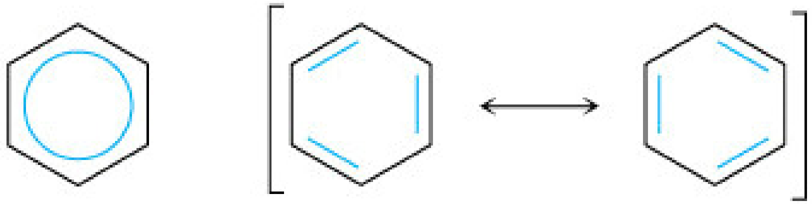
$\Delta H^\circ = -49.8$ kcal/mol
(osservato)



Legame intermedio tra un singolo e un doppio legame

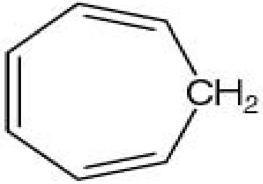




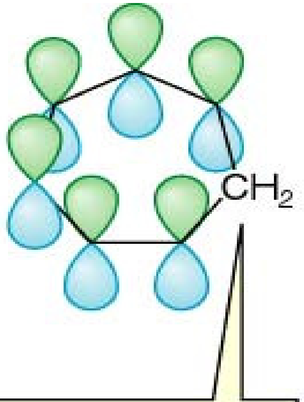


Rappresentazioni alternative del benzene. La rappresentazione con il cerchio deve essere usata con attenzione dal momento che non indica in numero degli elettroni **π** nell'anello.

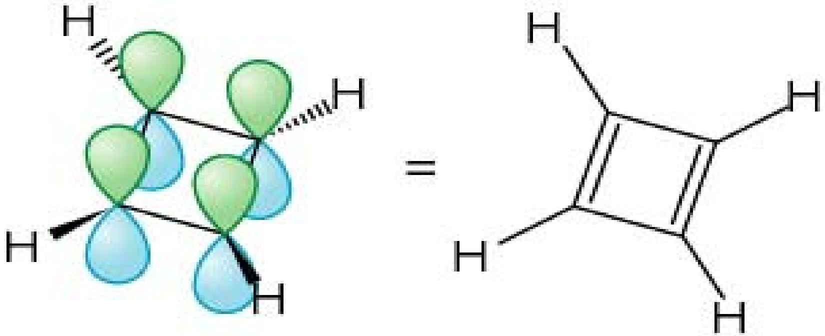
Composti non-aromatici



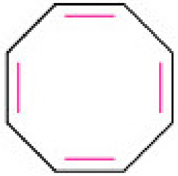
1,3,5-Cycloheptatriene



2*p* Orbital connectivity at C(7) broken here by the CH$_2$ group (no 2*p* orbital)

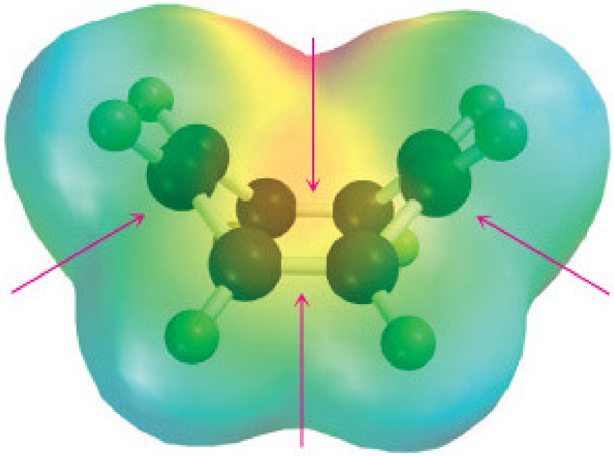


A most unstable molecule even though it is planar, cyclic, and fully conjugated



Cicloottatetraene

Quattro doppi legami;
otto elettroni π



- Le molecole sono aromatiche se sono soddisfatte le seguenti condizioni:
    - La molecule è ciclica
    - La molecula è interamente coniugata
    - La molecula è planare (atomi di carbonio con ibridazione sp^2)
    - regola di Hückel: la molecula contiene ($4n + 2$) elettroni-p (con $n = 1, 2, 3......$)

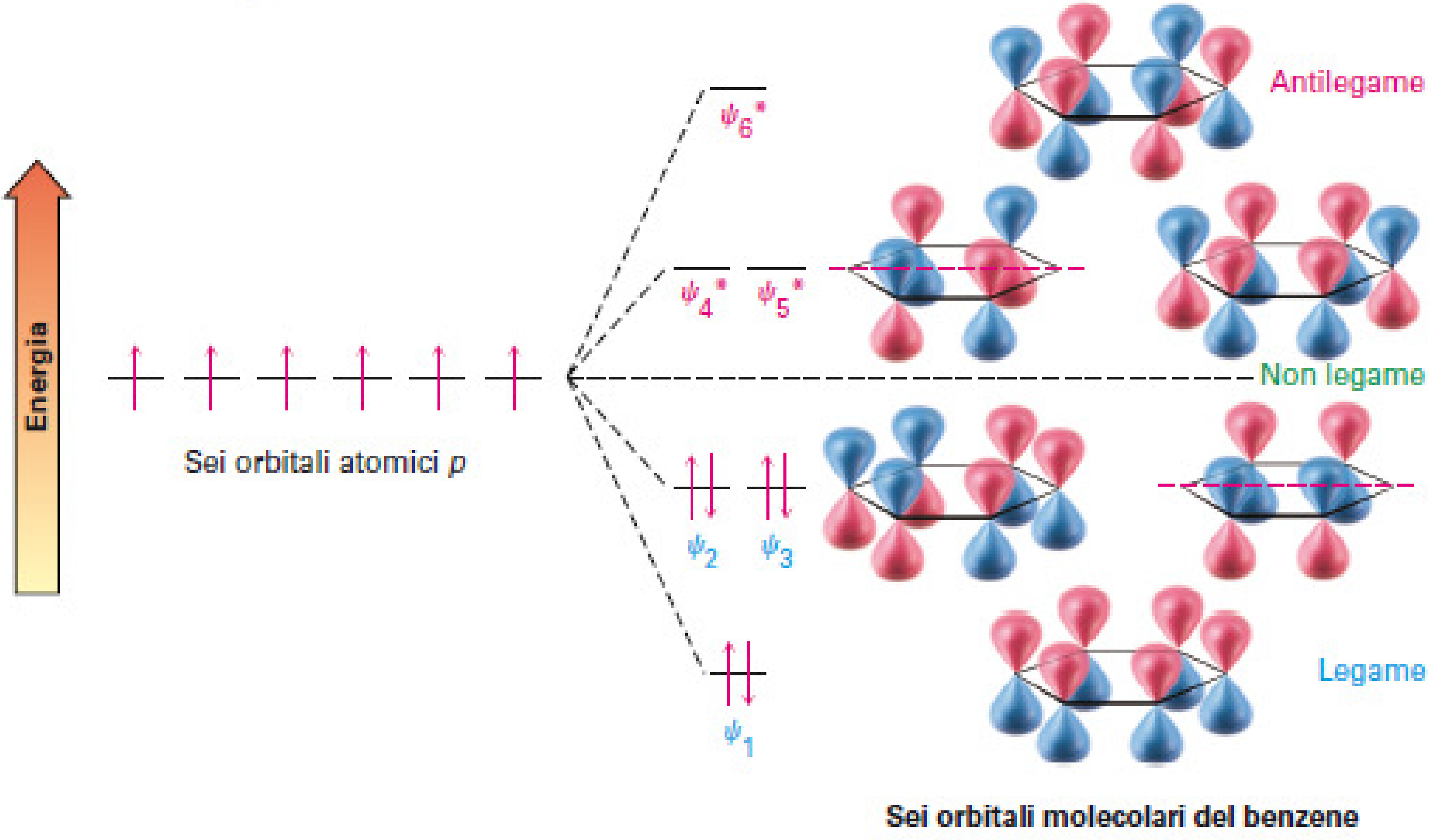
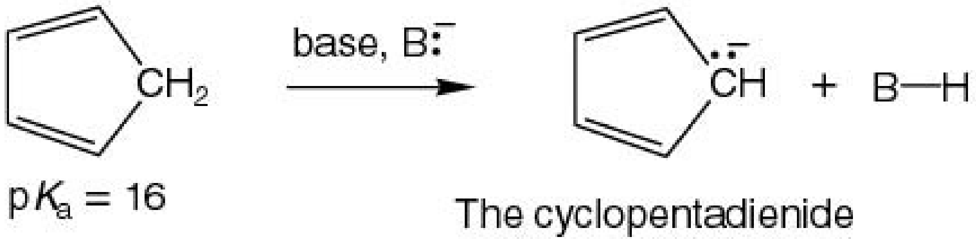
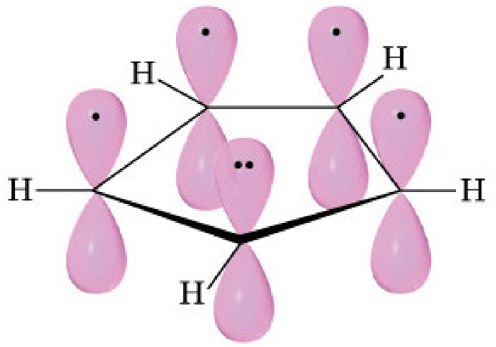


Figura 15.4 I sei orbitali molecolari π del benzene. Gli orbitali di legame ψ_2 e ψ_3 hanno la stessa energia e vengono definiti degeneri, come lo sono gli orbitali di antilegame ψ_4^* e ψ_5^*. Gli orbitali ψ_3 e ψ_4^* non presentano densità elettronica π su due atomi di carbonio a causa di un nodo passante attraverso questi atomi.

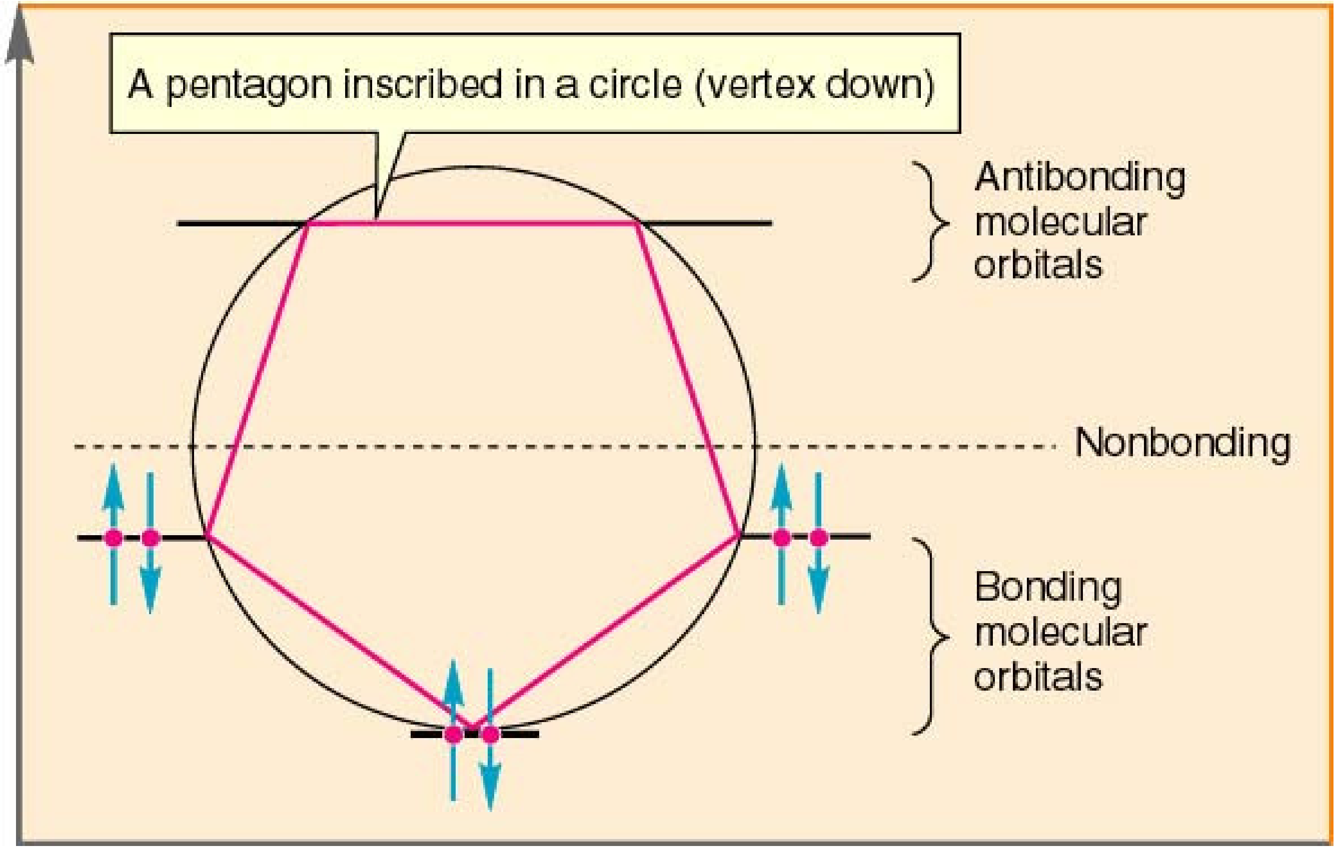
ioni aromatici

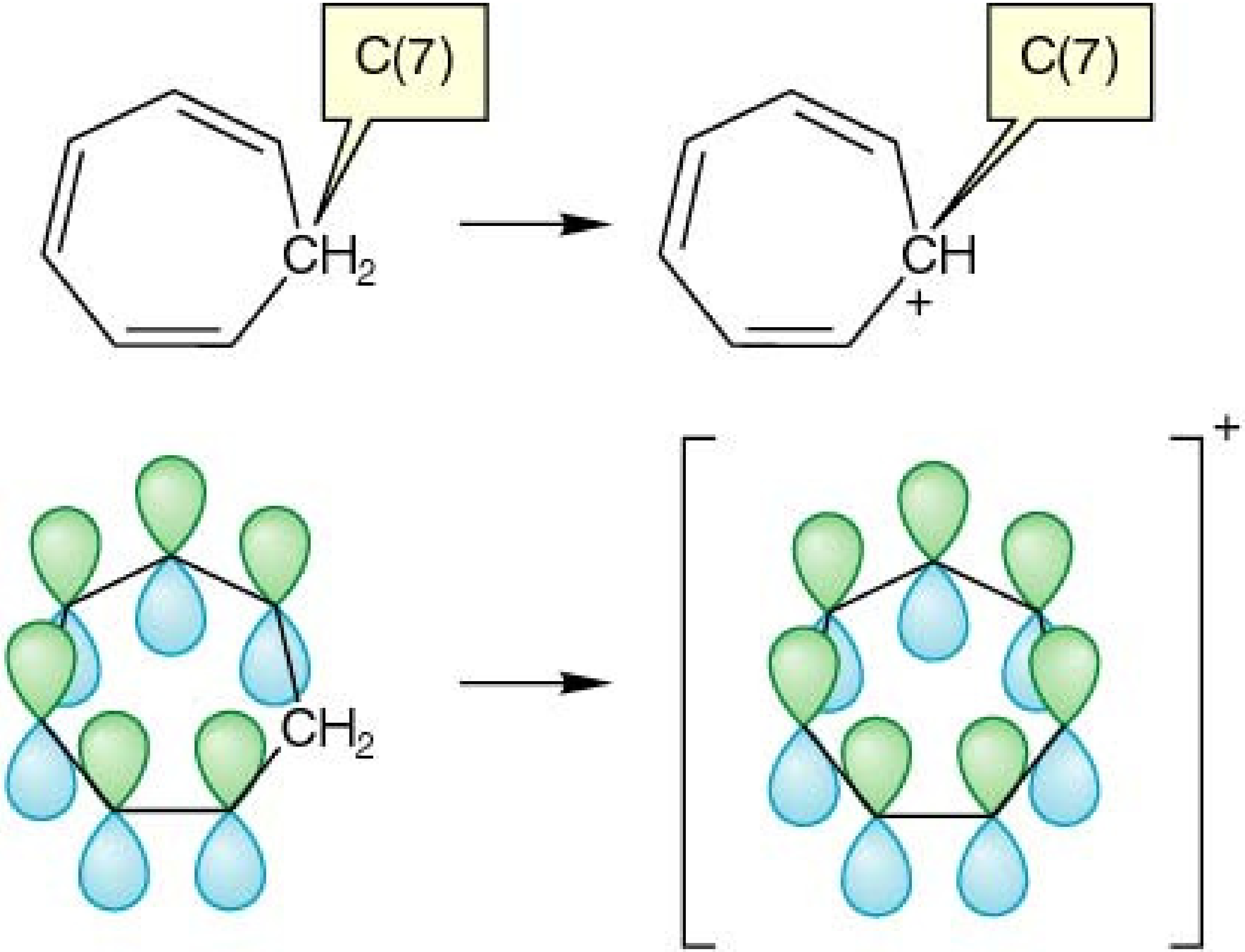


The cyclopentadienide anion is easily formed



L'anione aromatico ciclopentadienile, con sei elettroni π

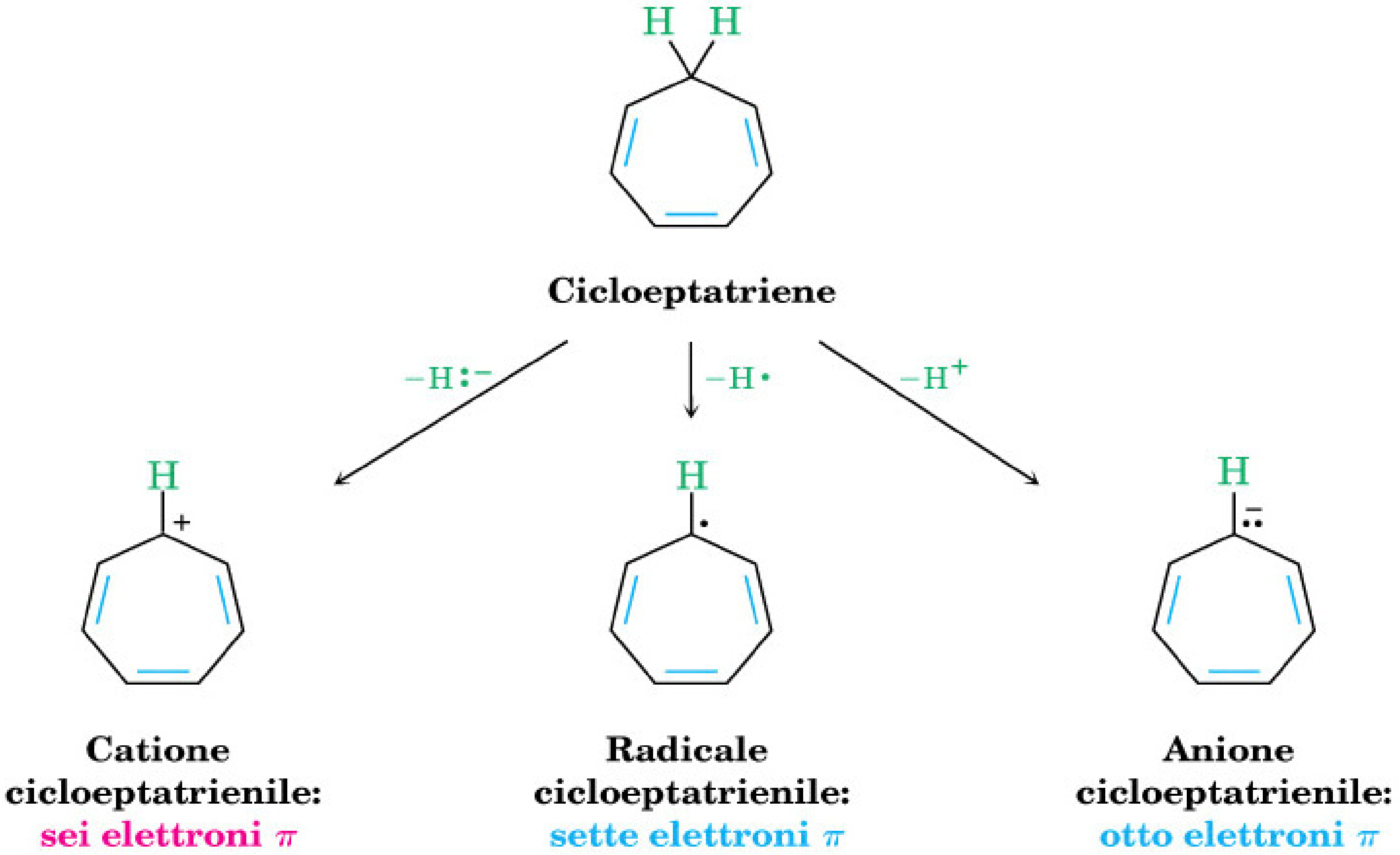




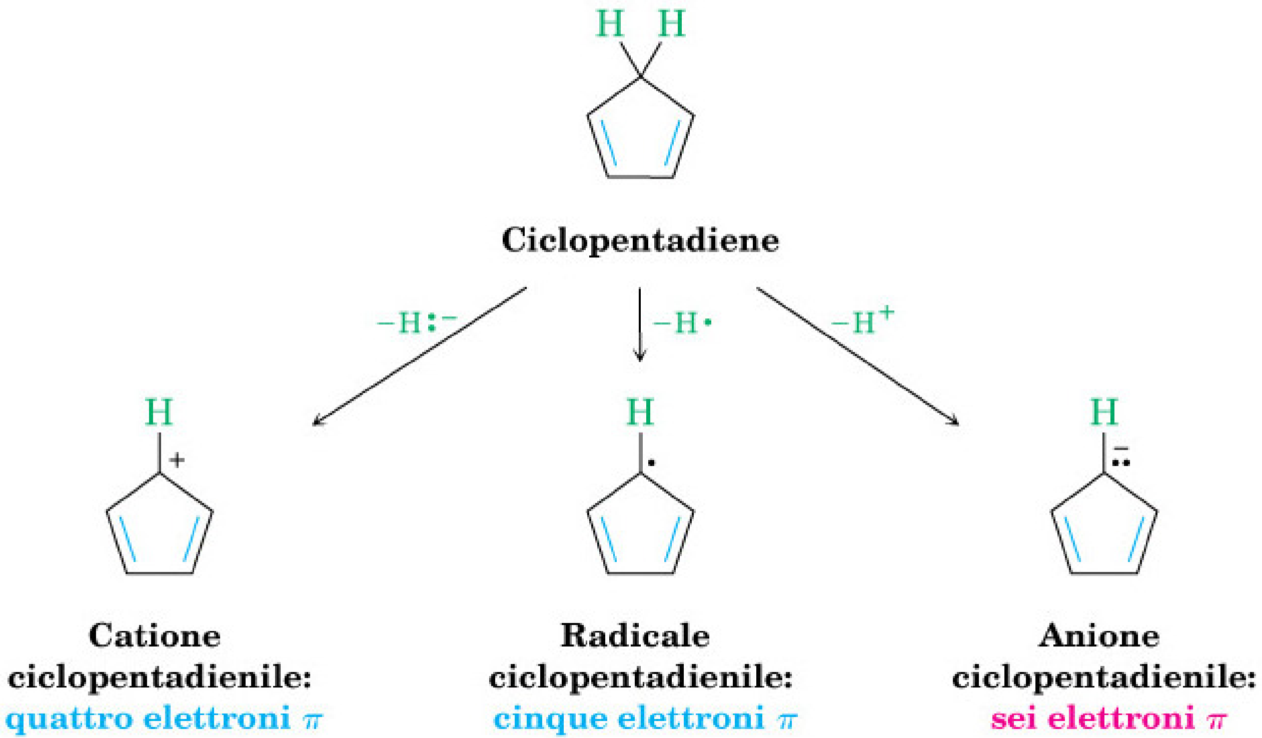
1,3,5-Cycloheptatriene is
not fully conjugated

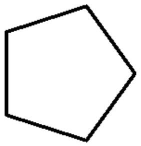
The cycloheptatrienylium
(tropylium) ion is fully conjugated

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



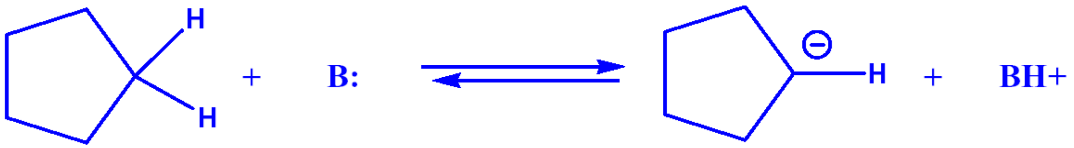
Formazione del catione, radicale e anione ciclopentadienile per estrazione di un atomo di idrogeno dal ciclopentadiene.



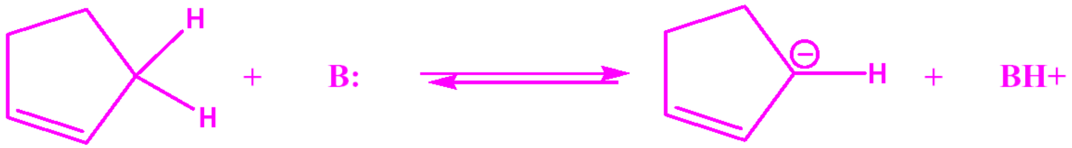


pKa = 60

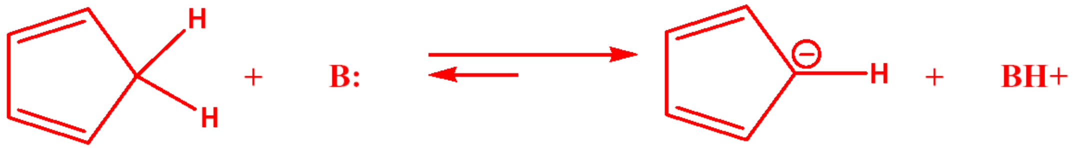
pKa



60

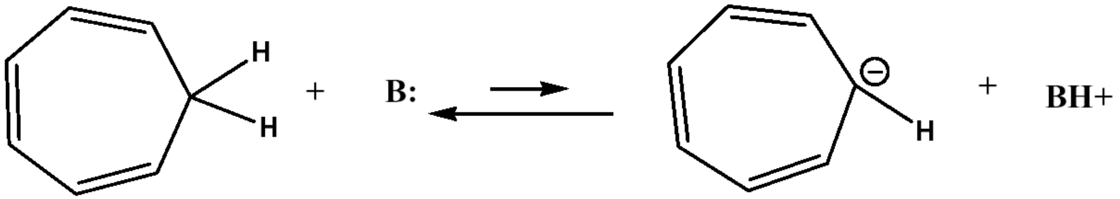


43



Aromatic

15



Anti-Aromatic

39

The pKa of the substance decreases when the compound get Aromatic character

eterocicli aromatici

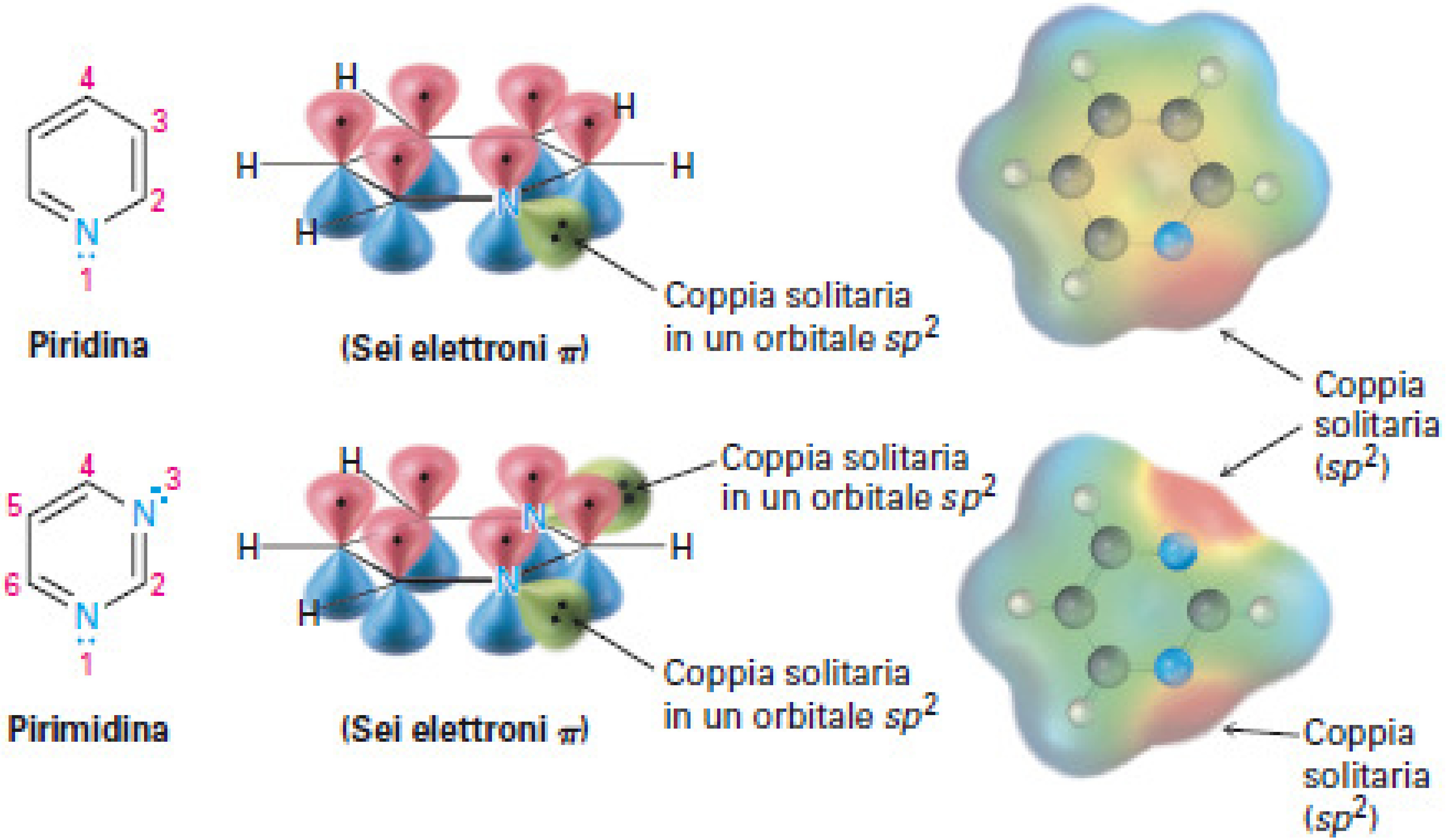


Figura 15.8 La piridina e la pirimidina sono eterocicli aromatici con una disposizione degli elettroni π molto simile a quella del benzene. Entrambe hanno una coppia solitaria di elettroni sull'azoto in un orbitale sp^2 nel piano dell'anello.

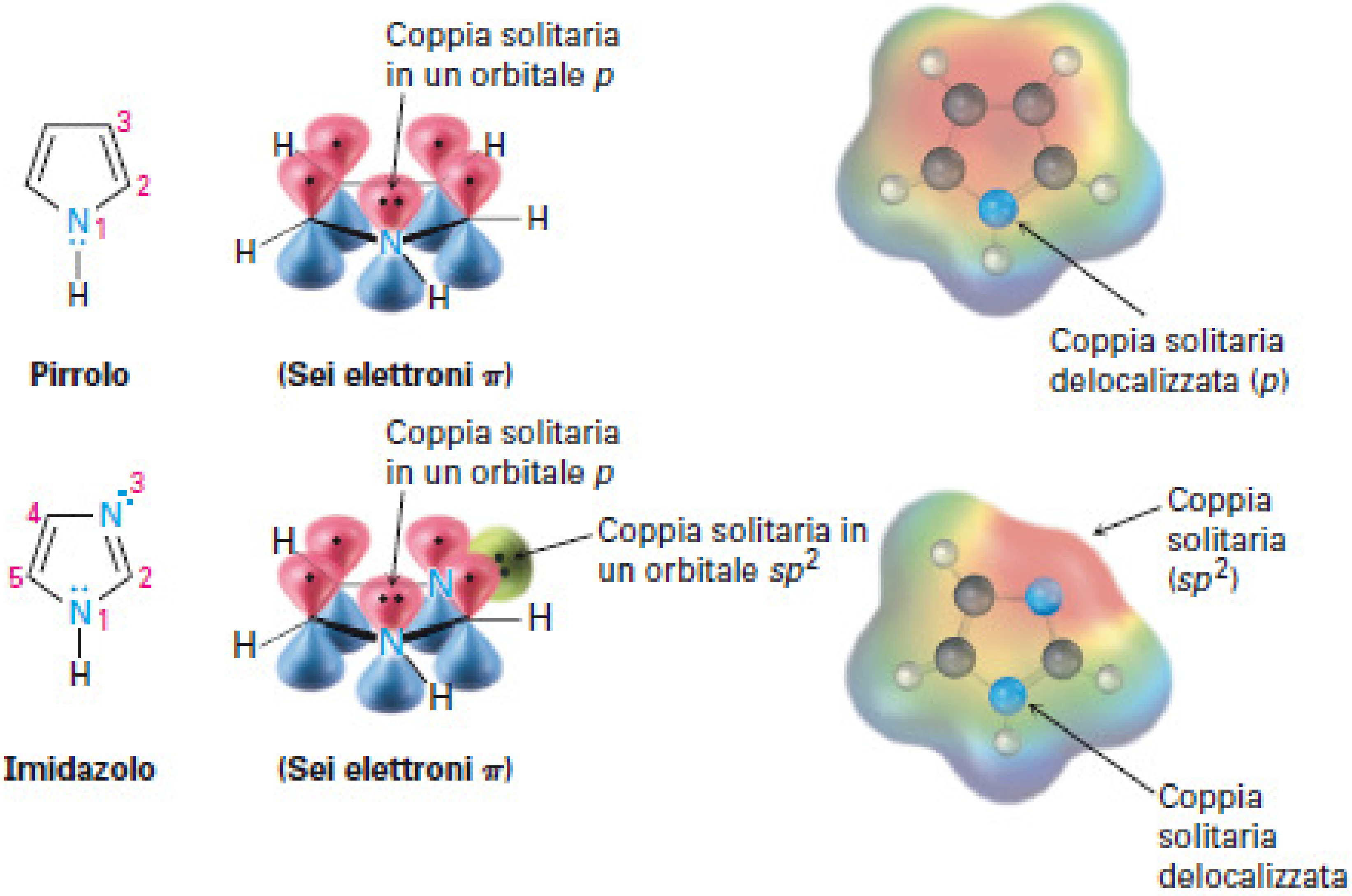
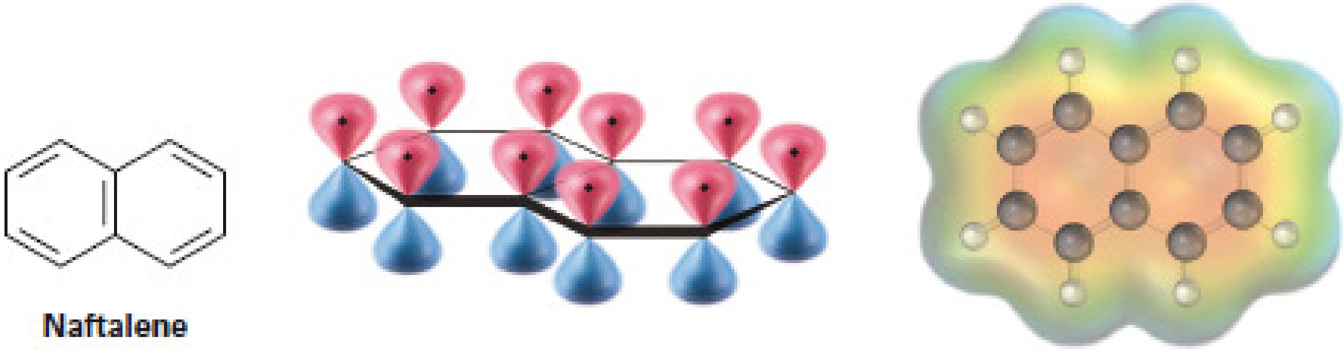
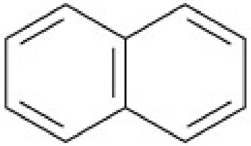


Figura 15.9 Il pirrolo e l'imidazolo sono eterocicli aromatici a cinque termini contenenti azoto, ma hanno una disposizione dei sei elettroni π molto simile a quella dell'anione ciclopentadienile. Entrambi hanno una coppia solitaria di elettroni sull'azoto in un orbitale *p* perpendicolare rispetto all'anello.

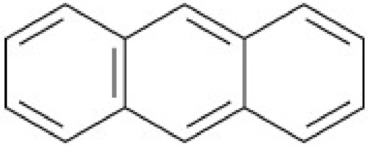
Figura 15.10 Il disegno degli orbitali e la mappa di potenziale elettrostatico del naftalene mostrano che i dieci elettroni π sono completamente delocalizzati su entrambi gli anelli.



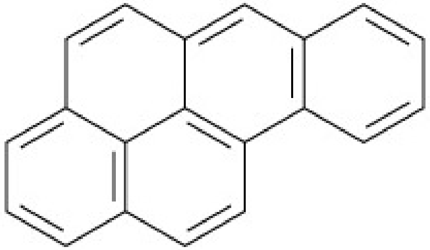
Naftalene



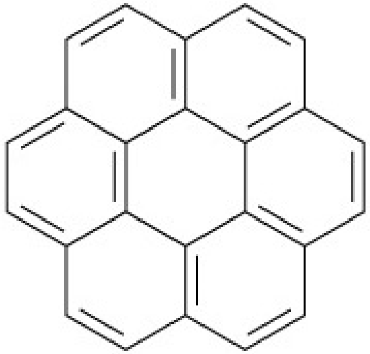
Naftalene



Antracene

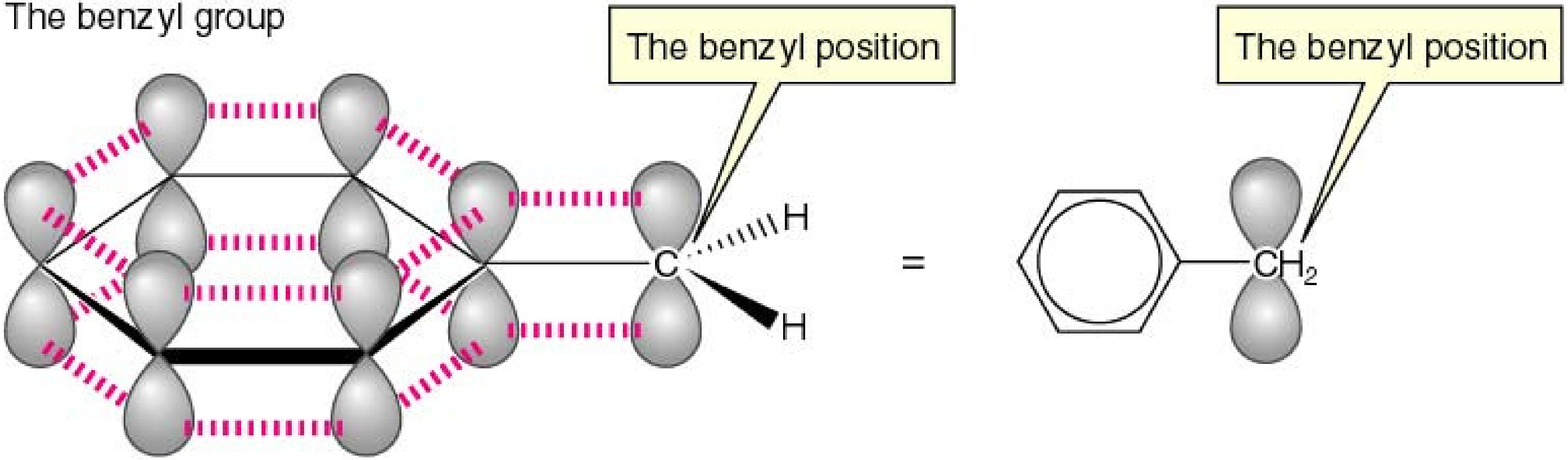


Benzo[a]pirene

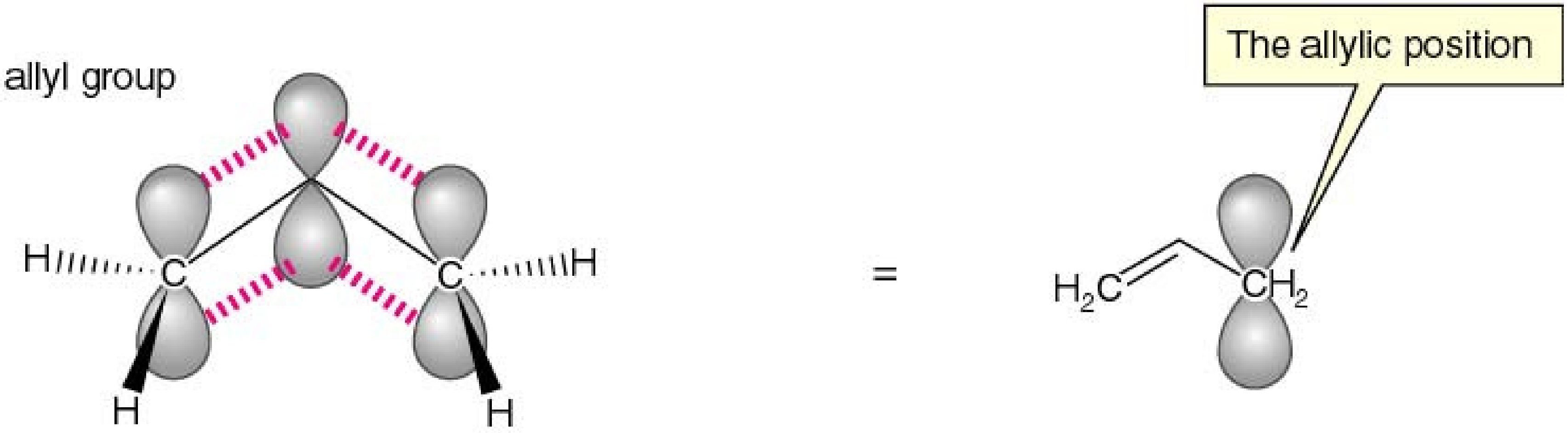


Coronene

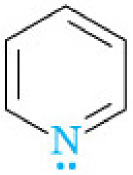
The benzyl group

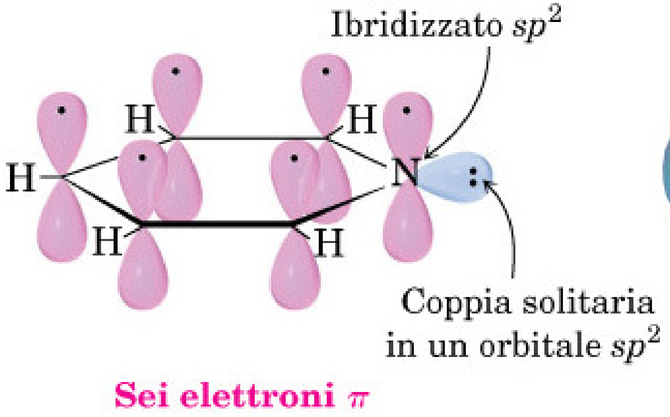


The allyl group



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





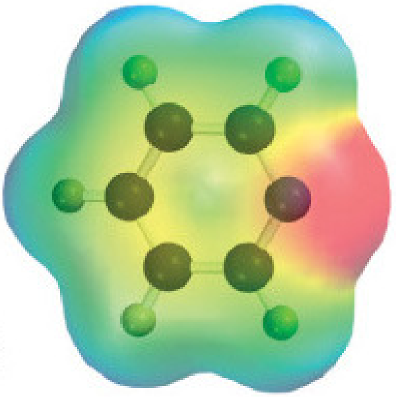
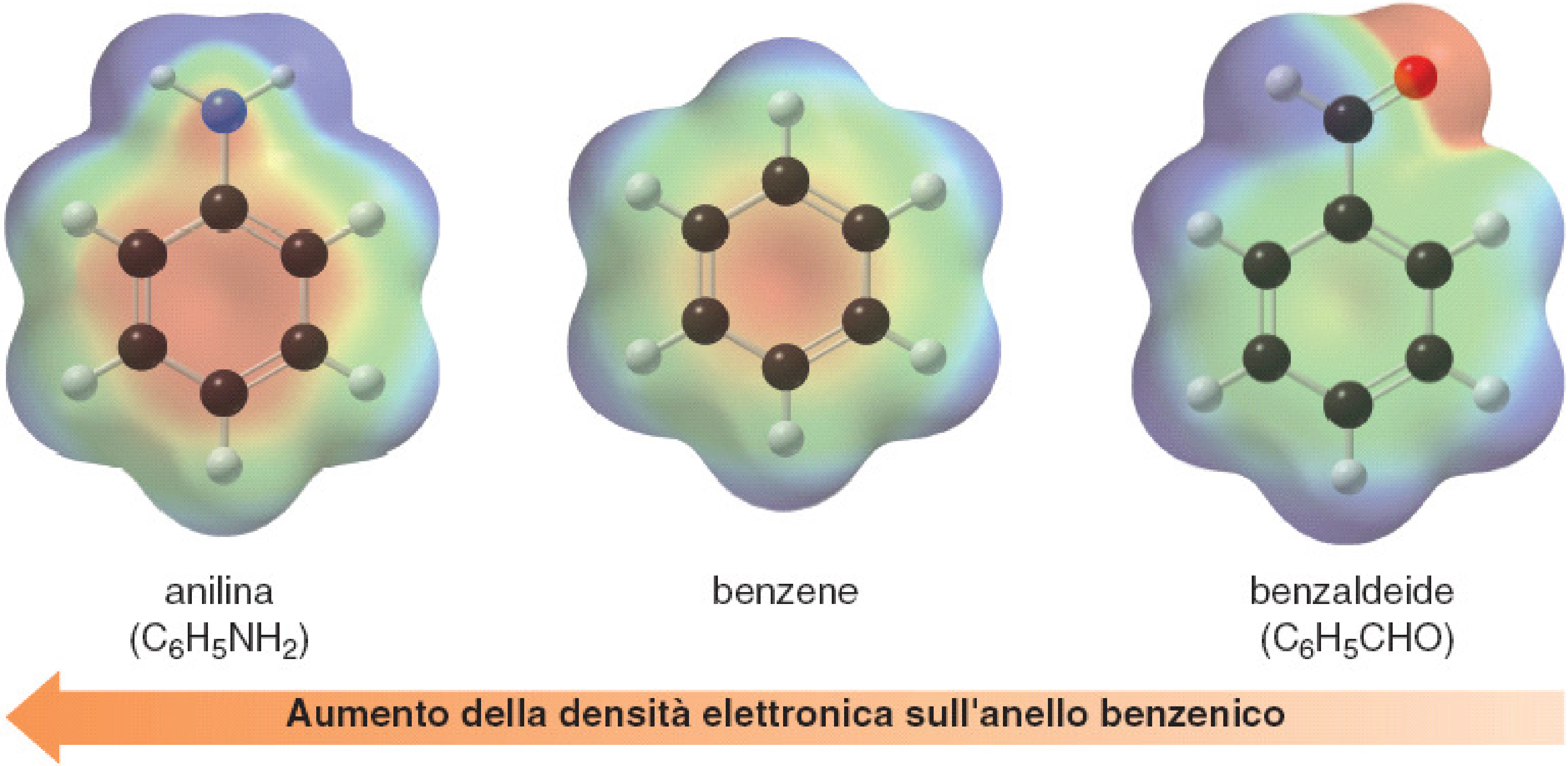


Figura 18.5 L'effetto dei sostituenti sulla densità elettronica nei benzeni sostituiti

- Il gruppo NH_2 dona densità elettronica, rendendo l'anello benzenico più ricco di elettroni (più rosso), mentre il gruppo -CHO attrae densità elettronica, rendendo l'anello benzenico meno ricco di elettroni (più verde).



anilina ($C_6H_5NH_2$)

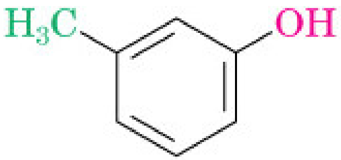
benzene

benzaldeide (C_6H_5CHO)

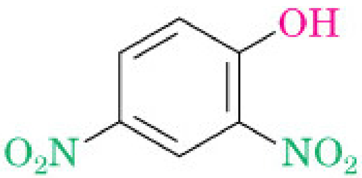
Aumento della densità elettronica sull'anello benzenico

Fenoli: nomenclatura

Termine fenolo: usato sia per il singolo composto che per l’intera classe



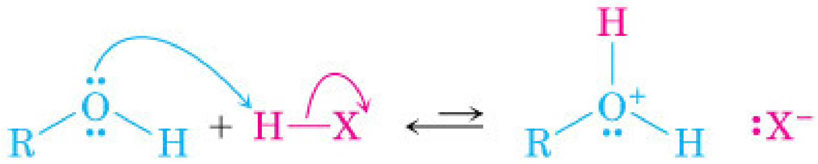
***m*-Metilfenolo**
(*m*-Cresolo)



2,4-Dinitrofenolo

qui il composto base è fenolo, non benzene

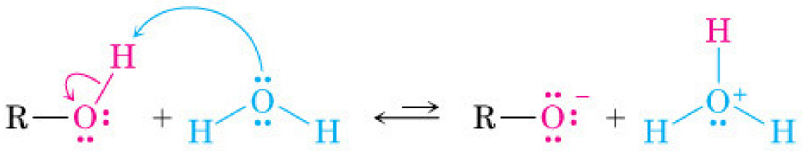
Alcoli e fenoli: proprietà acido-base



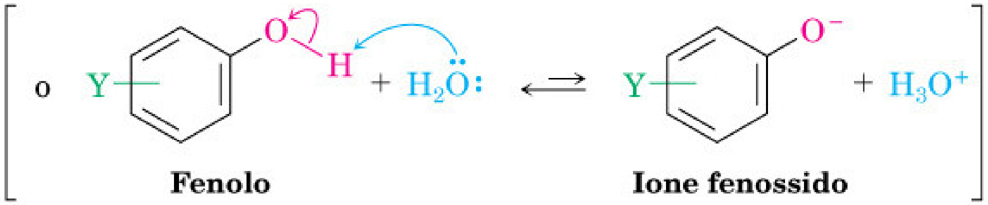
Alcol **Ione ossonio**

$$\left[\text{o} \quad \mathrm{ArOH} + \mathrm{HX} \rightleftharpoons \mathrm{Ar}\overset{+}{\mathrm{O}}\mathrm{H_2} \quad \mathrm{X^-}\right]$$

Basi deboli



Alcol **Ione alcossido**



Fenolo **Ione fenossido**

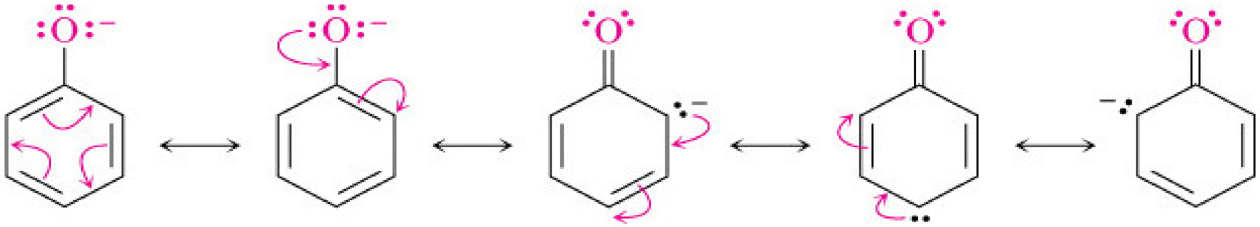
Acidi deboli

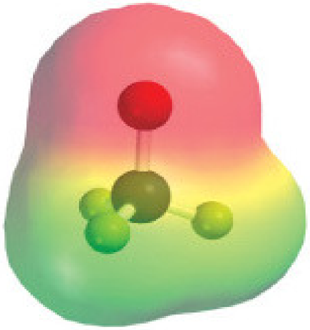
Alcoli e fenoli: proprietà acido-base

I fenoli sono molto più acidi degli alcoli e reagiscono bene con NaOH
sono solubili in soluzioni alcaline diluite

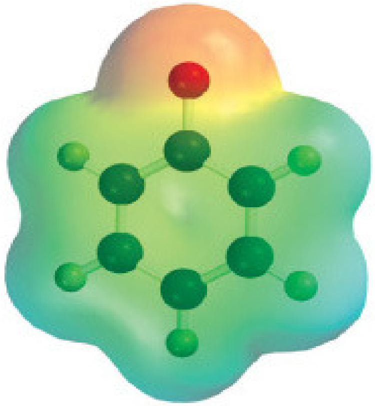
Fenolo **Sodio fenossido**

Lo ione fenossido, stabilizzato per risonanza, è più stabile di uno ione alcossido. Le mappe di potenziale elettrostatico mostrano come la carica negativa sia concentrata sull'ossigeno nello ione metossido, mentre sia delocalizzata sull'anello aromatico nel caso dello ione fenossido.



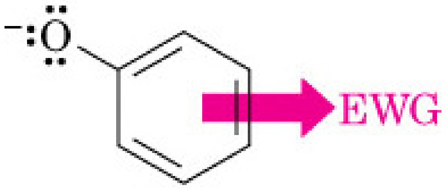


CH_3O^-

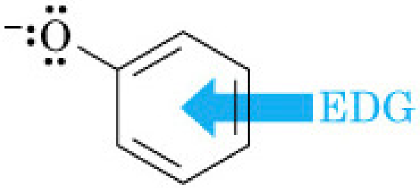


$C_6H_5O^-$

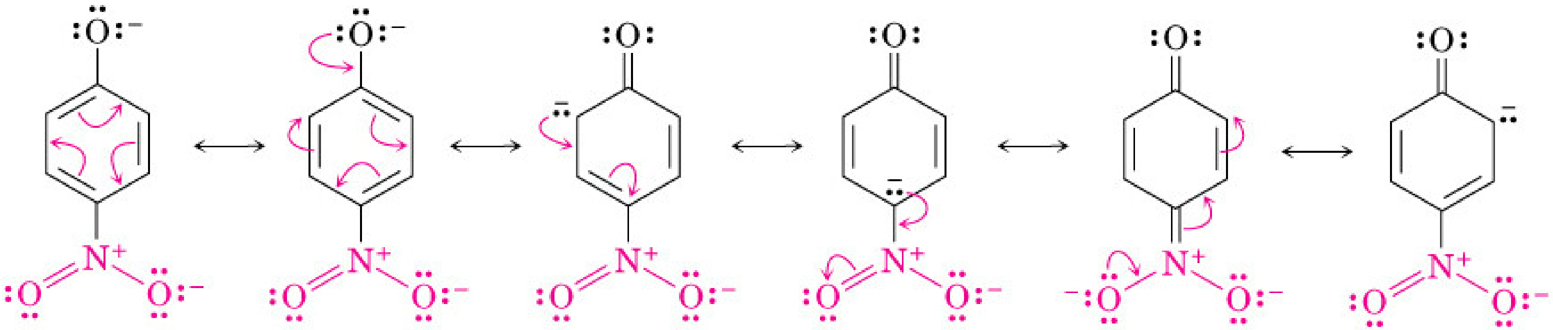
Alcoli e fenoli: proprietà acido-base



I gruppi elettron-attrattori (EWG)
stabilizzano lo ione fenossido,
determinando così un aumento
dell'acidità del fenolo

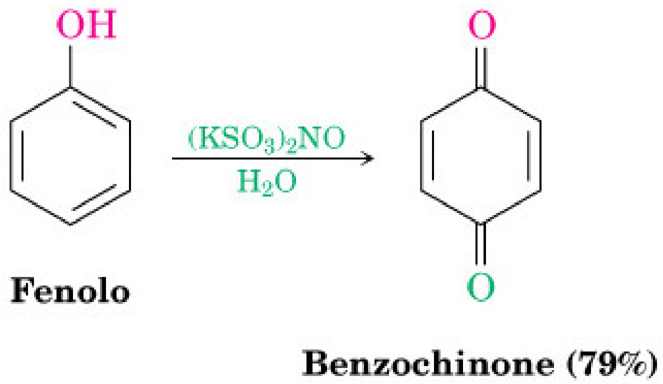


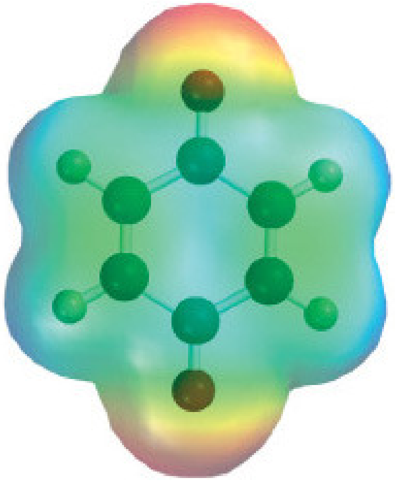
I gruppi elettron-donatori (EDG)
destabilizzano lo ione fenossido,
determinando così una diminuzione
dell'acidità del fenolo



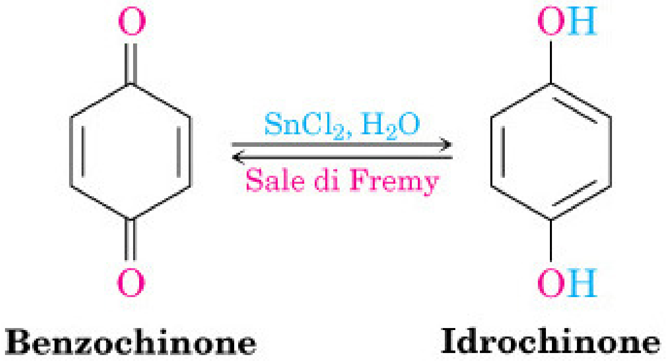
Fenoli: ossidazione

Ossidazione avviene con meccanismo radicalico

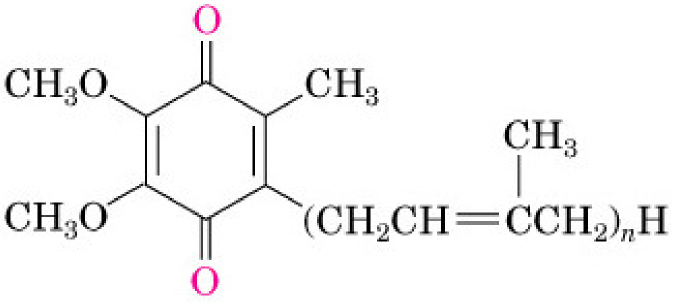




Composti usati come agenti redox: facilmente ossidabili e riducibili



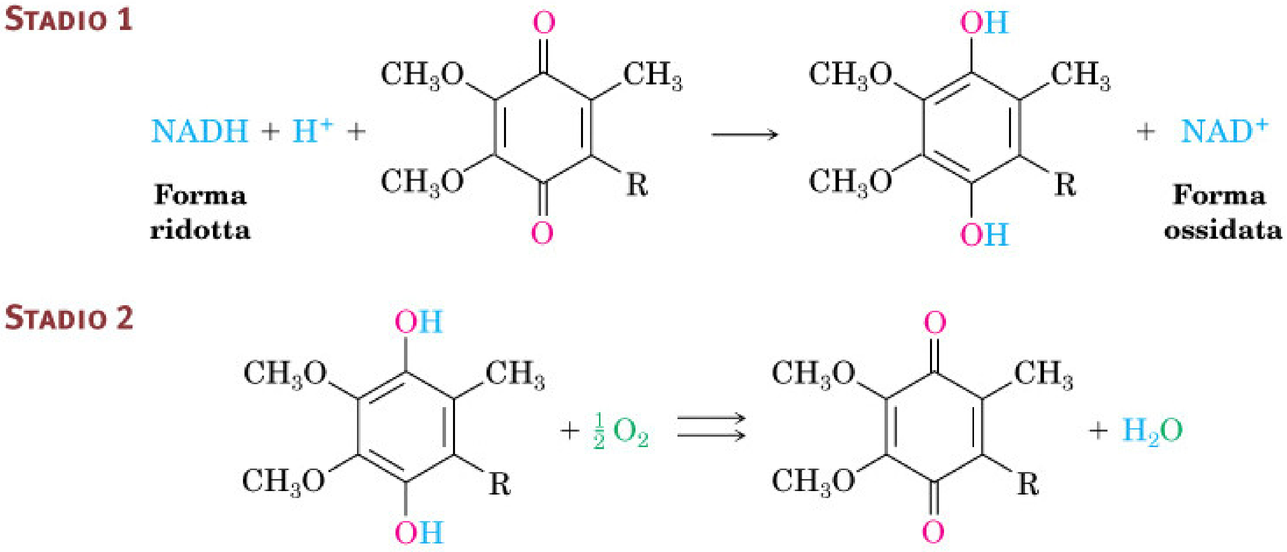
Fenoli: ossidazione



Ubichinoni (n = 1–10)

Coenzimi Q: ossidanti biologici

Importanti per il funzionamento delle cellule



NADH: riducente biologico

Reazione complessiva: $NADH + \frac{1}{2} O_2 + H^+ \longrightarrow NAD^+ + H_2O$

Reazione che libera energia