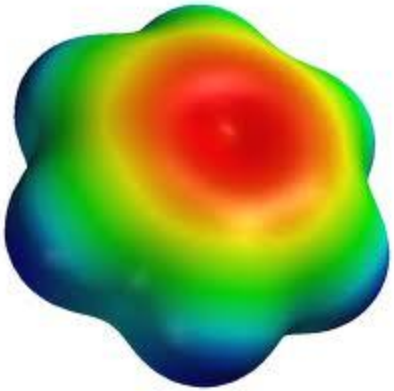
Areny

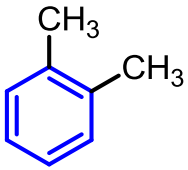


Aromatické uhlovodíky

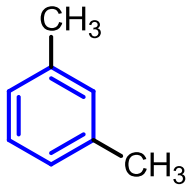
Aromatické uhlovodíky získávané destilací ropy:

Benzen
t.v. 80°C

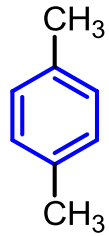
Toluen
t.v. 111°C



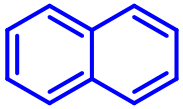
o-Xylen
t.v. 144°C



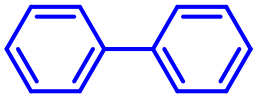
m-Xylen
t.v. 139°C



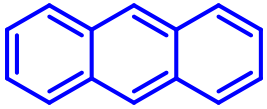
p-Xylen
t.v. 138°C



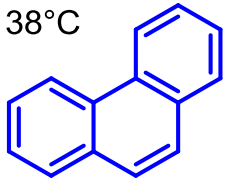
Naftalen
t.t. 80°C



Bifenyl
t.t. 71°C

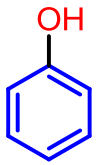


Anthracen
t.t. 216°C

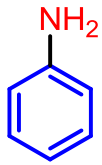


Fenanthren
t.t. 101°C

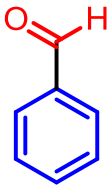
Triviální názvy některých dalších důležitých derivátů benzenu:



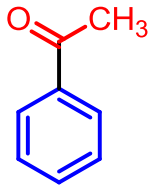
Fenol
t.t. 43°C



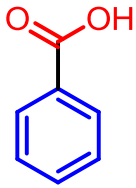
Anilin
t.v. 184°C



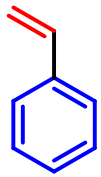
Benzaldehyd
t.v. 178°C



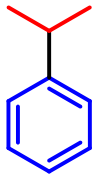
Acetofenon
t.t. 21°C



Kyselina benzoová
t.v. 178°C

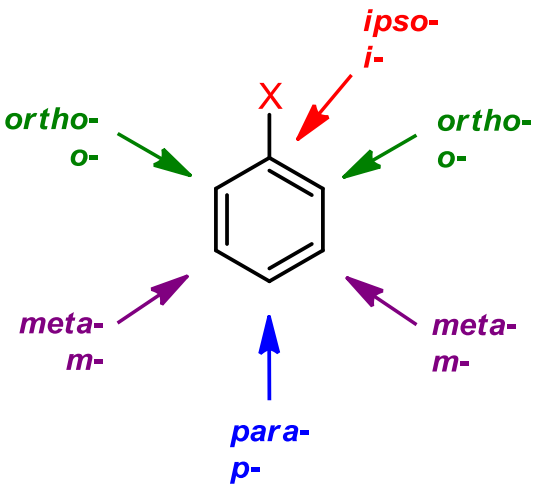


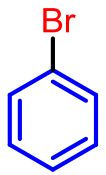
Styren
t.v. 145°C



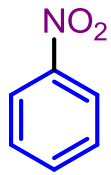
Kumen
t.v. 152°C

Deriváty benzenu - názvosloví

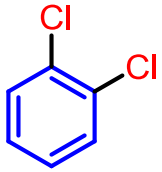




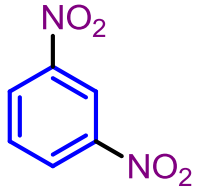
brombenzen



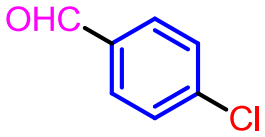
nitrobenzen



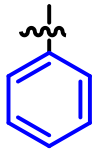
o-dichlorbenzen
ortho-dichlorbenzen
1,2-dichlorbenzen



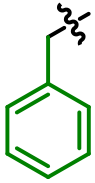
m-dinitrobenzen
meta-dinitrobenzen
1,3-dinitrobenzen



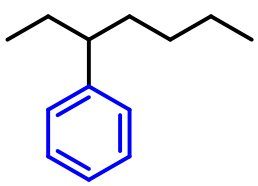
p-chlorbenzaldehyd
para-chlorbenzaldehyd
4-chlorbenzaldehyd



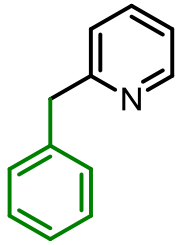
fenyl



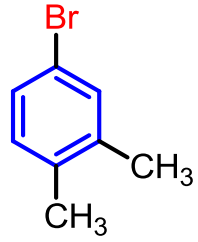
benzyl



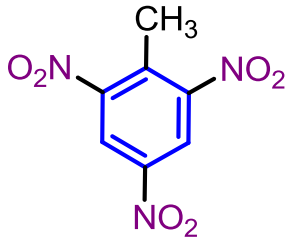
3-fenylheptan



2-benzylpyridin



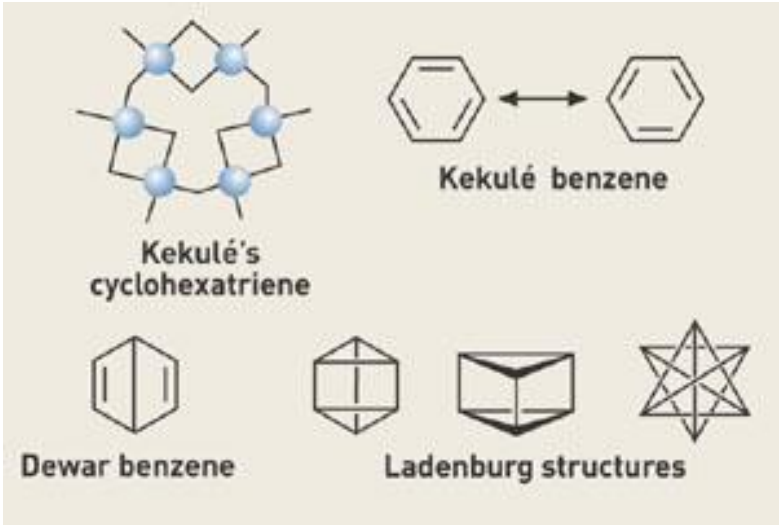
4-brom-1,2-dimethylbenzen



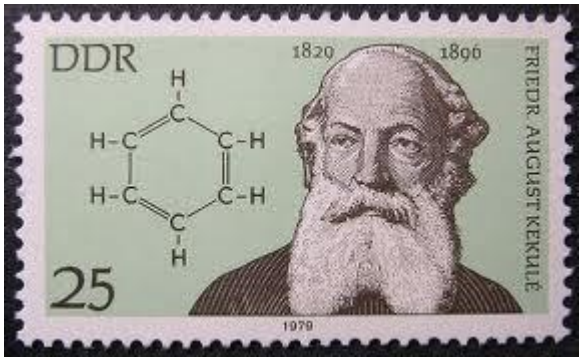
2,4,6-trinitrotoluen

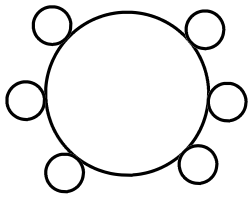
Struktura benzenu - historie

C_6H_6, symetrická molekula, neprobíhají adiční reakce



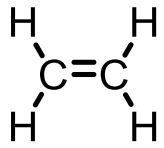
1865



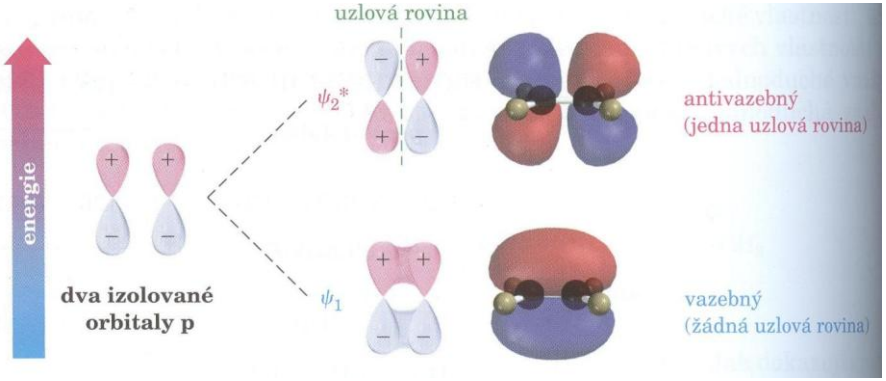


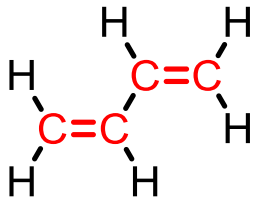
Loschmidt 1861

Konjugované π-systémy a delokalizace elektronů

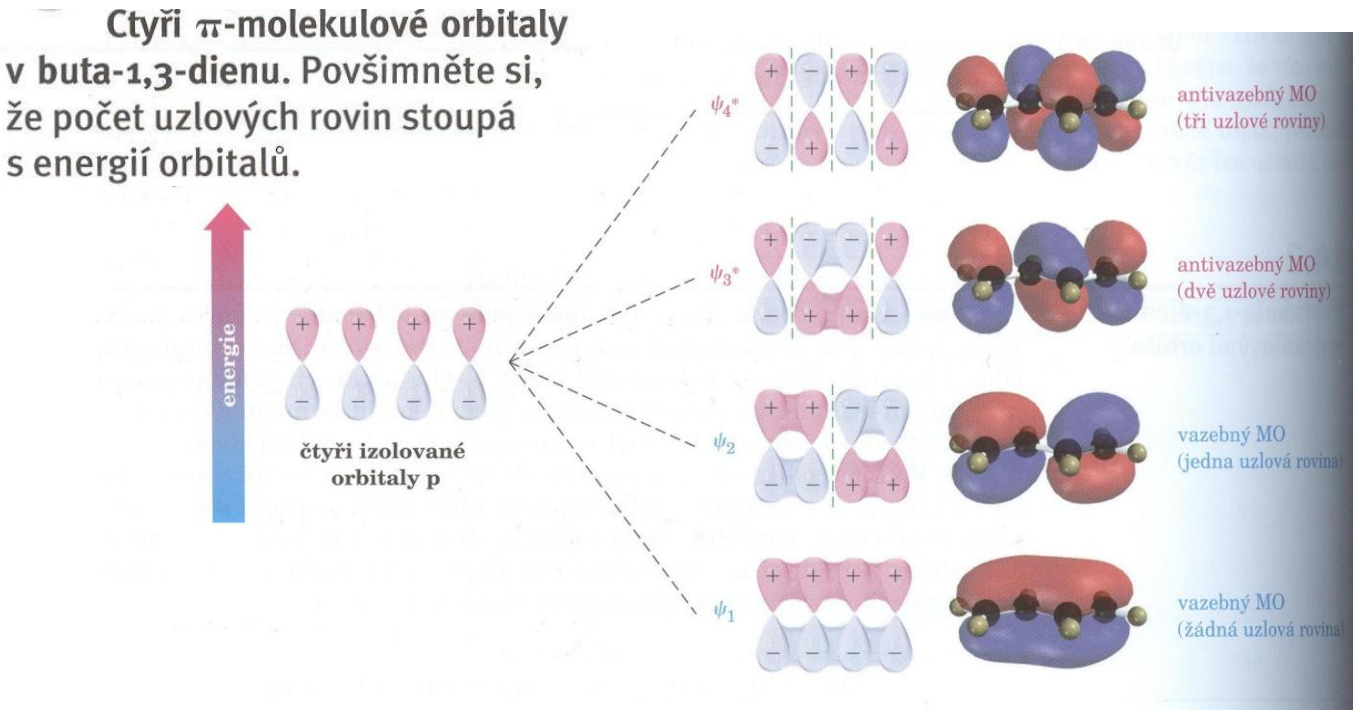


Ethen - izolovaná dvojná vazba

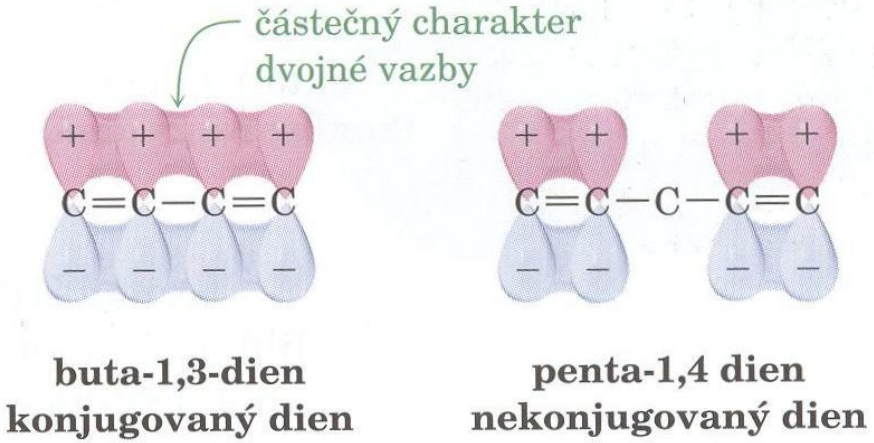




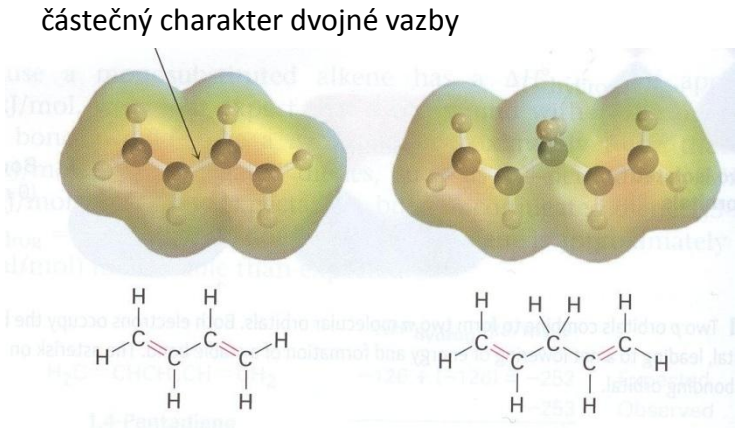
Butadien - konjugované dvojné vazby

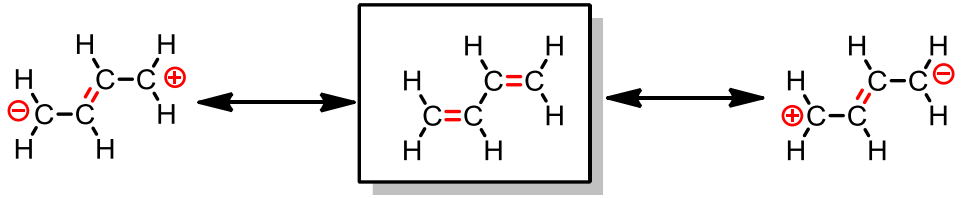


Konjugované π-systémy a delokalizace elektronů

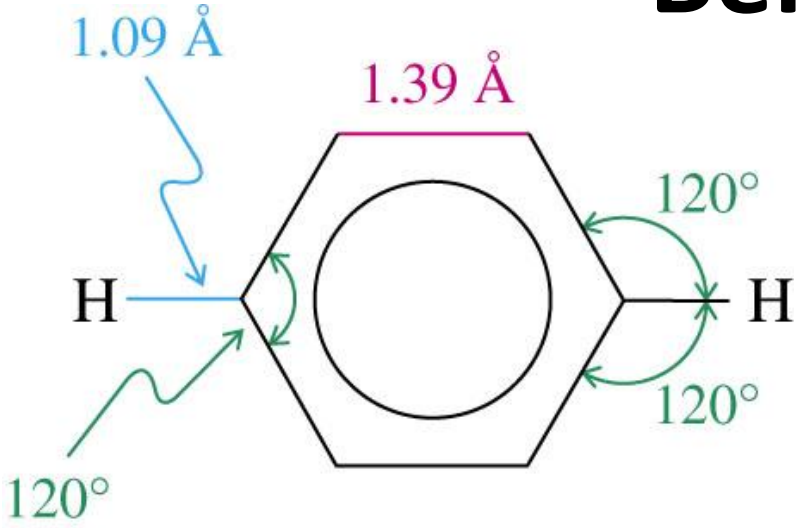


Dochází k částečné delokalizaci elektronů v rámci celého konjugovaného π-systému

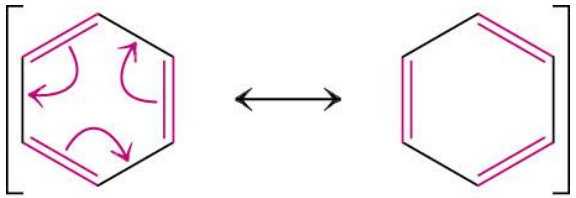




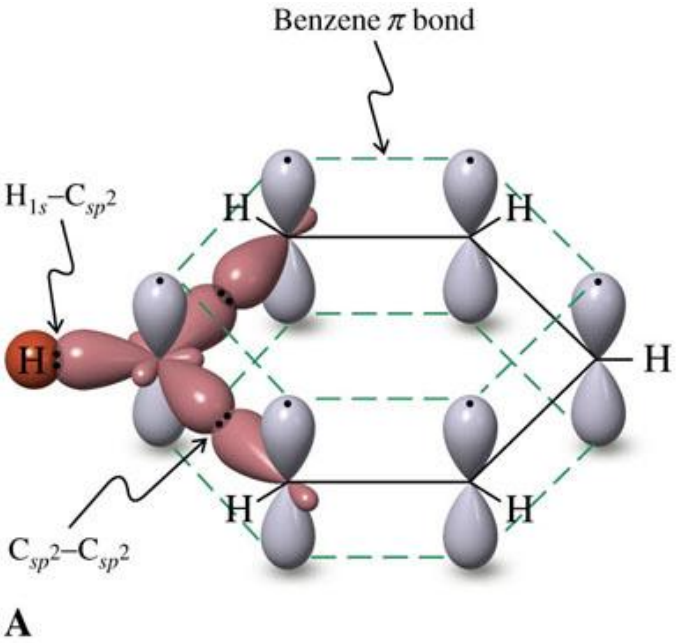
Benzen

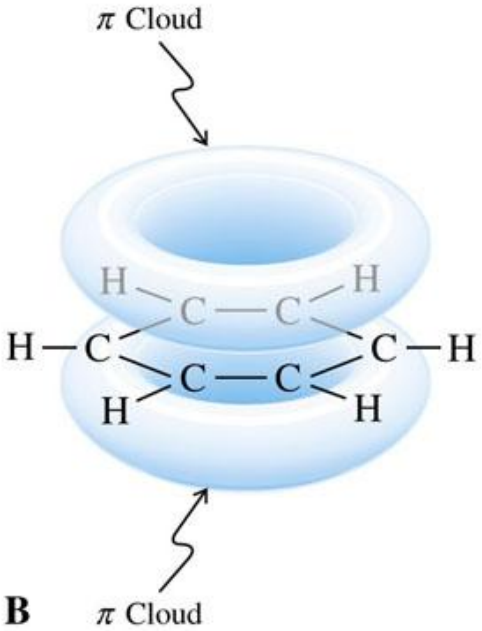


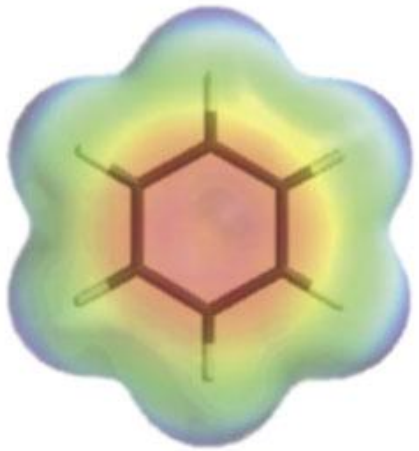
řád vazby 1.5

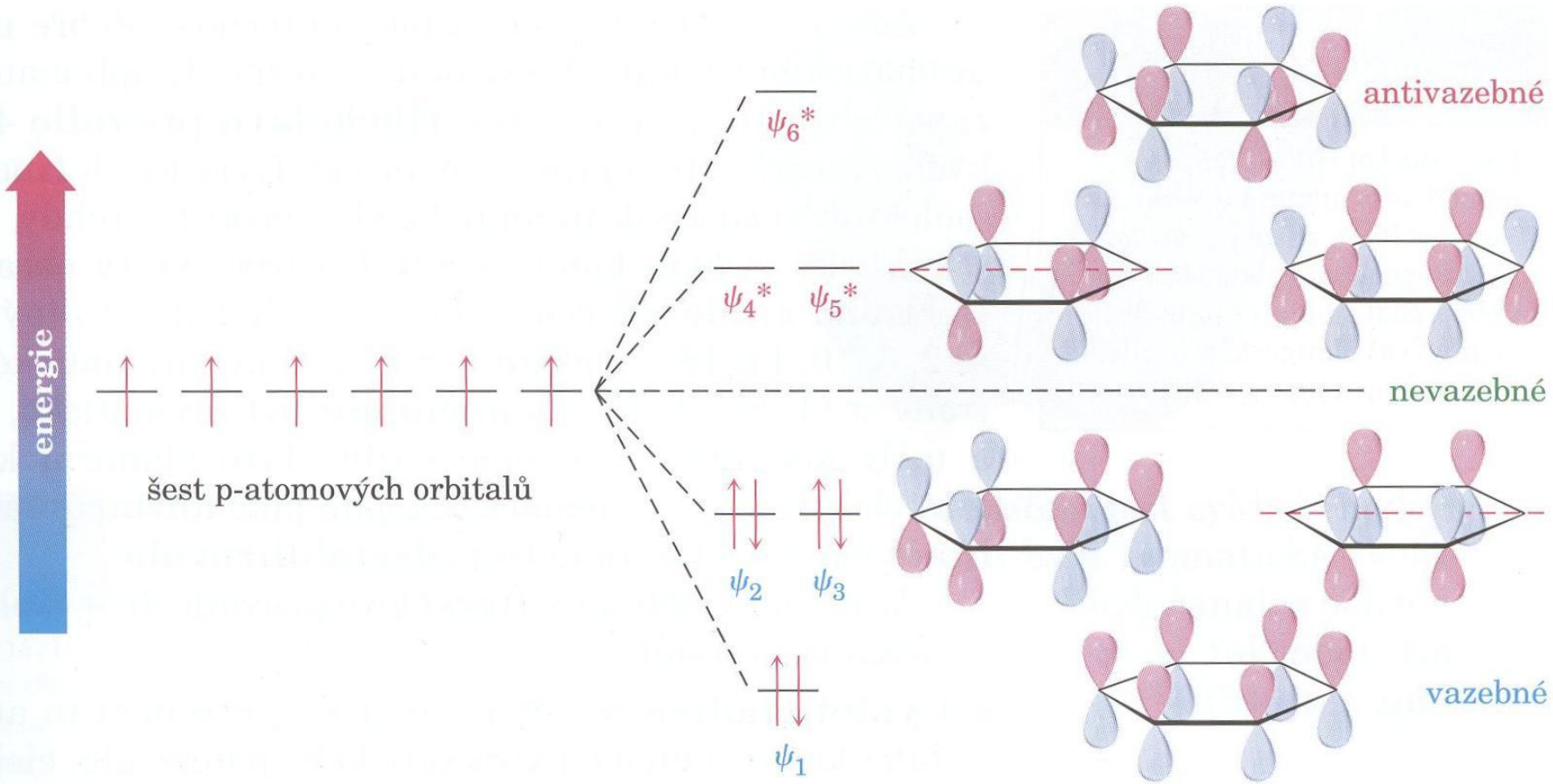


is the same as

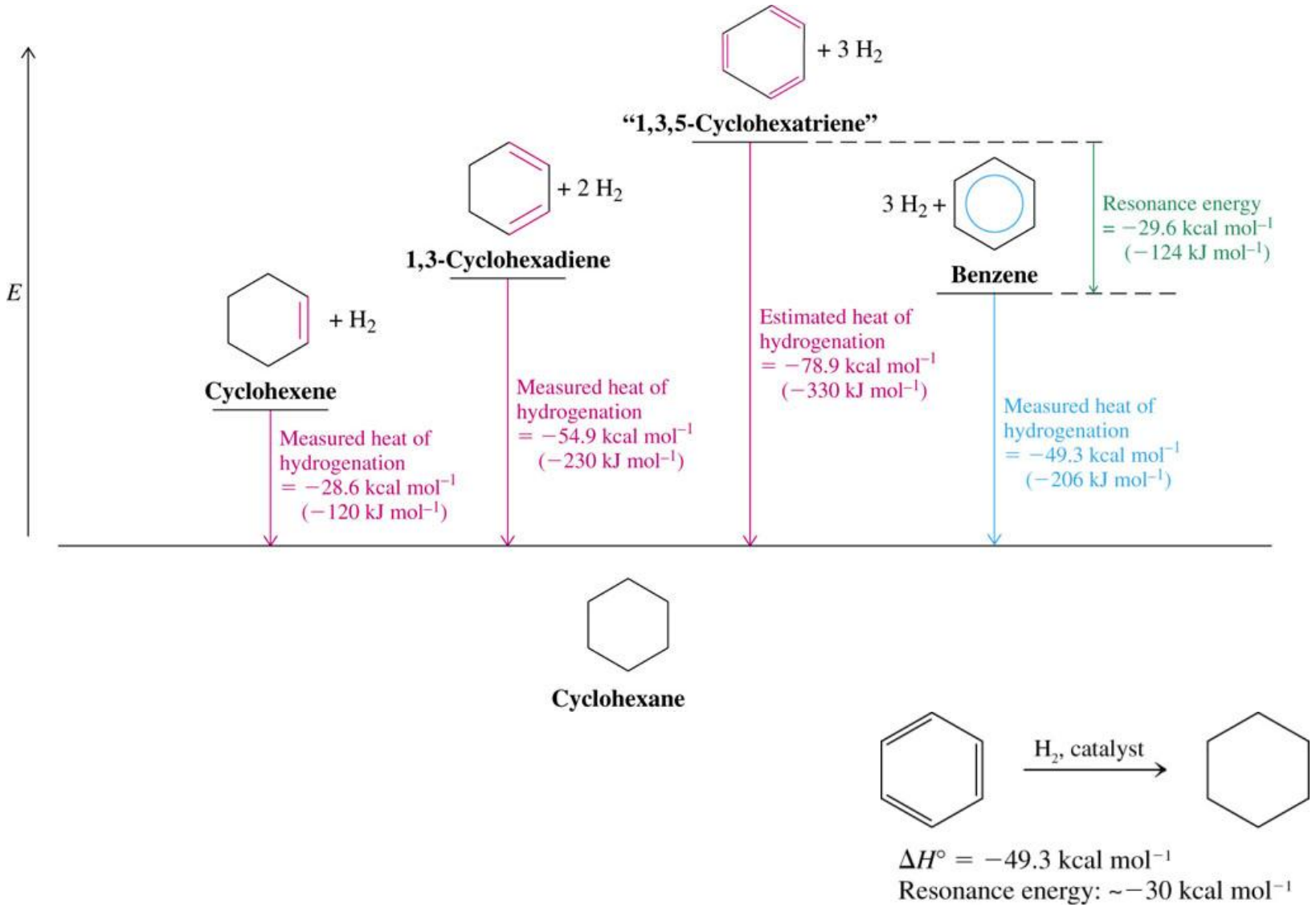








šest molekulových orbitalů benzenu



$\Delta H^\circ = -49.3$ kcal mol^{-1}

Resonance energy: ~−30 kcal mol^{-1}

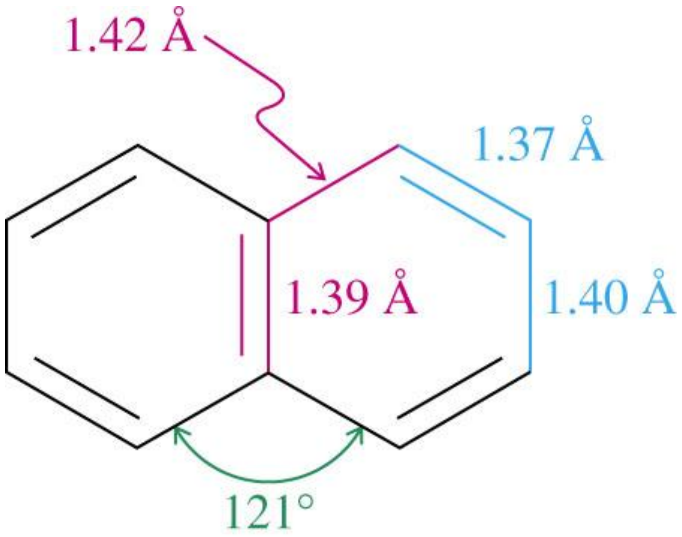
Hückelovo pravidlo a aromaticita

Hückelovo pravidlo
Planární cyklické systémy s **(4n+2) konjugovanými π elektrony** (n = 0, 1, 2 atd.),
tj. systémy s 2, 6, 10, 14, atd. konjugovanými π elektrony, jsou **aromatické**
Delokalizace π elektronů systém stabilizuje

Planární cyklické systémy s **4n konjugovanými π elektrony**, tj. systémy s 4, 8, 12, 16, atd. konjugovanými π elektrony, jsou **antiaromatické**
Delokalizace π elektronů by systém destabilizovala (nejsou delokalizovány)

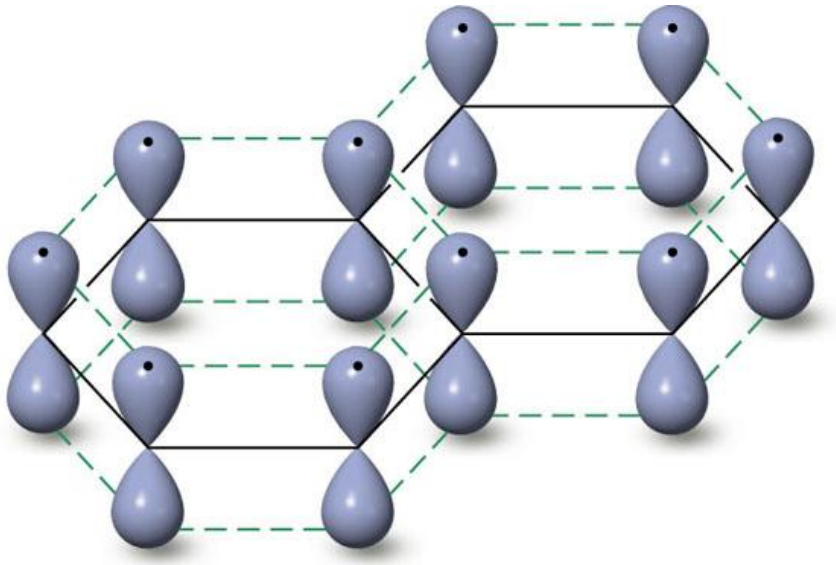
Neplanární nebo acyklické systémy s **nekonjugovanými π elektrony**, jsou **nearomatické**.
Delokalizace π elektronů v těchto systémech není možná

Naftalen

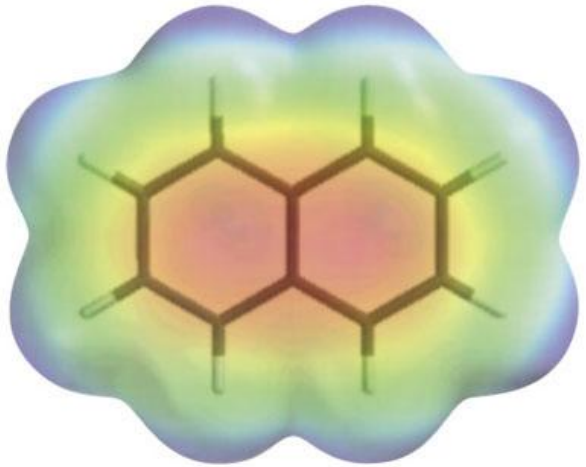


10 (4 x 2 + 2) π elektronů

Aromatický



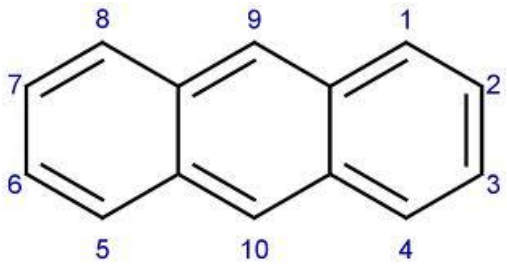
A



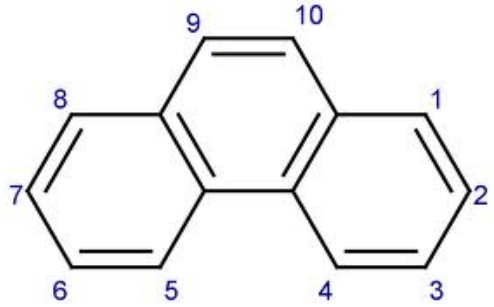
B

Kondenzované aromatické sloučeniny

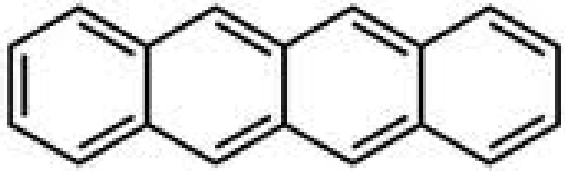
Anthracen



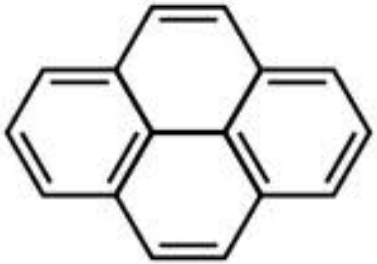
Fenanthren



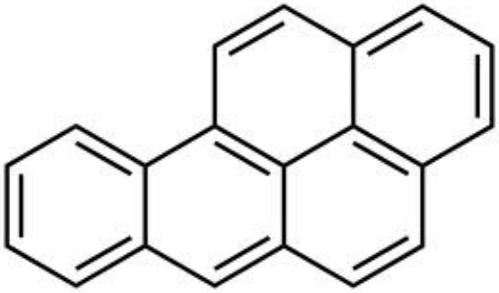
Tetracen



Pyren

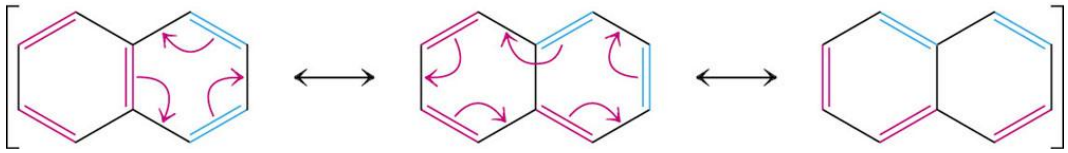


Benzo[a]pyren

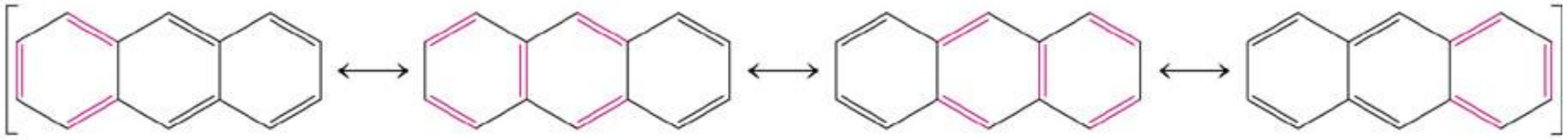


Rezonance v kondenzovaných aromatických sloučeninách

Resonance Forms of Naphthalene

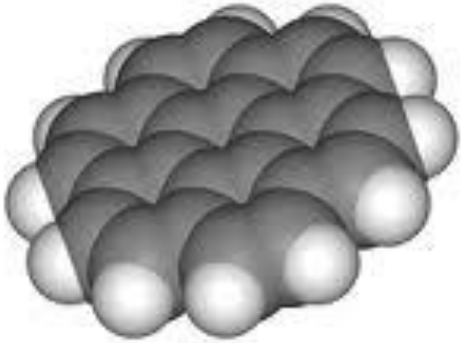


Resonance in Anthracene

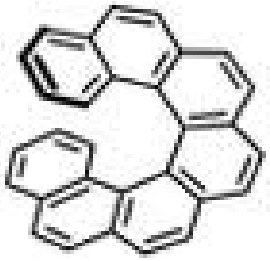


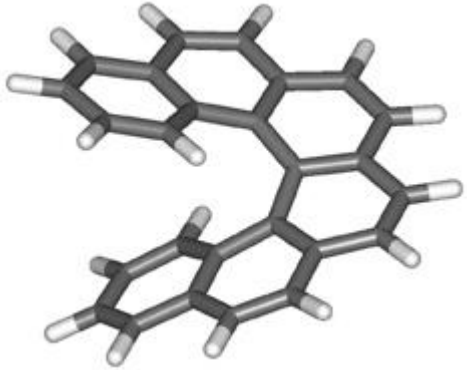
Resonance in Phenanthrene

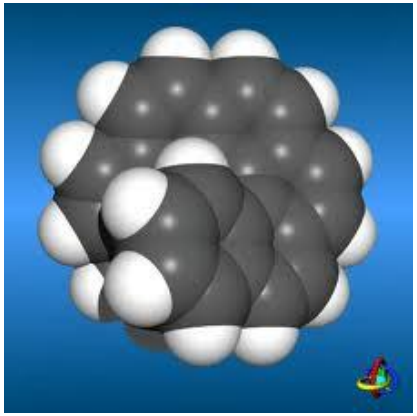
Koronen



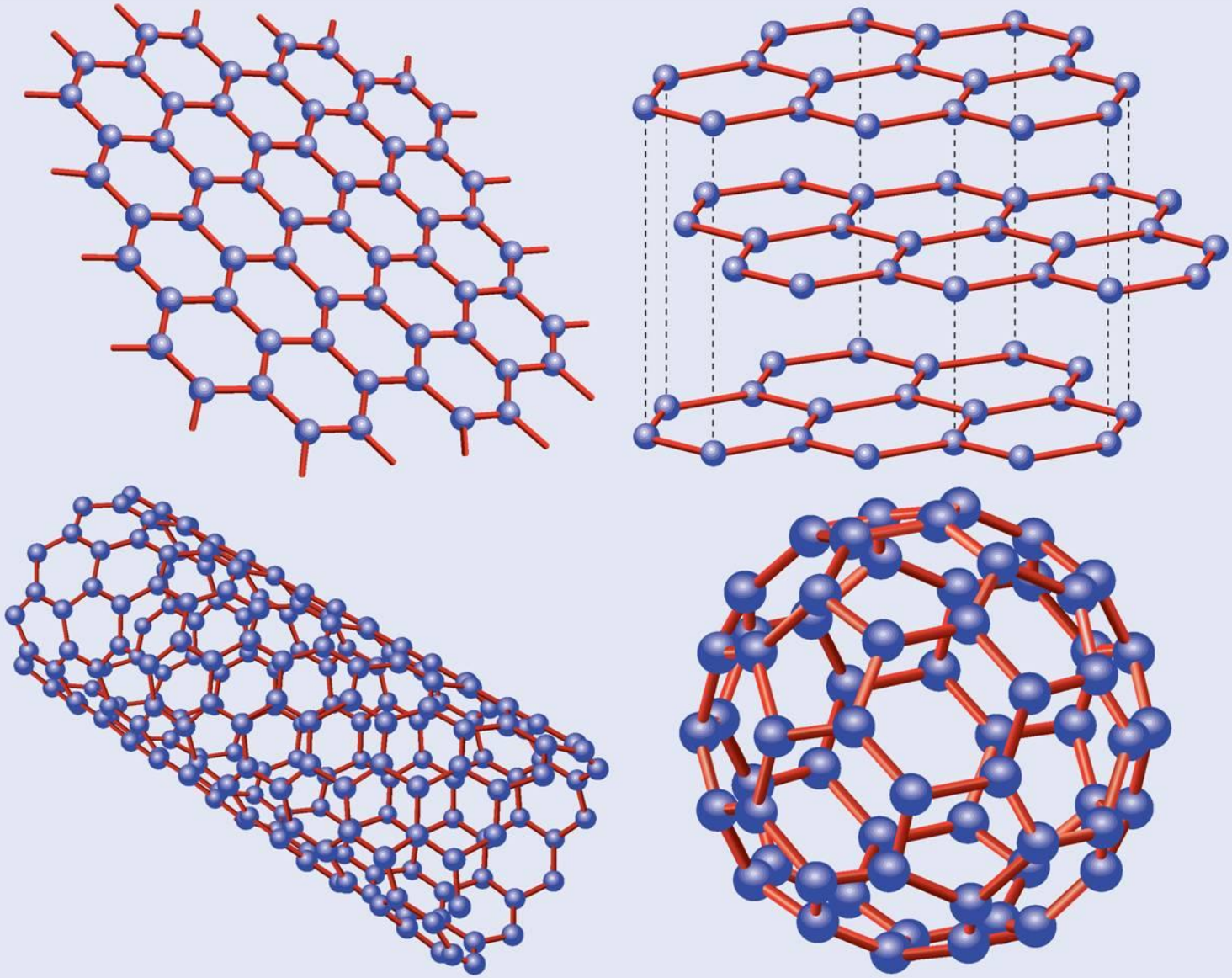
[6]-Helicen





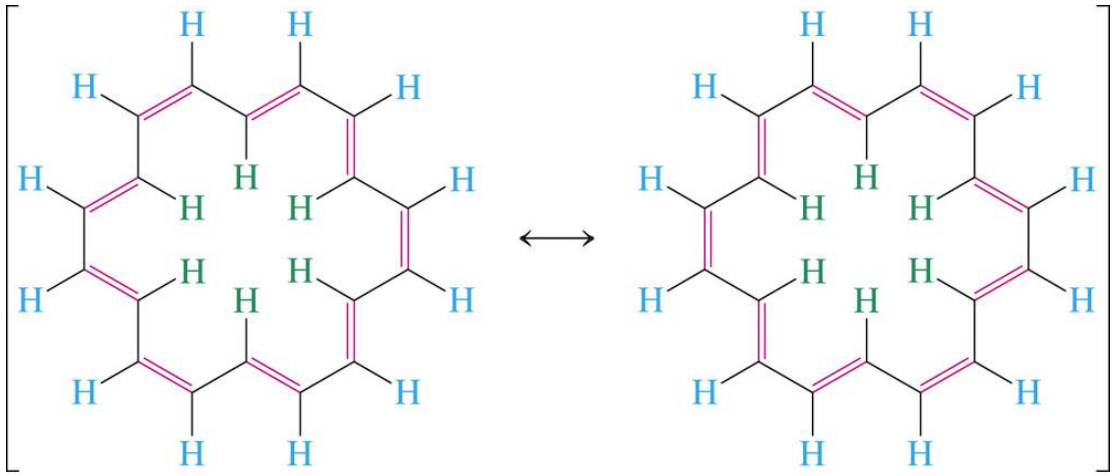


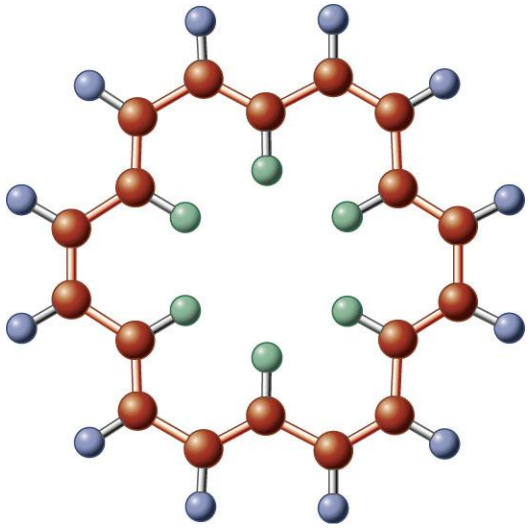
2 Graphene: mother of them all



Graphene (top left) consists of a 2D hexagonal lattice of carbon atoms. Each atom is covalently bonded to three others; but since carbon has four valence electrons, one is left free – allowing graphene to conduct electricity. Other well-known forms of carbon all derive from graphene: graphite is a stack of graphene layers (top right); carbon nanotubes are rolled-up cylinders of graphene (bottom left); and a buckminsterfullerene (C_{60}) molecule consists of graphene balled into a sphere by introducing some pentagons as well as hexagons into the lattice (bottom right).

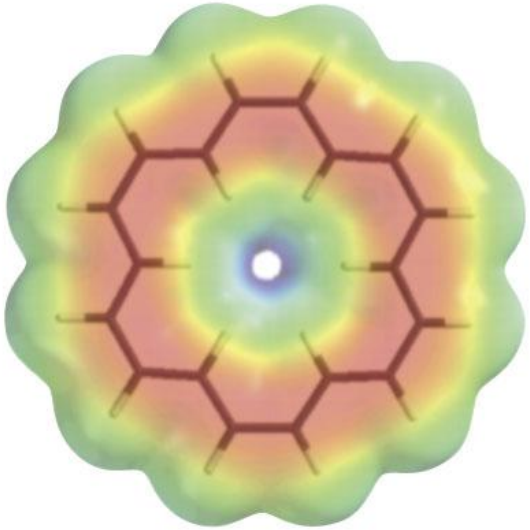
[18]anulen (cyklooktadeka-1,3,5,7,9,11,13,15,17-nonaen)





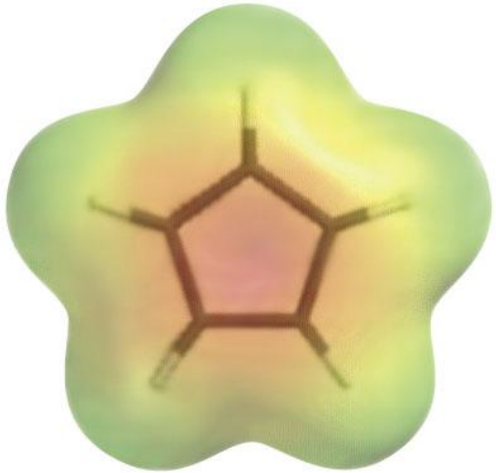
18 (4 x 4 + 2) π elektronů

Aromatický



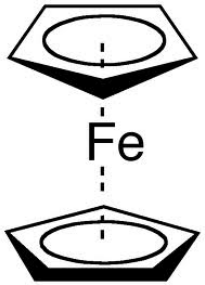
Cyklopentadienylový anion

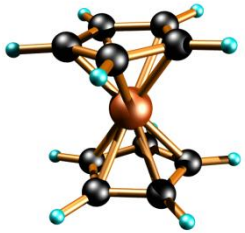
6 π elektronů



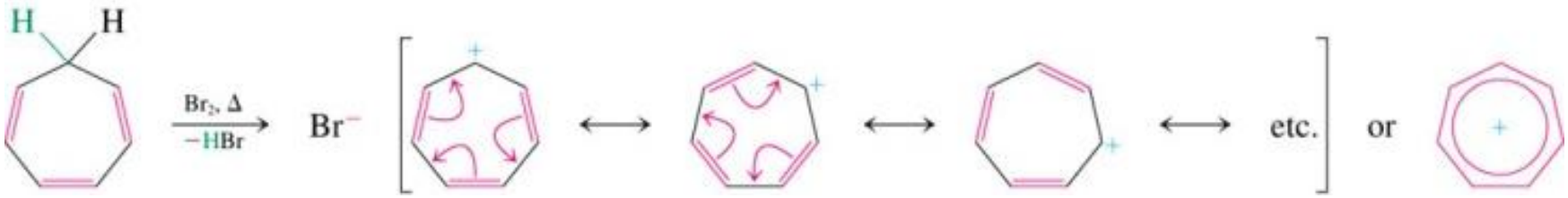
Aromatický

Ferrocen



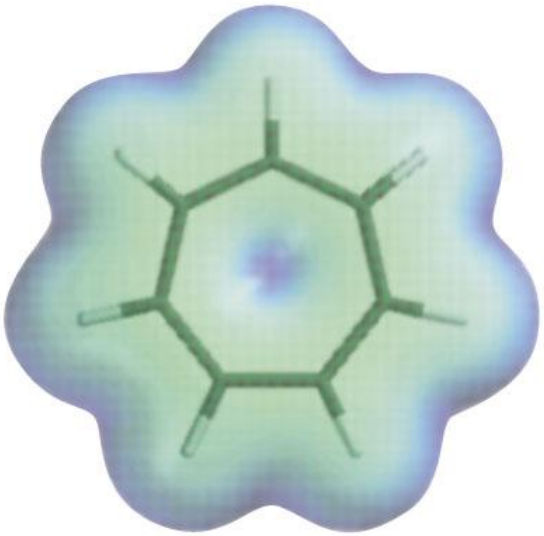


Cykloheptatrienový kation (tropylium)

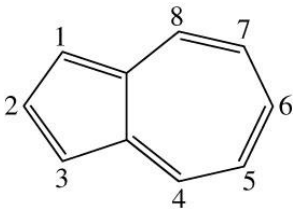


6 π elektronů

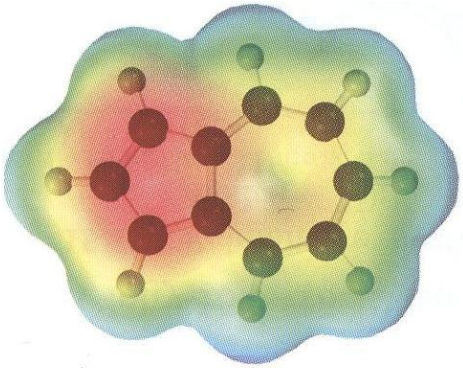
Aromatický

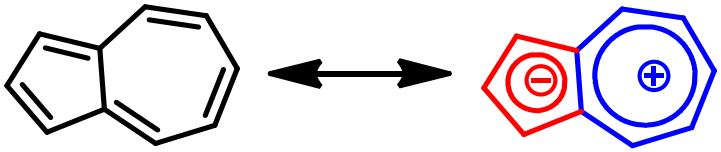


Azulen



aromatický

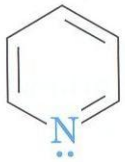


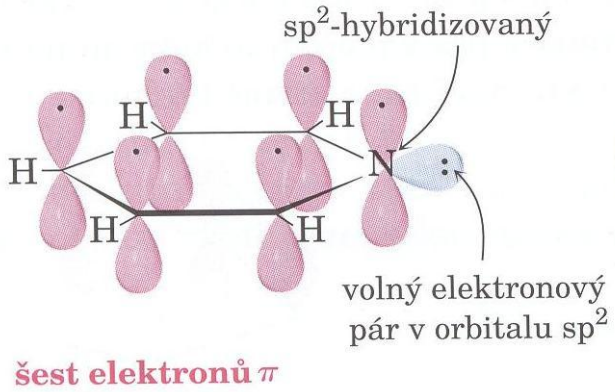


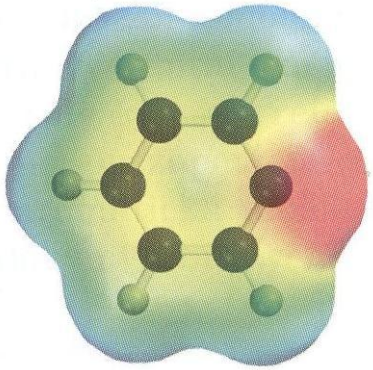
Lactarius indigo obsahuje (7-isopropenyl-4-methylazulen-1-yl)methyl stearate.

Heteroaromatické sloučeniny

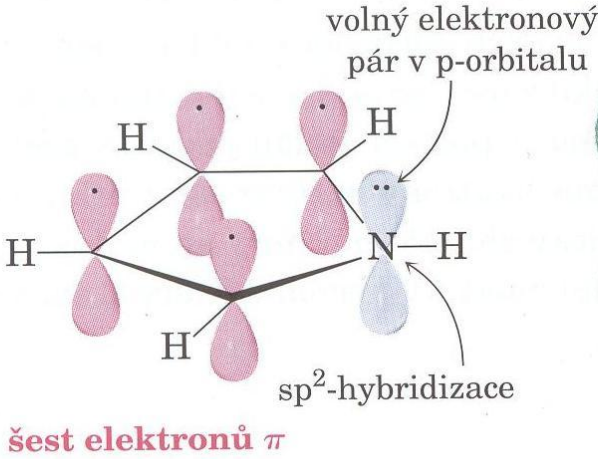
Pyridin

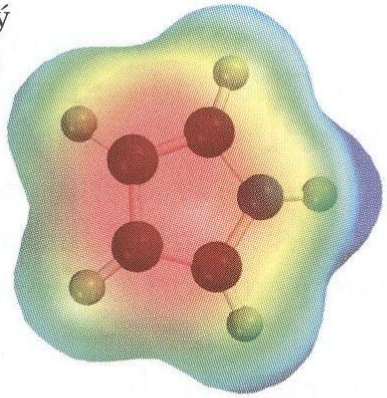




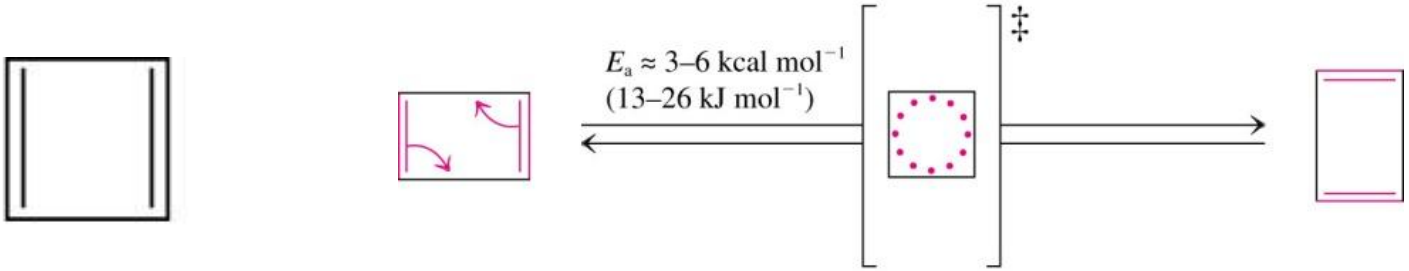


Pyrrol





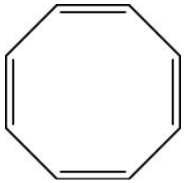
Cyklobutadien

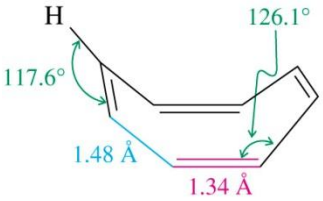


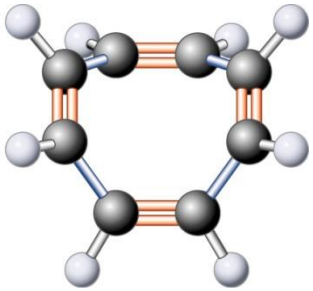
4 π elektronů

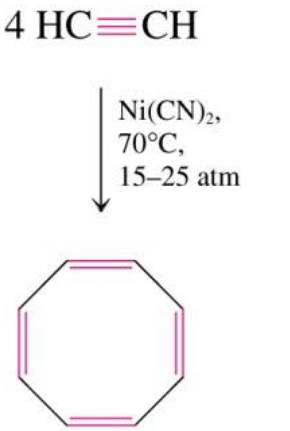
Antiaromatický

Cyklookta-1,3,5,7-tetraen





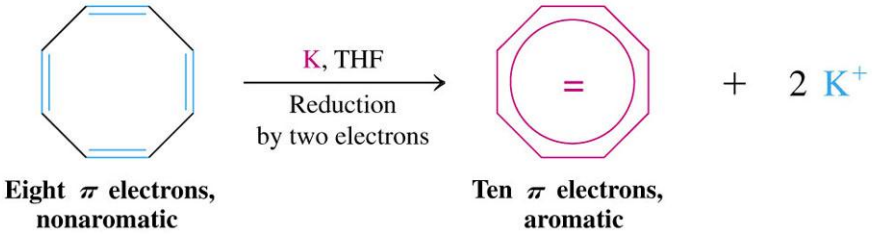




8 π elektronů, neplanární

Nearomatický

Nonaromatic Cyclooctatetraene Forms an Aromatic Dianion

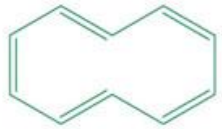


The Annulenes and Other Cyclic Polyenes

Cyclobutadiene:
planar, antiaromatic

Benzene:
planar, aromatic

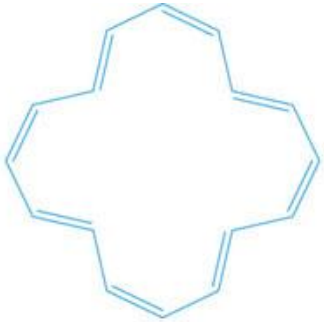
Cyclooctatetraene:
nonplanar = nonaromatic



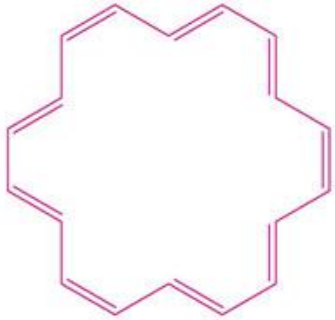
[10]Annulene:
nonplanar = nonaromatic

[12]Annulene:
planar = antiaromatic

[14]Annulene:
planar = aromatic



[16]Annulene:
planar = antiaromatic



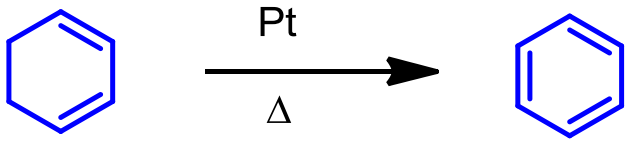
[18]Annulene:
planar = aromatic

1,3-Cyclopentadiene:
noncyclically delocalized
= nonaromatic

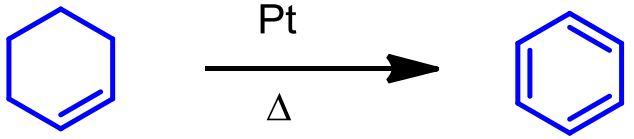
1,4-Cyclohexadiene:
nondelocalized
= nonaromatic

Syntéza benzenu a dalších aromátů

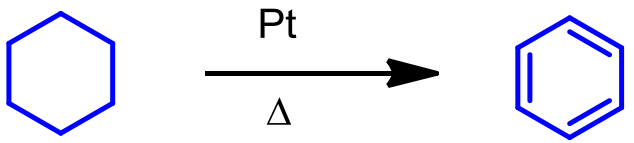
Kalalytická dehydrogenace



+ H_2 **nejsnadnější**

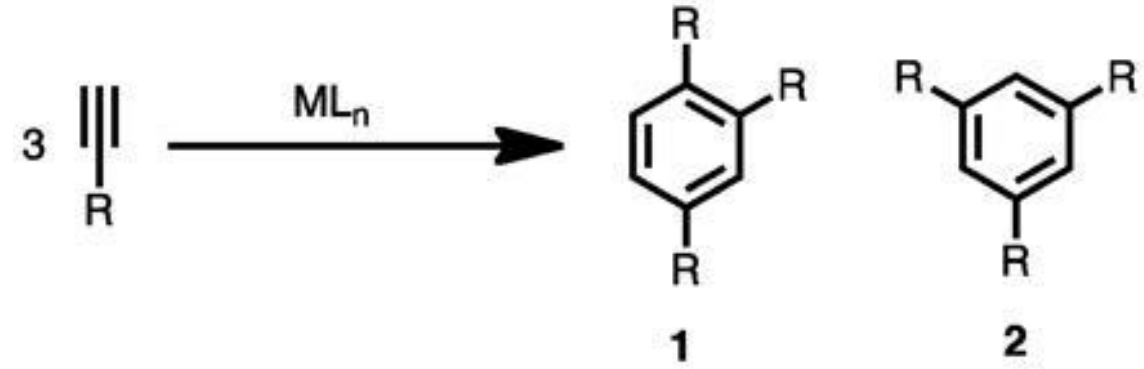


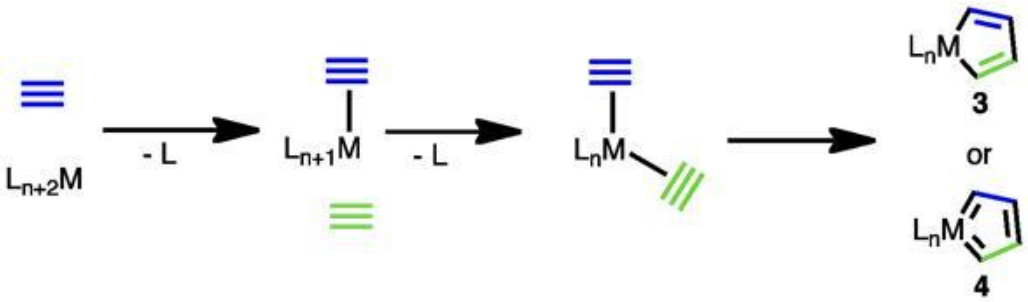
+ 2 H_2

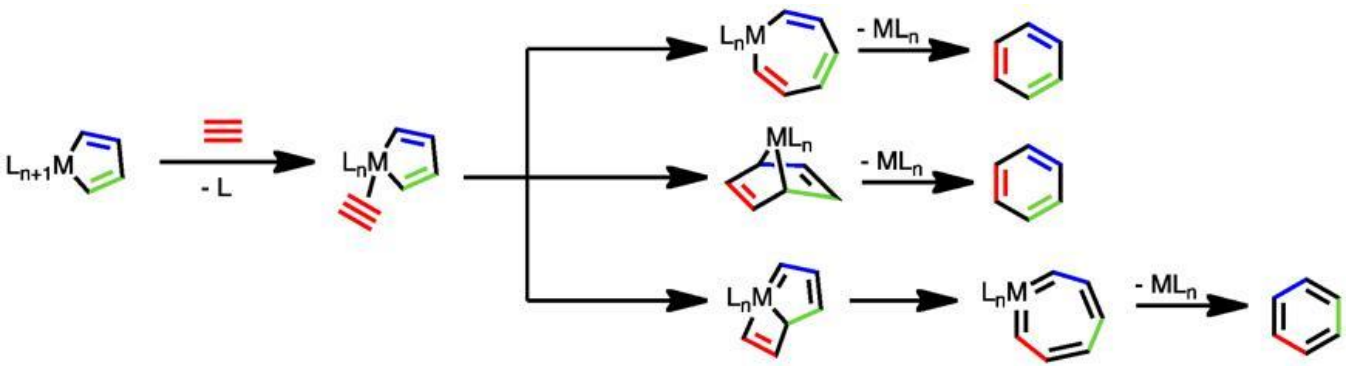


+ 3 H_2 **nejobtížnější**

Syntéza benzenu [2+2+2]-cyklotrimerizací alkynů

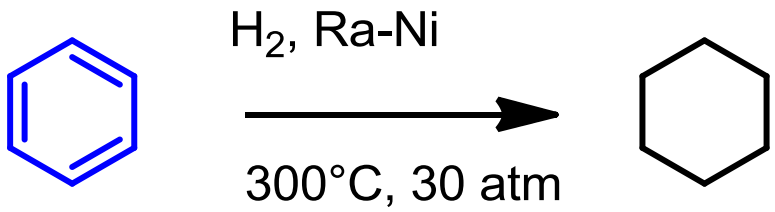




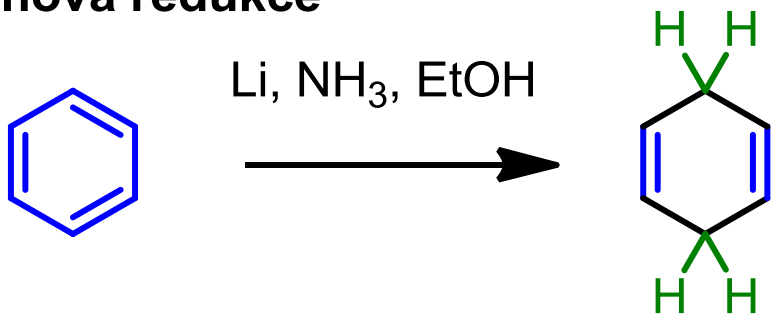


Reaktivita benzenu – redukce (velmi obtížně)

Kalalytická hydrogenace

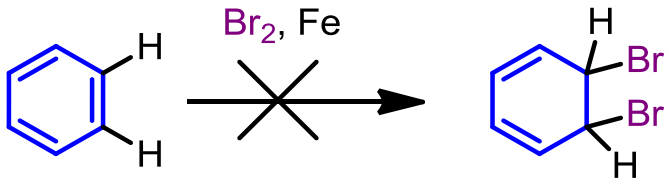


Birchova redukce

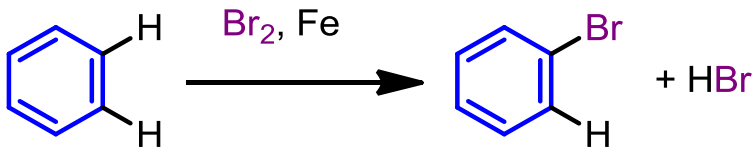


Reaktivita benzenu – adice a substituce

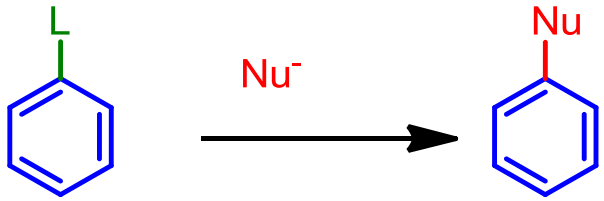
Adiční reakce neprobíhají



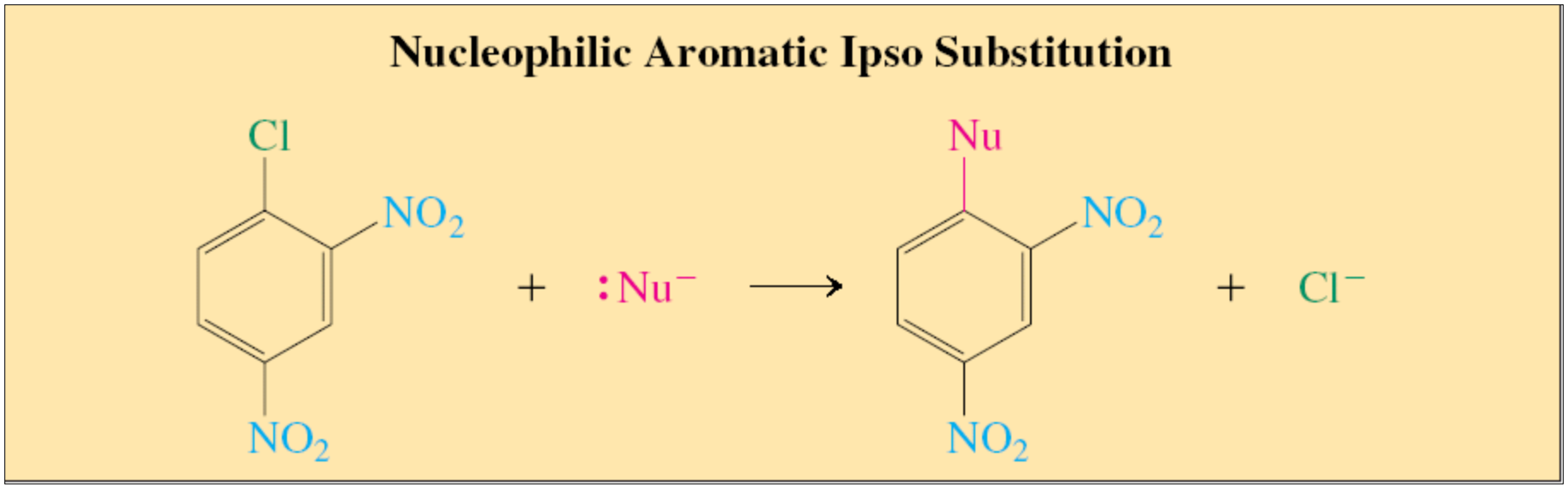
Elektrofilní substituce probíhají snadno

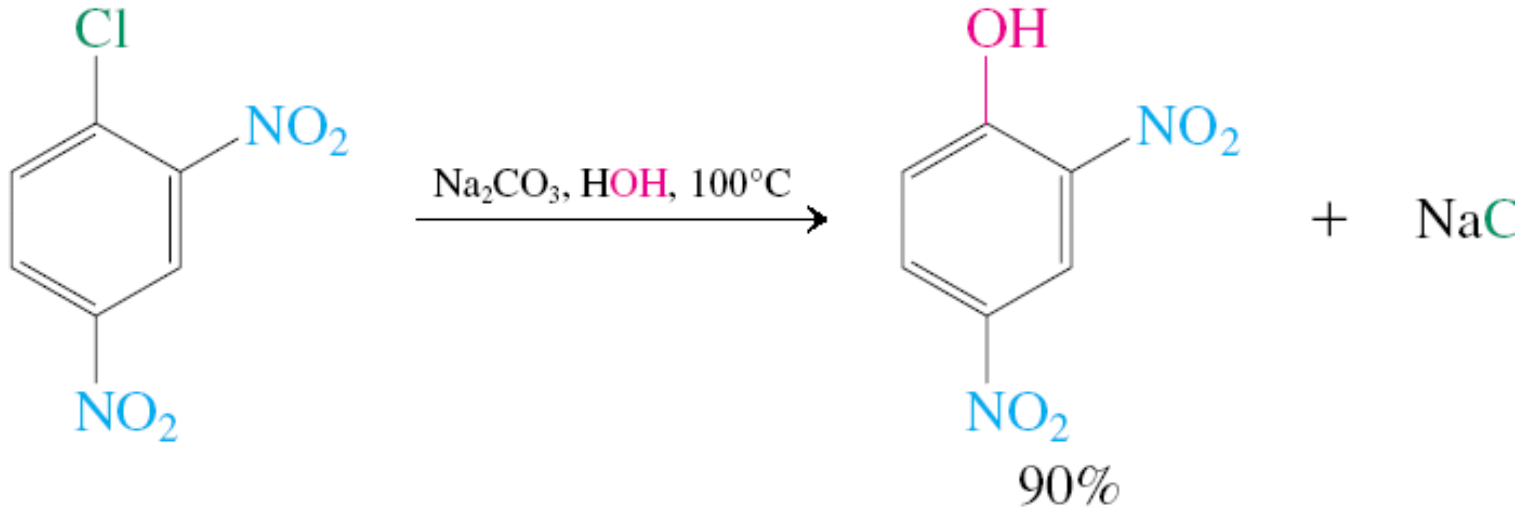


Nukleofilní substituce probíhají obtížně – pouze pro elektronově chudší systémy



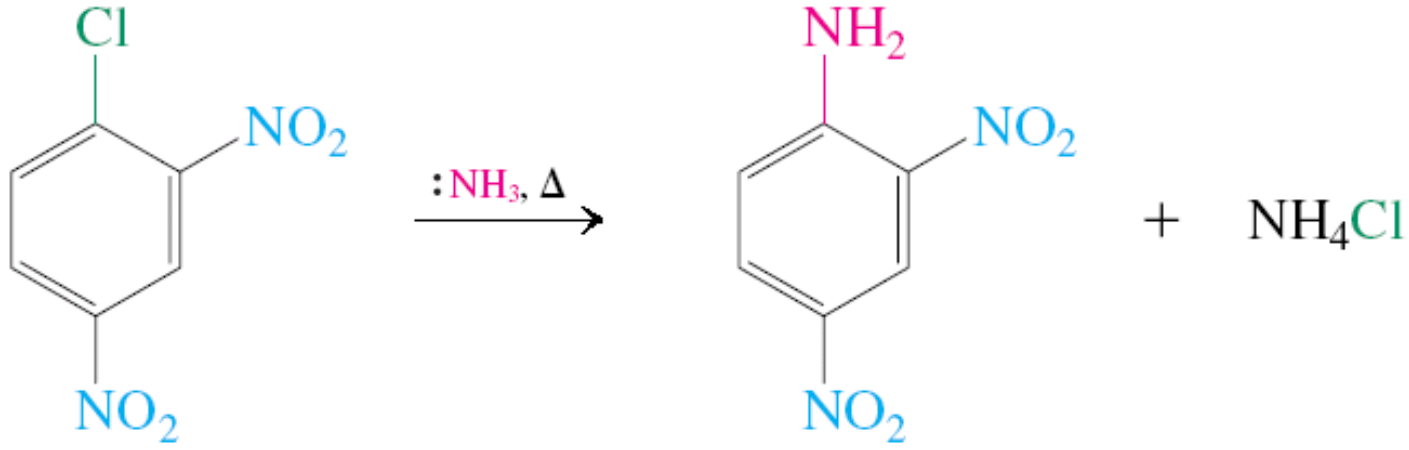
Nukleofilní substituce probíhají obtížně – pouze pro elektronově chudší systémy





1-Chloro-2,4-dinitrobenzene

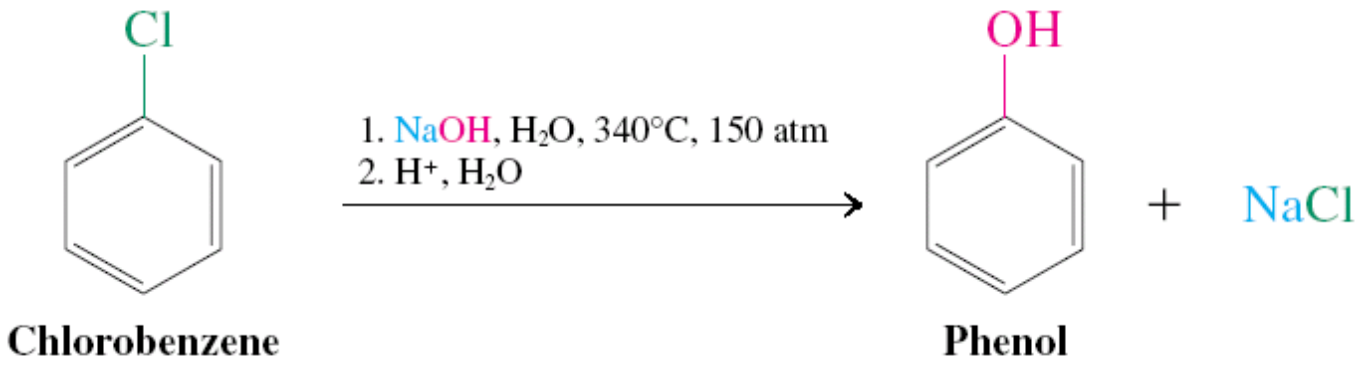
2,4-Dinitrophenol

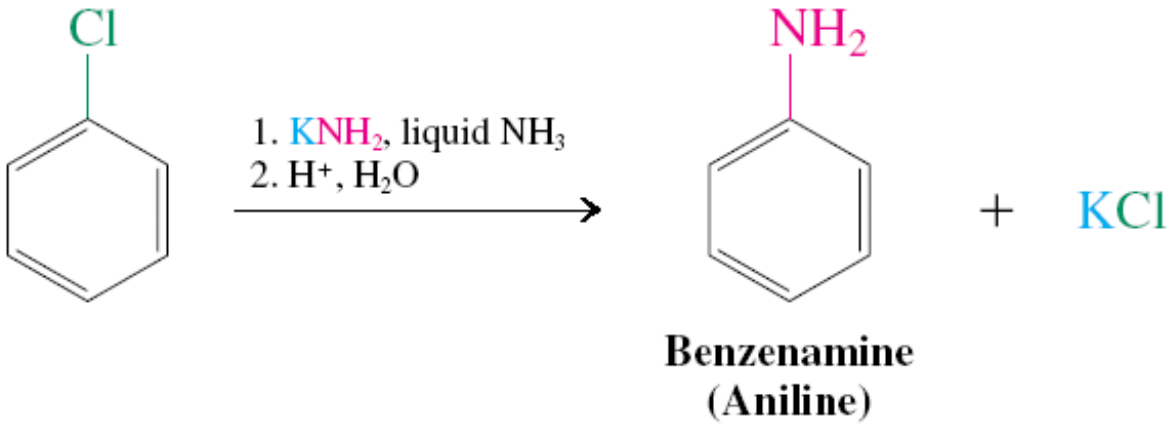


2,4-Dinitrobenzenamine (2,4-Dinitroaniline)

Nukleofilní substituce elektronově-bohatých halogenarenů

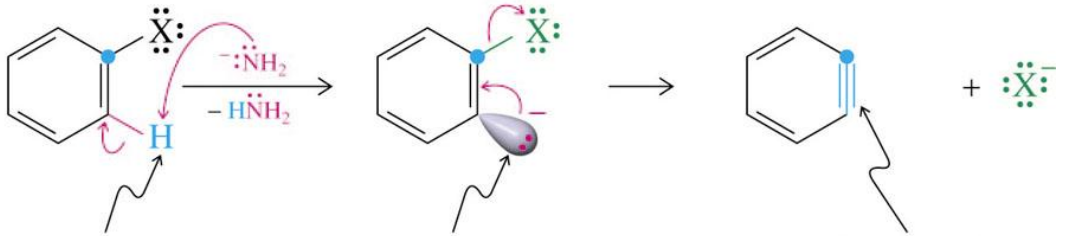
Halogenareny bez elektron-odtahujících skupin mohou poskytovat nukleofilní substituci ze vysokých teplot a tlaků – tato reakce probíhá před benzynový intermediát.





Mechanism of Nucleophilic Substitution of Simple Haloarenes

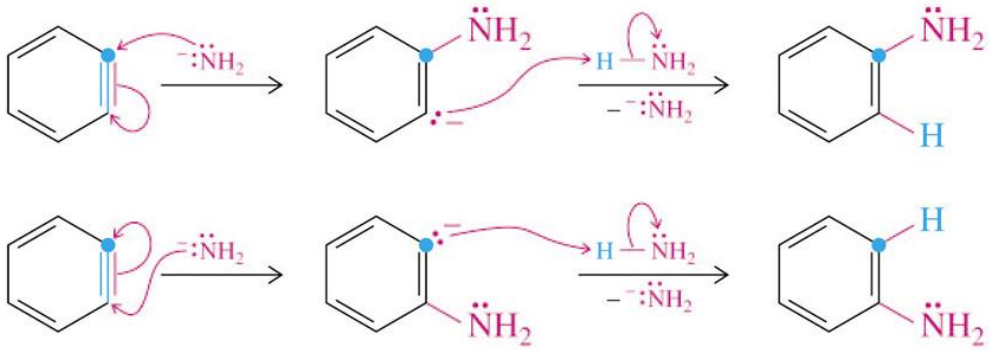
Step 1. Elimination occurs stepwise

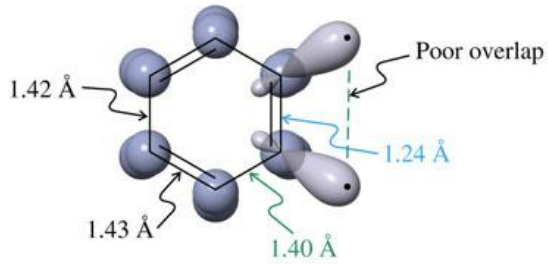


Phenyl anion
(Intermediate)

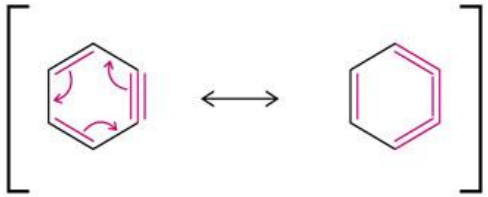
Benzyne
(Reactive intermediate; not isolated)

Step 2. Addition occurs to both strained carbons

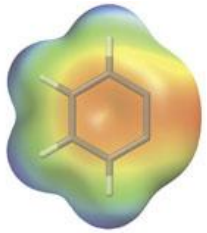




A



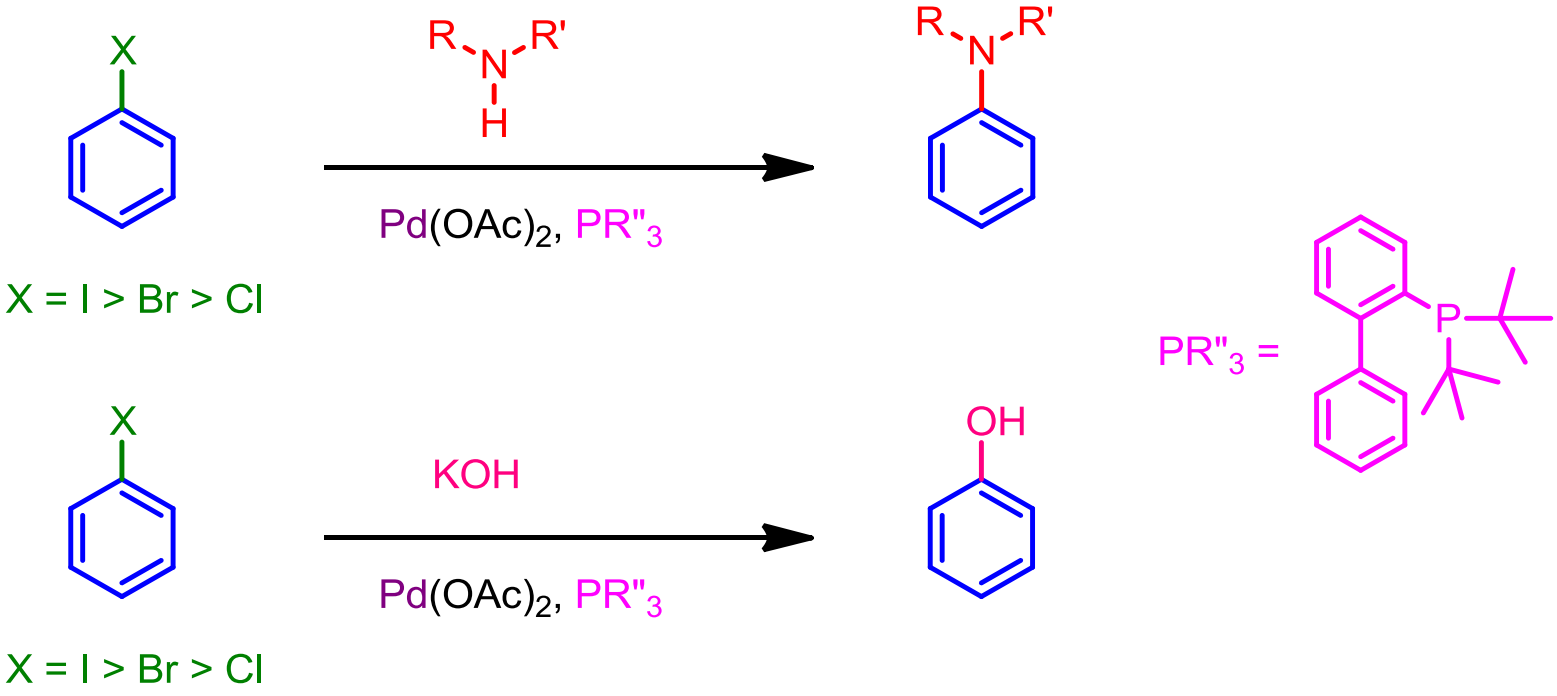
B



C

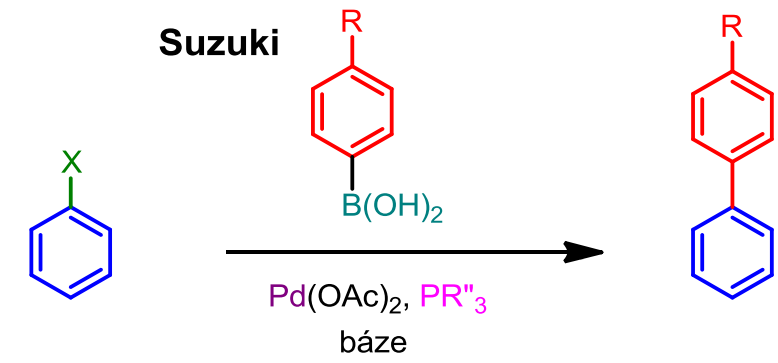
Moderní katalytické metody „nukleofilní substituce“ halogenarenů

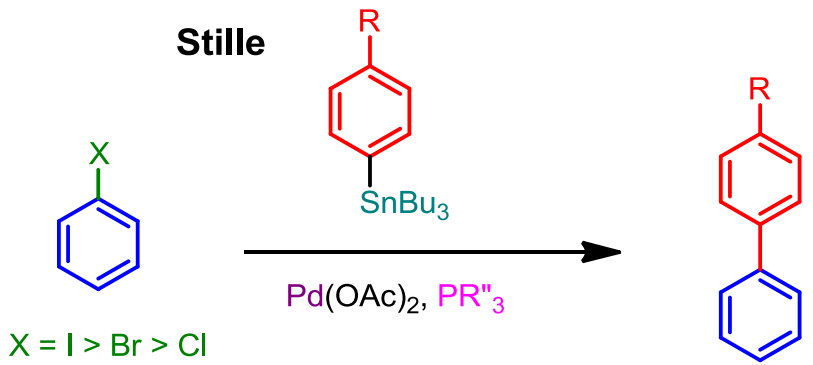
- Pd-katalyzované C-X cross-couplingy (Buchwald-Hartwigovy reakce)

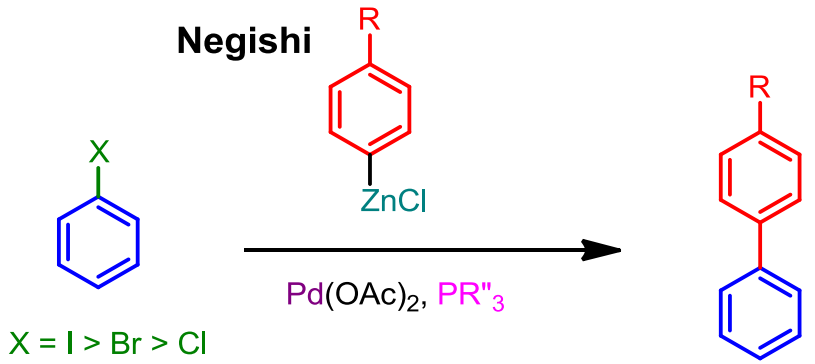


Moderní katalytické metody „nukleofilní substituce“ halogenarenů

- Pd-katalyzované C-C cross-couplingy (Suzukiho, Negishiho nebo Stilleho reakce)







Nobelova cena za chemii 2010