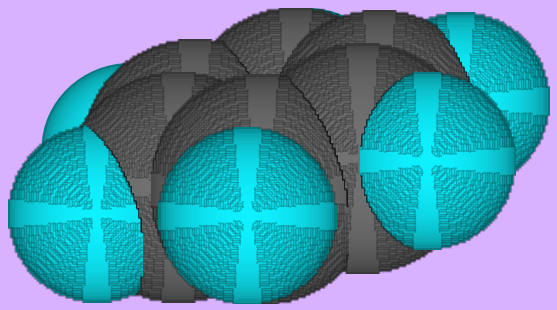
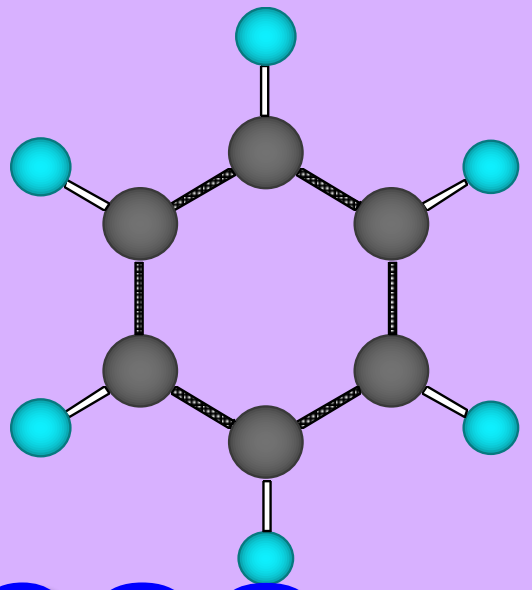
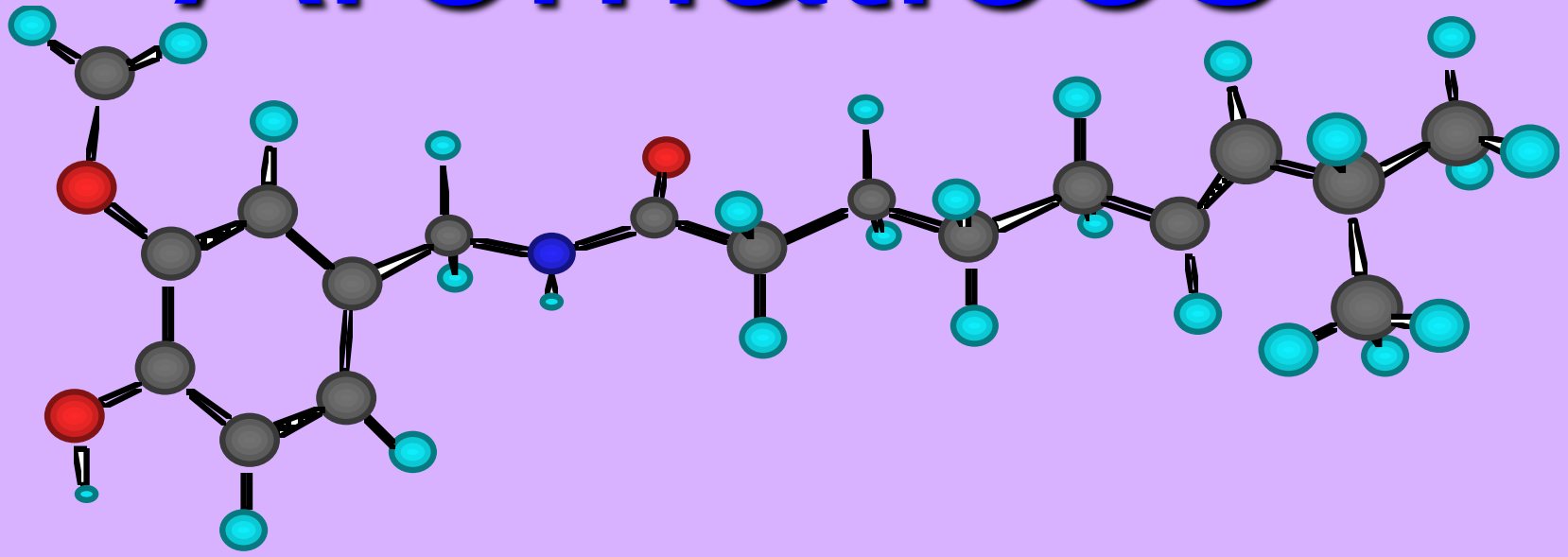




# Aromáticos




# Michael Faraday (1791-1867)

•Mais conhecido por suas descobertas sobre fenômenos elétricos. Contudo, iniciou sua carreira com estudos na área da química.

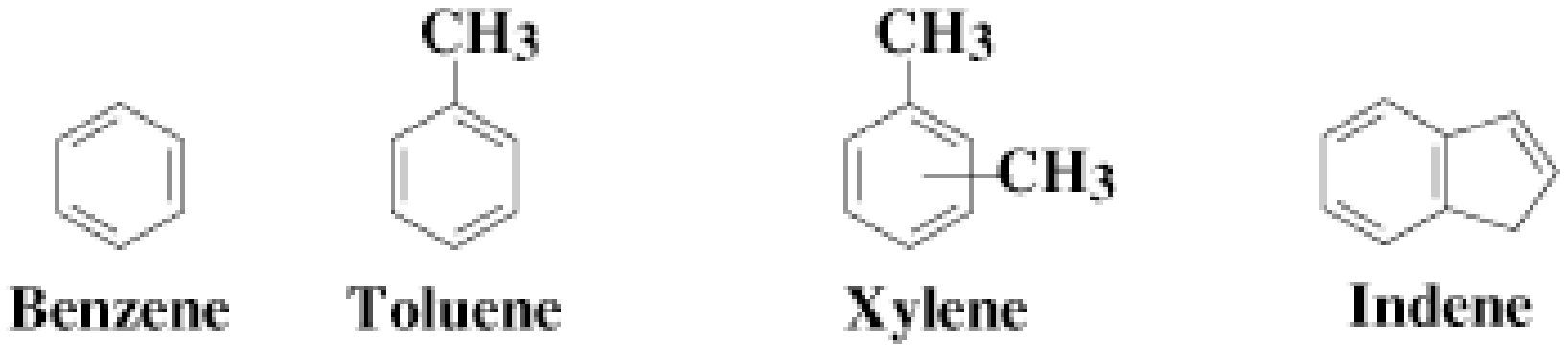
• Isolou o benzeno do resíduo oleoso encontrado nos postes de iluminação à gás das ruas de Londres e determinou que a razão C:H era de 1:1.

•O nome do grupamento ***fenila***, usado quando o uma unidade de benzeno encontra-se como um substituinte, deriva de sua origem, pois a palavra grega *pheno* significa *“Eu tenho a luz”.*

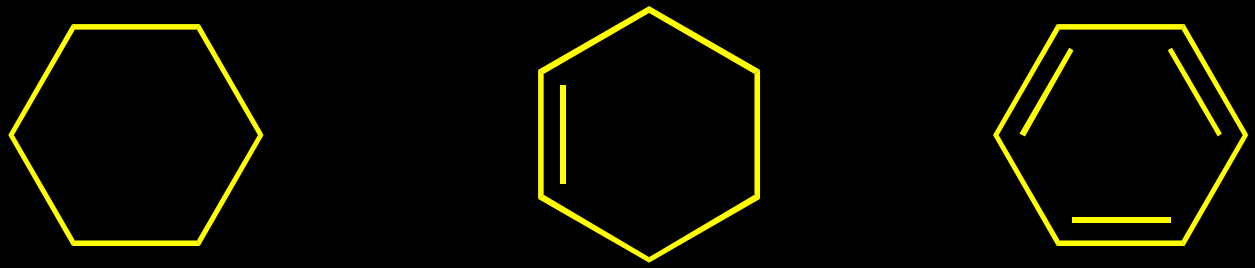
•O benzeno foi sintetizado em 1834 por Eilhard Mitscherlich, o qual determinou sua fórmula molecular como $C_6H_6$.

# Aromatic Compounds

- *Aromatic* was used to described some fragrant compounds in early 19$^{th}$ century
- later they are grouped by chemical behavior (unsaturated compounds that undergo substitution rather than addition)
- Current: distinguished from *aliphatic* compounds by electronic configuration



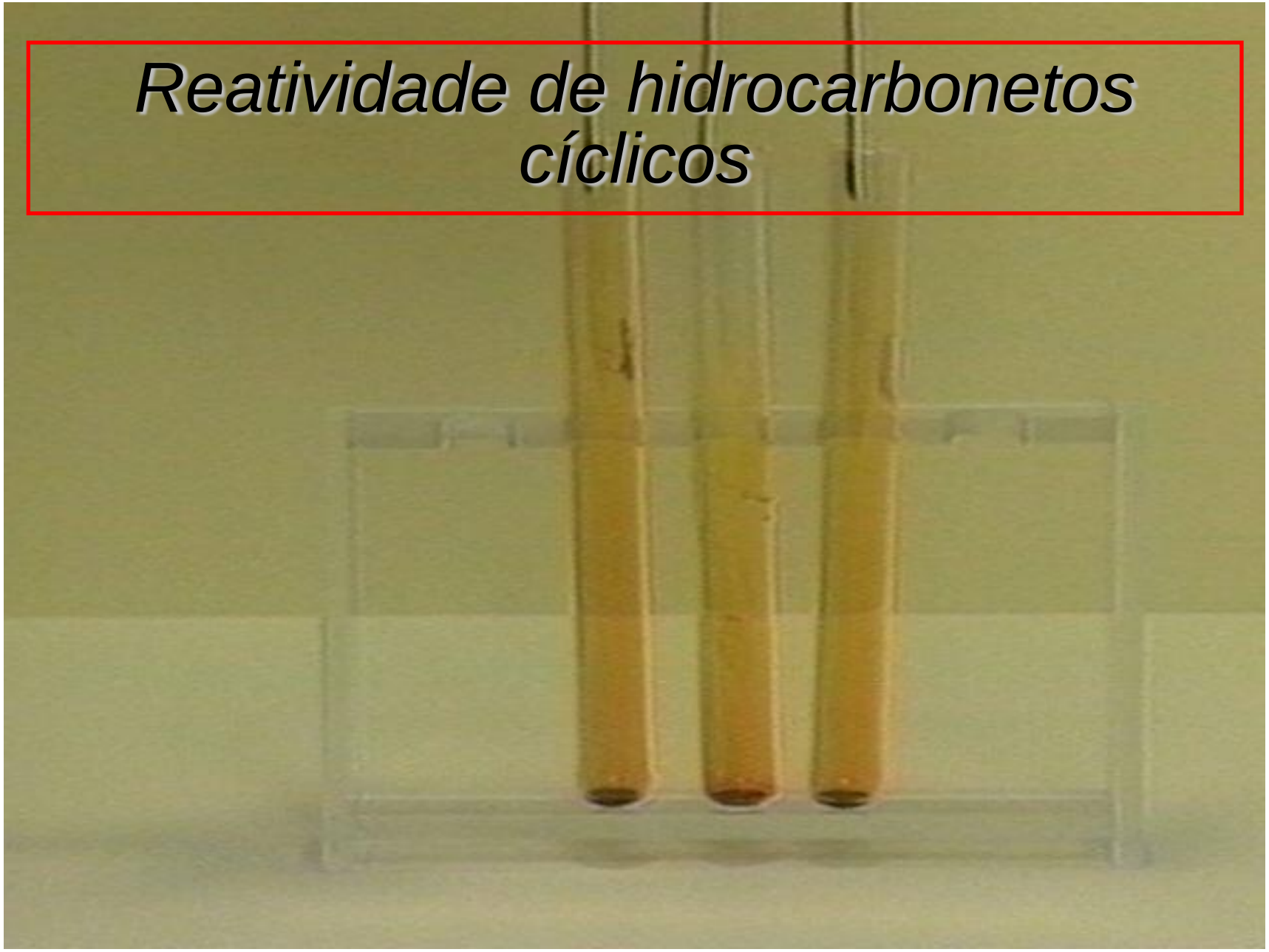
# *Reatividade de hidrocarbonetos cíclicos: um exemplo*



**ciclo-hexano  ciclo-hexeno  benzeno**

**Entretanto, há exceções: na reação desses três compostos com $Br_2$: o que se observou?**

# *Reatividade de hidrocarbonetos cíclicos*



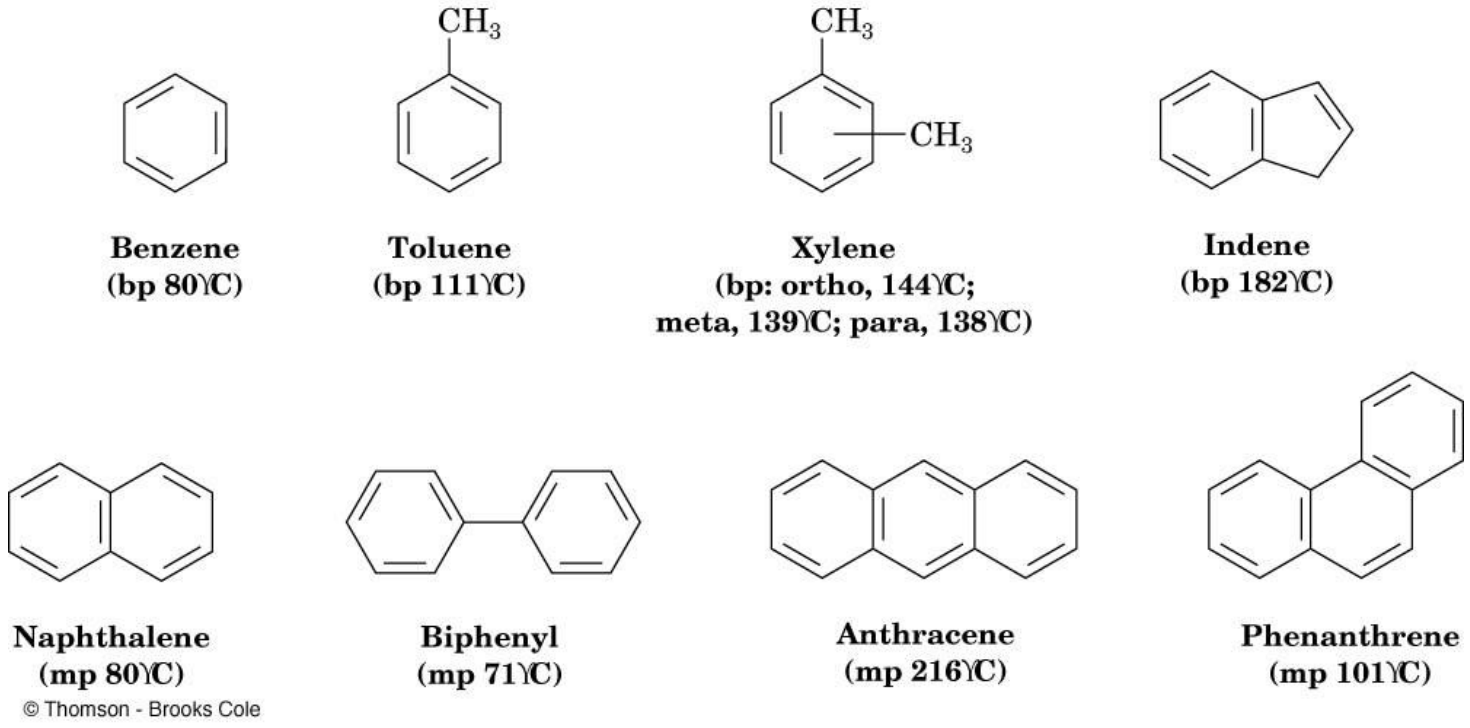

Bromine


Cyclohexane
Cyclohexene
Benzene


Cyclohexane
Cyclohexene
Benzene

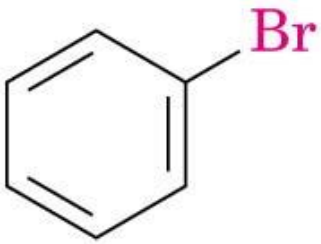
# Sources of Aromatic Hydrocarbons

- From high temperature distillation of coal tar
- Heating petroleum at high temperature and pressure over a catalyst



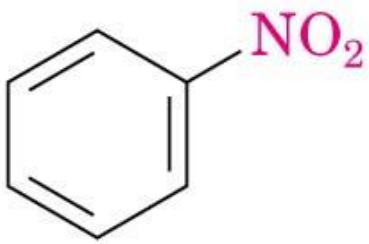
# Naming Aromatic Compounds

- Many common names (toluene = methylbenzene; aniline = aminobenzene)
- Monosubstituted benzenes systematic names as hydrocarbons with –*benzene*
  - $C_6H_5Br$ = bromobenzene
  - $C_6H_5NO_2$ = nitrobenzene, and $C_6H_5CH_2CH_2CH_3$ is propylbenzene

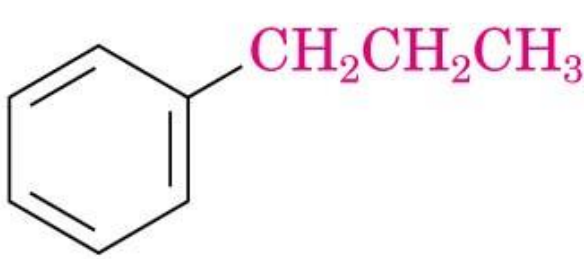



**Bromobenzene**





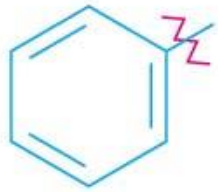

**Nitrobenzene**



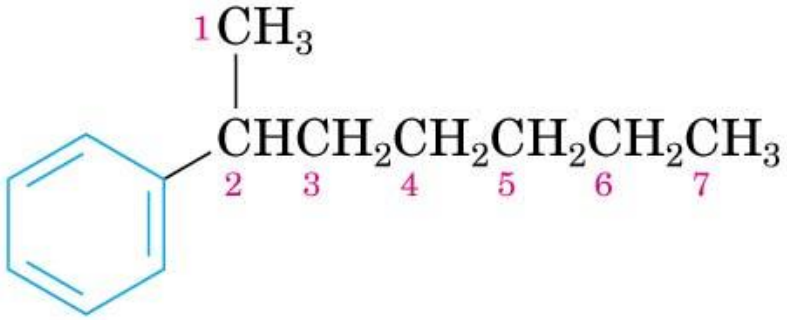

**Propylbenzene**

# O grupo fenila

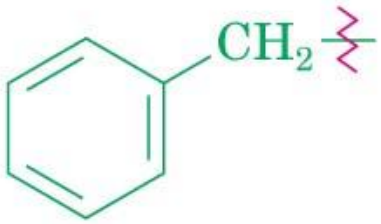
- When a benzene ring is a substituent, the term **phenyl** is used (for $C_6H_5$□)
  - You may also see “Ph” or “ϕ” in place of “$C_6H_5$”
- “**Benzila**” refere-se a “$C_6H_5CH_2$-”



**A phenyl group**



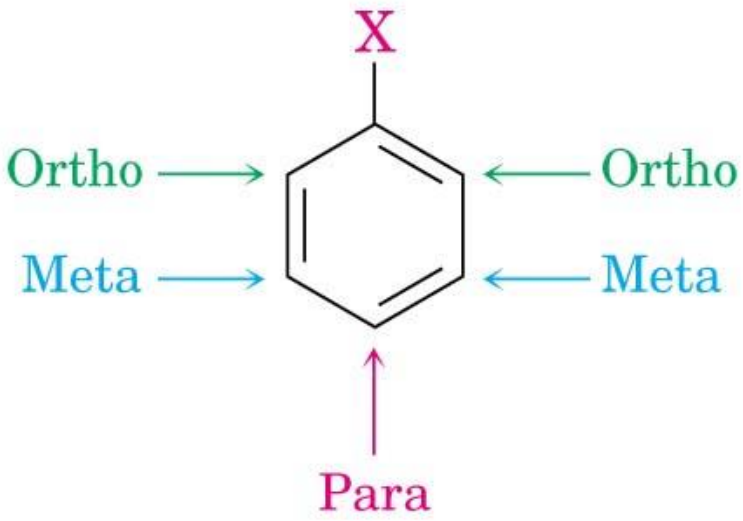

**2-Phenylheptane**

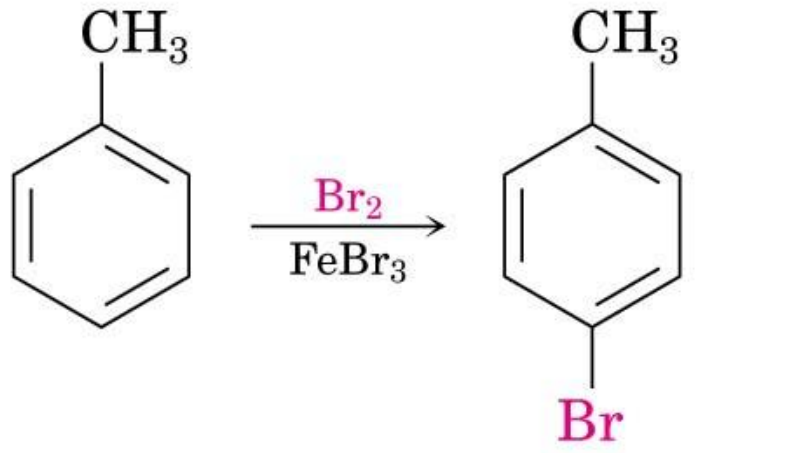



**A benzyl group**

# Disubstituted Benzenes

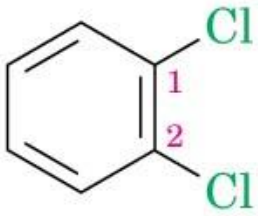
- Relative positions on a benzene ring
  - ***ortho- (o)*** on adjacent carbons (1,2)
  - ***meta- (m)*** separated by one carbon (1,3)
  - ***para- (p)*** separated by two carbons (1,4)
- Describes reaction patterns (“occurs at the para position”)

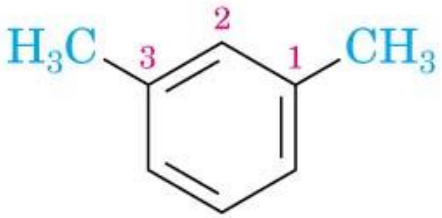


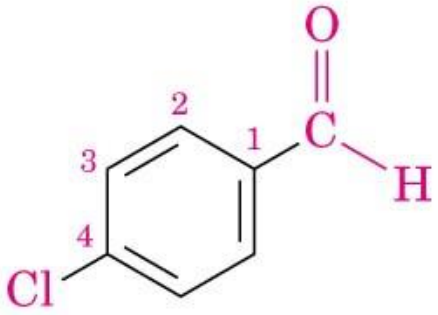




**Toluene** **p-Bromotoluene**





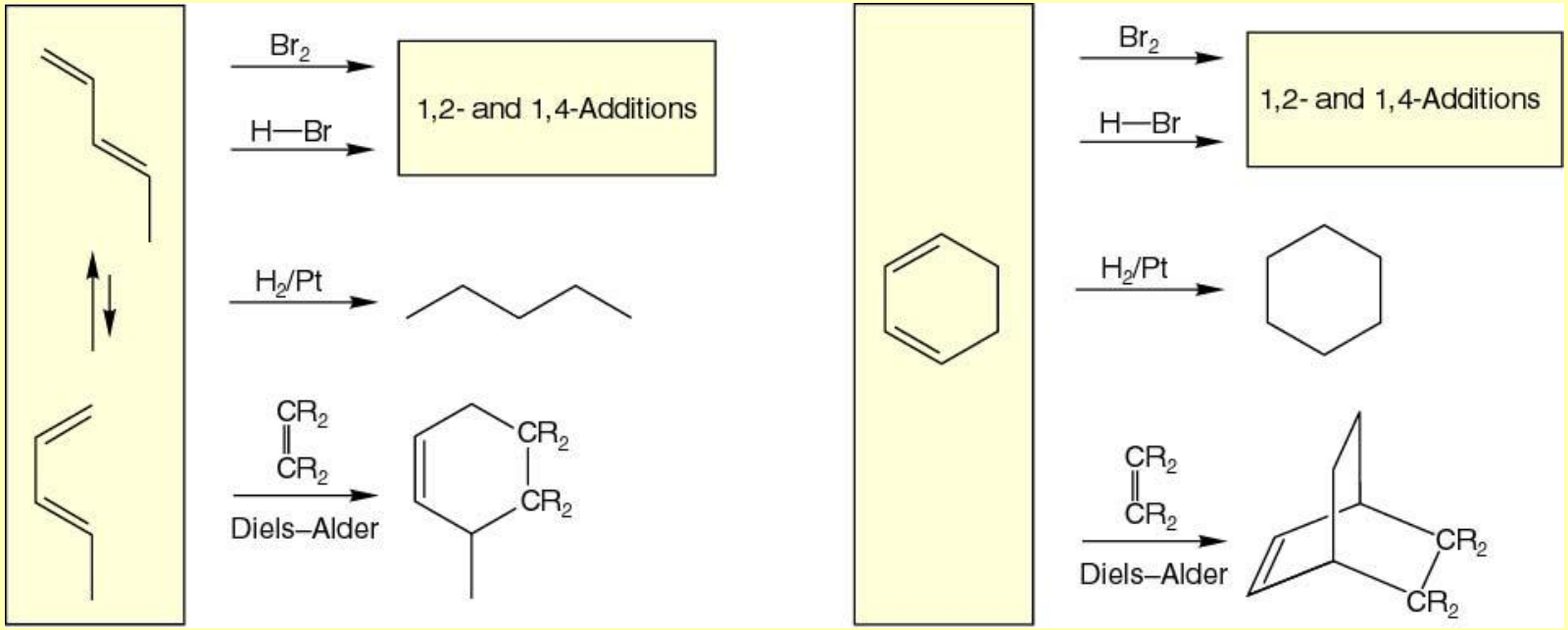

***ortho*-Dichlorobenzene**
**1,2 disubstituted**

***meta*-Xylene**
**1,3 disubstituted**

***para*-Chlorobenzaldehyde**
**1,4 disubstituted**

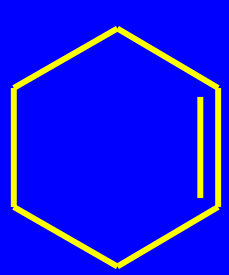
# Dienos conjugados lineares *vs* cíclicos

- Em geral, a reatividade dos dienos conjugados cíclicos é semelhante àquela exibida pelos lineares.

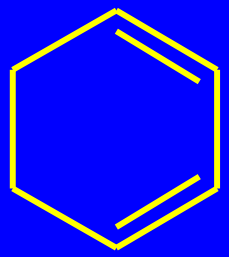


# *Entalpias de Hidrogenação*

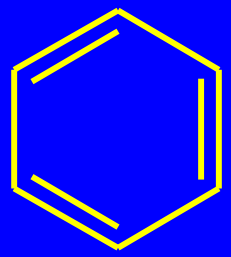
para obtenção de ciclo-hexano (kJ/mol)



120



231

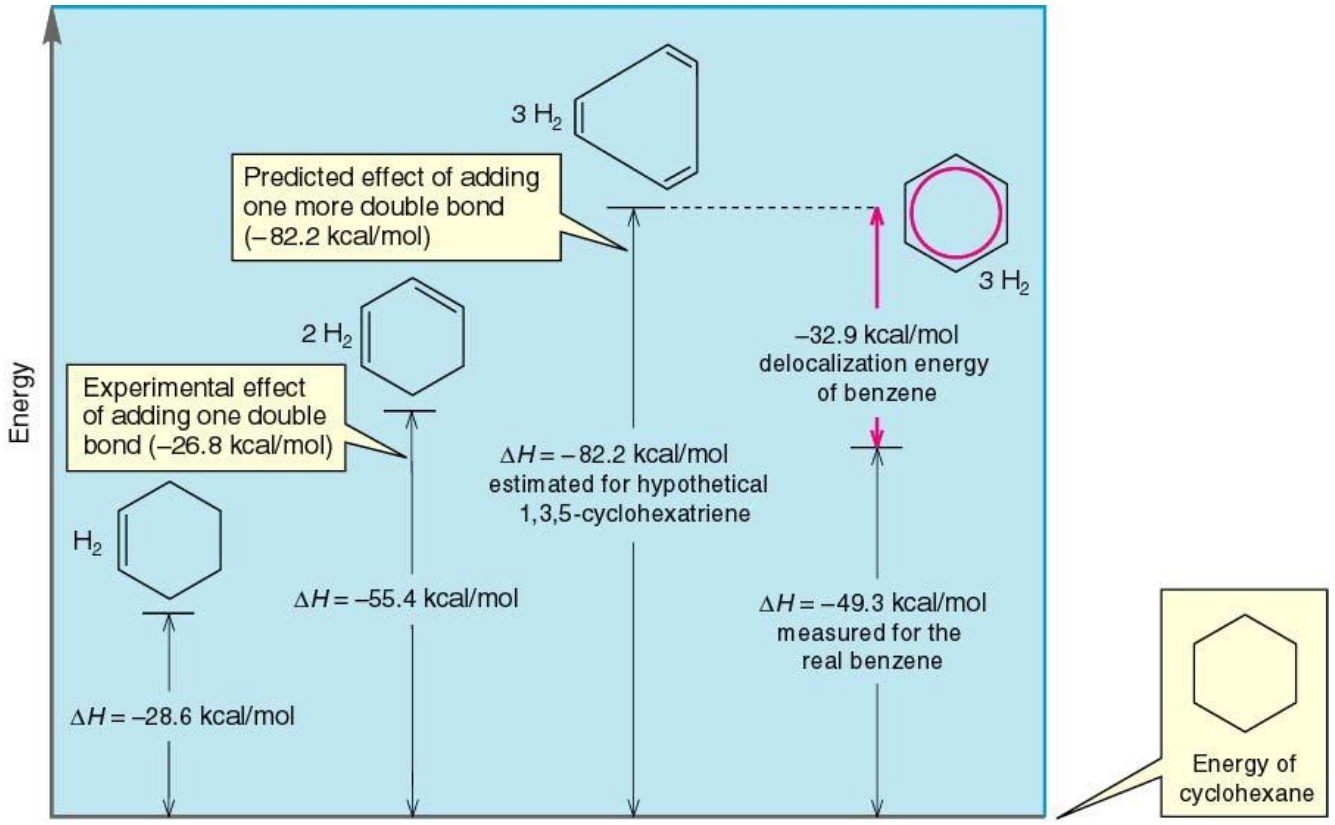


208

benzeno: 152 kJ/mol a menos do que o calculado

3 X 120 kJ/mol $\Rightarrow$ 360 kJ/mol, com base na hidrogenação de ciclo-hexeno.

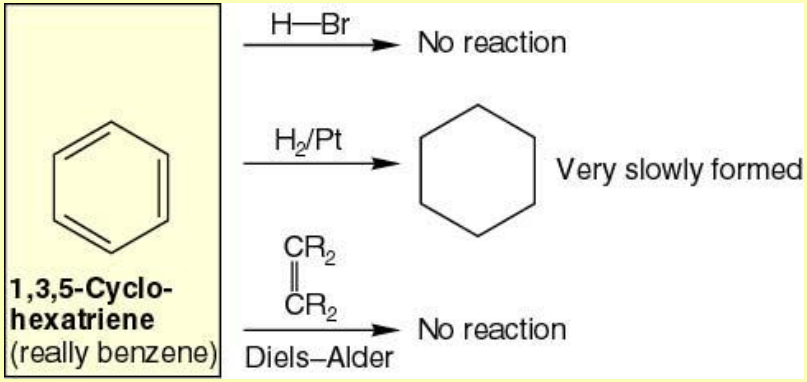
# A estabilidade do benzeno

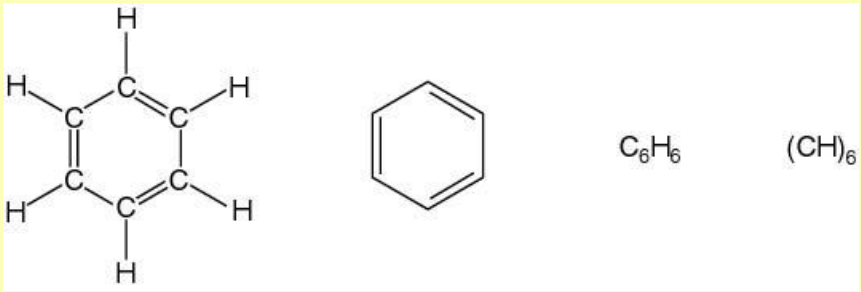


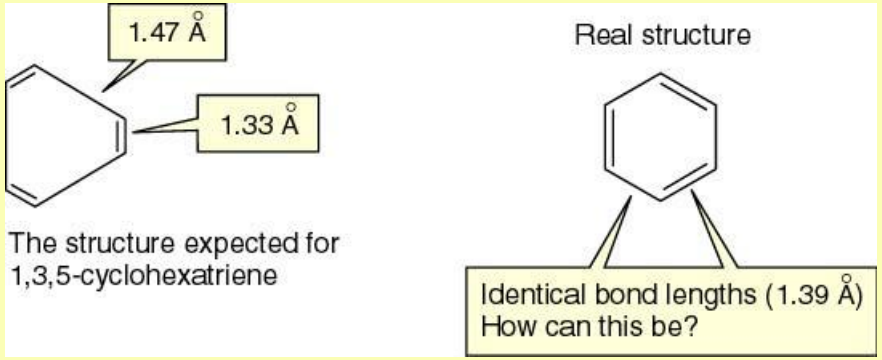

- A determinação da energia liberada ao se hidrogenar o benzeno também é uma evidência experimental da estabilidade dessa substância.

# Compostos cíclicos conjugados

- **Resumindo:** vários alcenos conjugados anulares têm uma reatividade completamente inesperada, sendo **significativamente menos reativos (mais estáveis)** do que os dienos conjugados "normais".



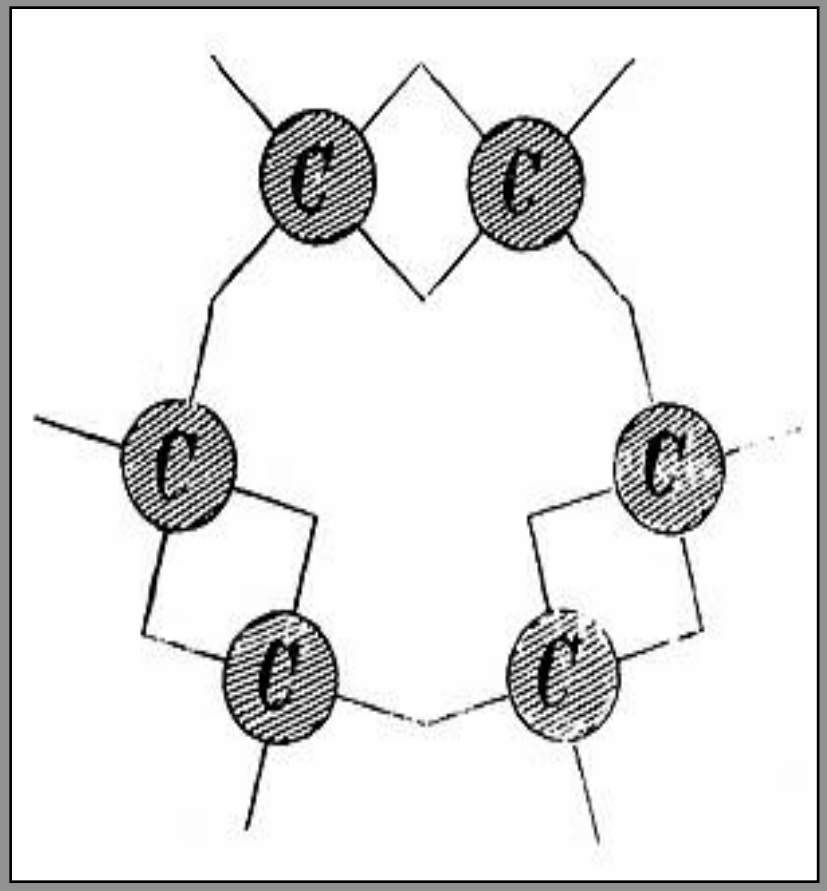
# Percepção da Aromaticidade:

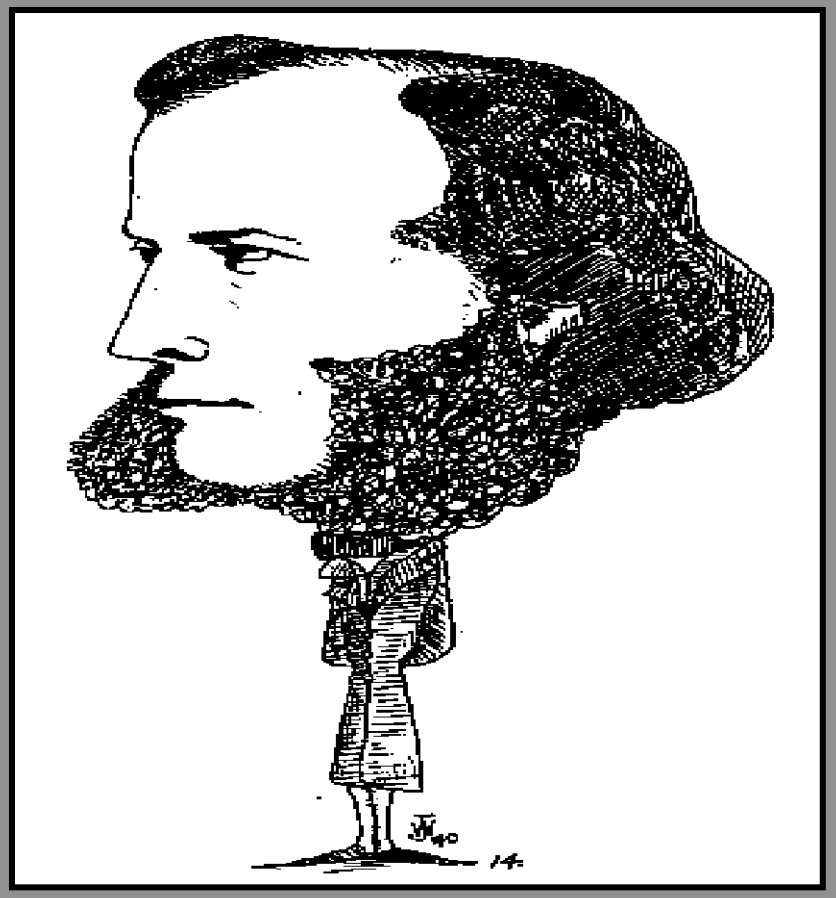
- Dados experimentais, tais como: entalpia de hidrogenação, reatividade.

- Estabilidade incomum, associada a sistemas cíclicos totalmente conjugados

**....I was sitting writing on my textbook, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by the repeated visions of the kind, could now distinguish larger structures of manifold conformation; long rows sometimes more closely fitted together all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis (KEKULE).**

**Royston M. Roberts, *Serendipidty, Accidental Discoveries in Science*, John Wiley and Sons, New York, NY,1989, pp. 75-81.**



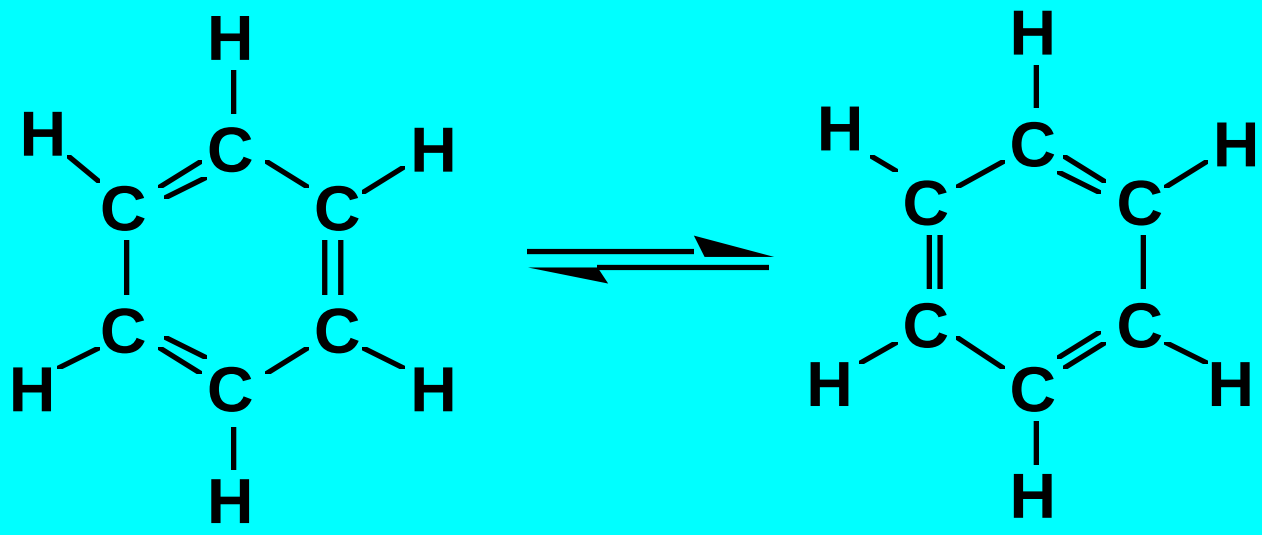
**Friedrich August KEKULE,** later **Kekulé von Stradonitz.**

**7 de setembro 7 de 1829, Darmstadt, Alemanha.**

**13 de julho de 1896, Bonn, Alemanha.**

# Benzeno de Kekulé: século XIX

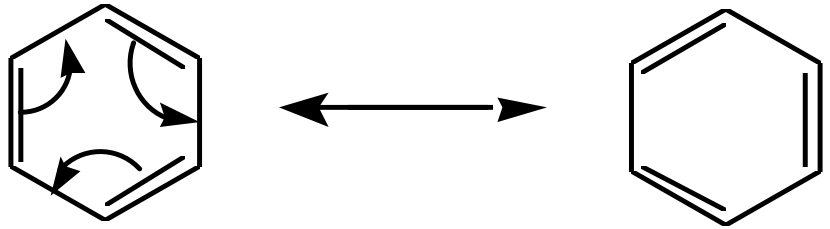
- August Kekulé: propôs a primeira estrutura para o benzeno, em 1872

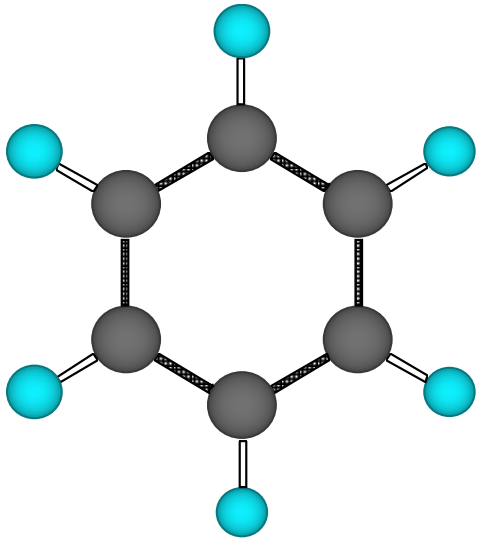


- Essa estrutura não explicava a inesperada reatividade exibida pelo benzeno

# Benzeno - Ressonância

- O benzeno é representado normalmente como um híbrido de duas estruturas equivalentes de Kekulé





**cada uma contribui igualmente para o híbrido, de modo que as ligações C-C não são simples ou duplas, mas sim, algo intermediário.**

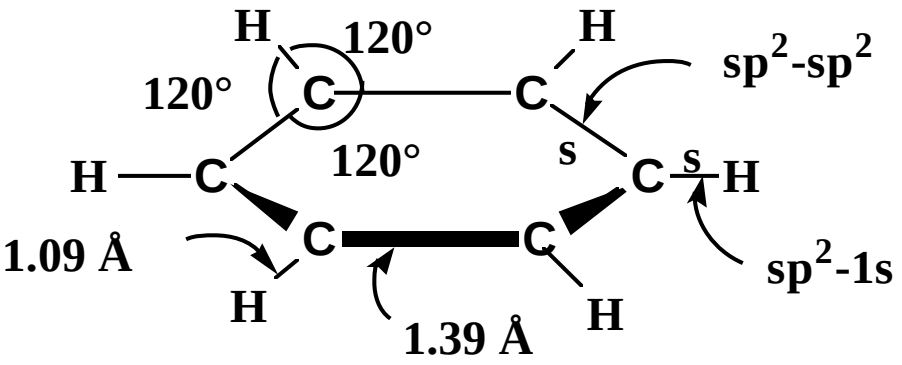
# Estrutura do Benzeno

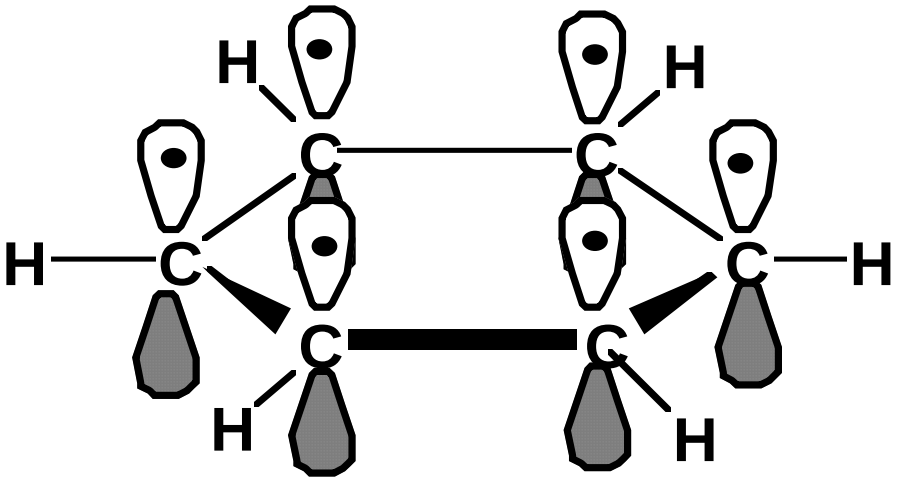
Considerando:

- a hibridação de orbitais atômicos
- a teoria da ressonância

Descreve-se a estrutura do benzeno:

- um hexágono regular, com todos os ângulos de ligação C-C-C e H-C-C iguais a 120°



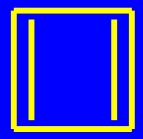



# Requisitos para a Aromaticidade

1. Composto cíclico
2. Composto planar
3. Sistema completamente conjugado
4. 4n + 2 $\pi$ elétrons (Regra de Huckel)

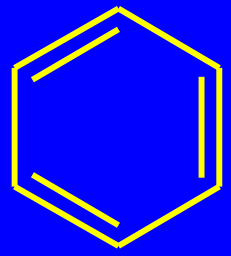
# Requisitos para a Aromaticidade

A conjugação no ciclo é necessária, *mas não suficiente.*

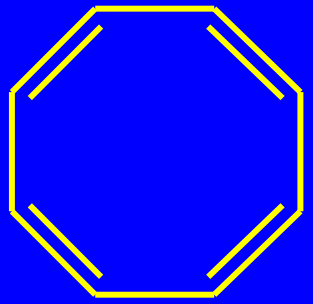


não aromático

Antiaromático quando quadrado



aromático



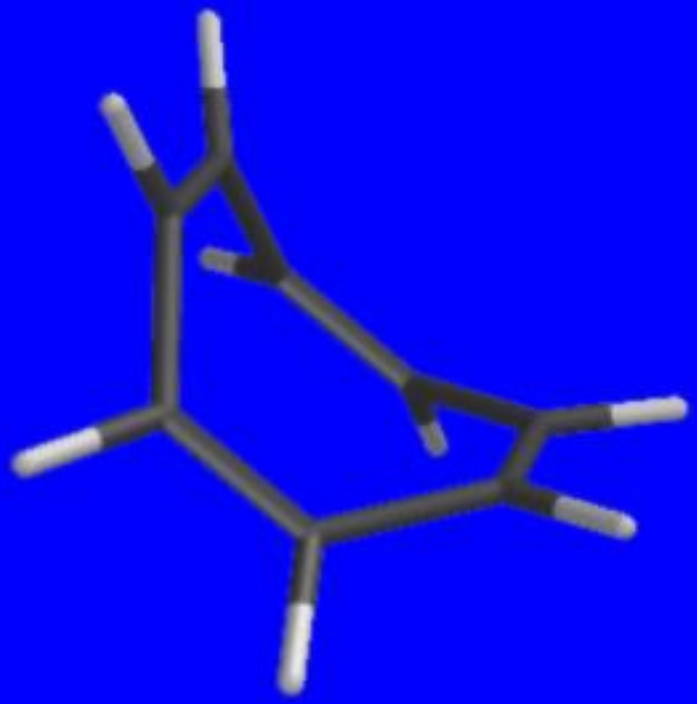
não aromático

Antiaromático quando planar

# *Estrutura do Ciclo-octatetraeno*

O Ciclo-octatetraeno não é planar

apresenta ligações longas (146 pm)
e curtas (133 pm) alternadas



# *Stability of Cyclobutadiene*

Cyclobutadiene is observed to be highly reactive, and too unstable to be isolated and stored in the customary way.

Not only is cyclobutadiene not aromatic, it is *antiaromatic*.

An antiaromatic substance is one that is *destabilized* by cyclic conjugation.

# *Conclusão*

Deve haver algum fator, além da conjugação cíclica, que seja determinante para que a molécula apresente aromaticidade.

**Regra de Hückel:**

O fator adicional que influencia na aromaticidade é o número de elétrons $\pi$

# *Hückel's Rule*

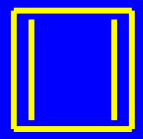
among planar, monocyclic, completely conjugated polyenes, only those with $4n + 2$ $\pi$ electrons possess special stability

| *n* | $4n+2$ | |
|---|---|---|
| 0 | 2 | |
| 1 | 6 | Benzene! |
| 2 | 10 | |
| 3 | 14 | |
| 4 | 18 | |

aromatic: $4n + 2\pi\ e^-$

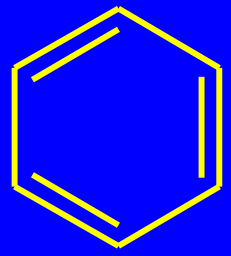
# *Requisito para a Aromaticidade: nº de Elétrons π*

4 elétrons π



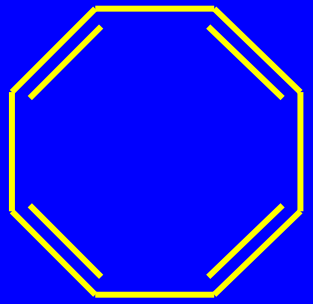
não aromático

6 elétrons π



aromático

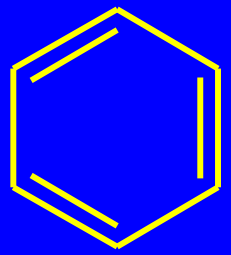
8 elétrons π



não aromático

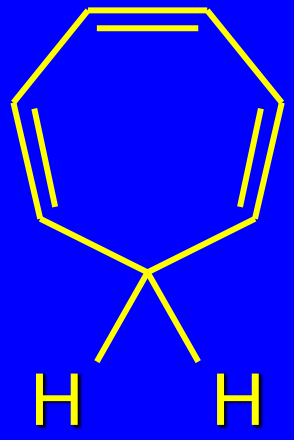
# *Polienos Completamente Conjugados*

6 $\pi$ electrons; completely conjugated



aromatic

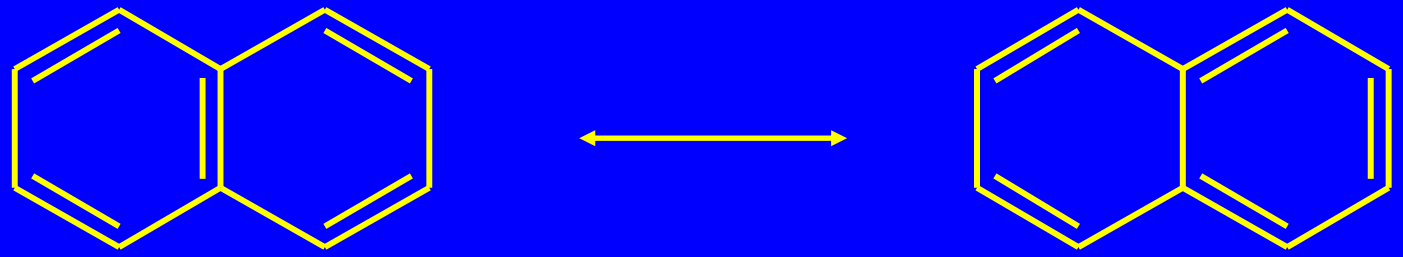
6 $\pi$ electrons; not completely conjugated




not aromatic

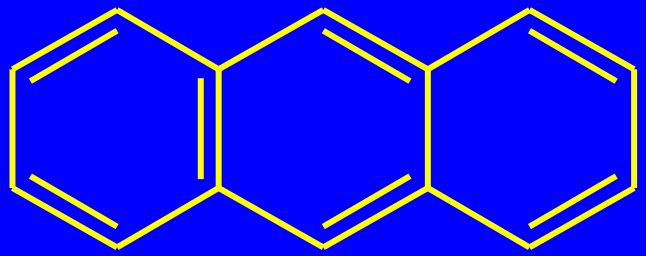
# *Naftaleno*

resonance energy = 255 kJ/mol

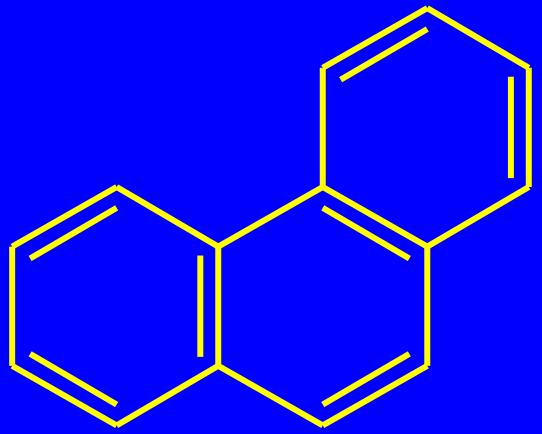


most stable Lewis structure;
both rings correspond to
Kekulé benzene

# *Antraceno e Fenantreno*



Antraceno



Fenantreno

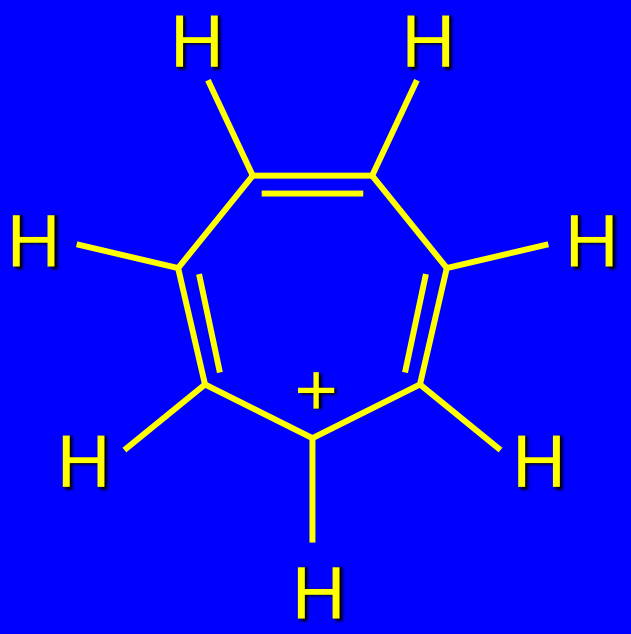
Energia de ressonância:

347 kJ/mol

381 kJ/mol

# Íons Aromáticos

# *Cátion Ciclo-heptatrienila*



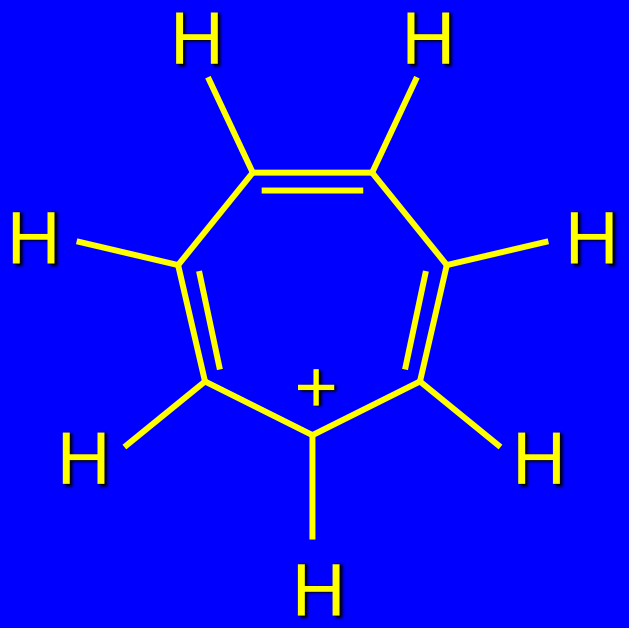

6 elétrons π deslocalizados ao longo de 7 carbonos

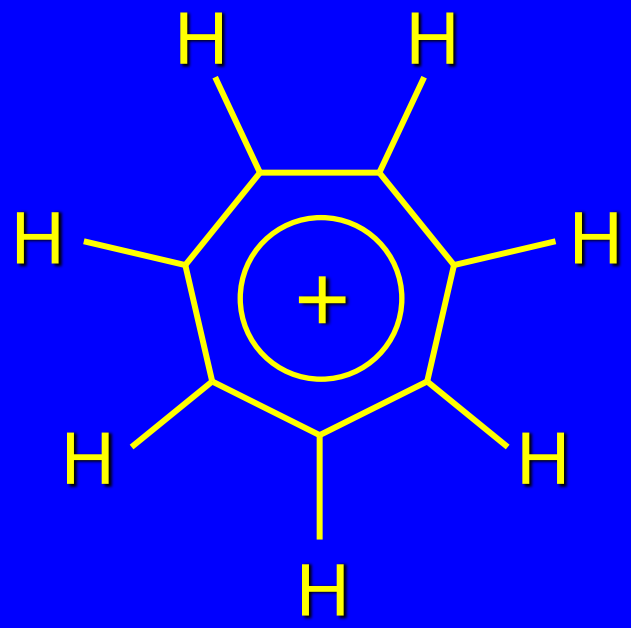
carga positiva dispersa pelos 7 carbonos

carbocátion muito estável

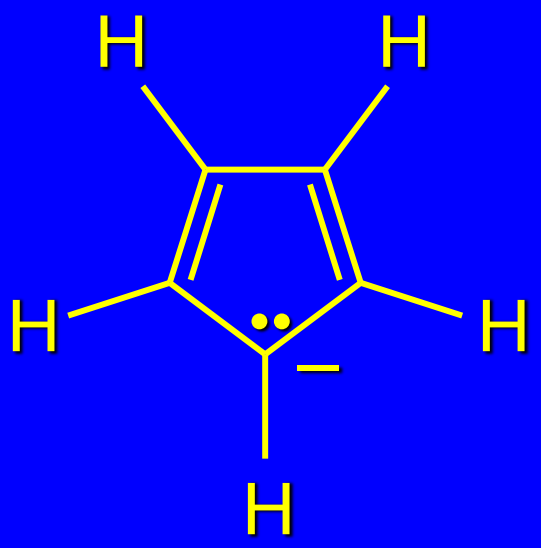
também chamado de cátion tropílio

# *Cátion Ciclo-heptatrienila*



# *Ânion Ciclopentadieneto*

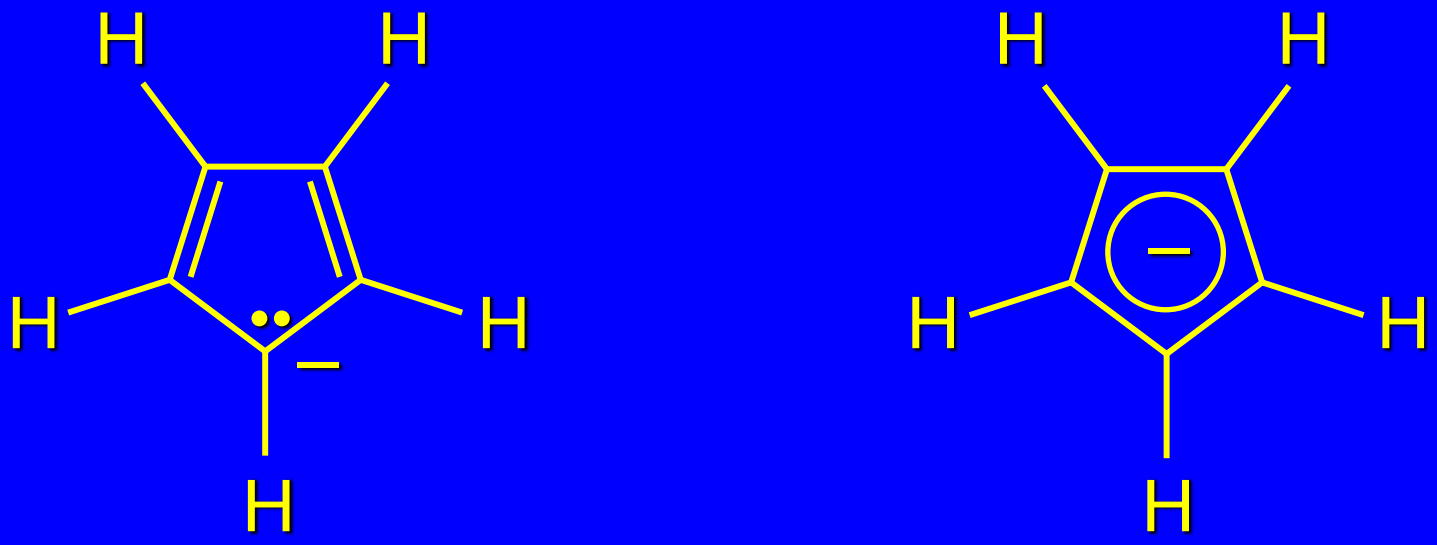



6 elétrons p deslocalizados ao longo de 5 carbonos

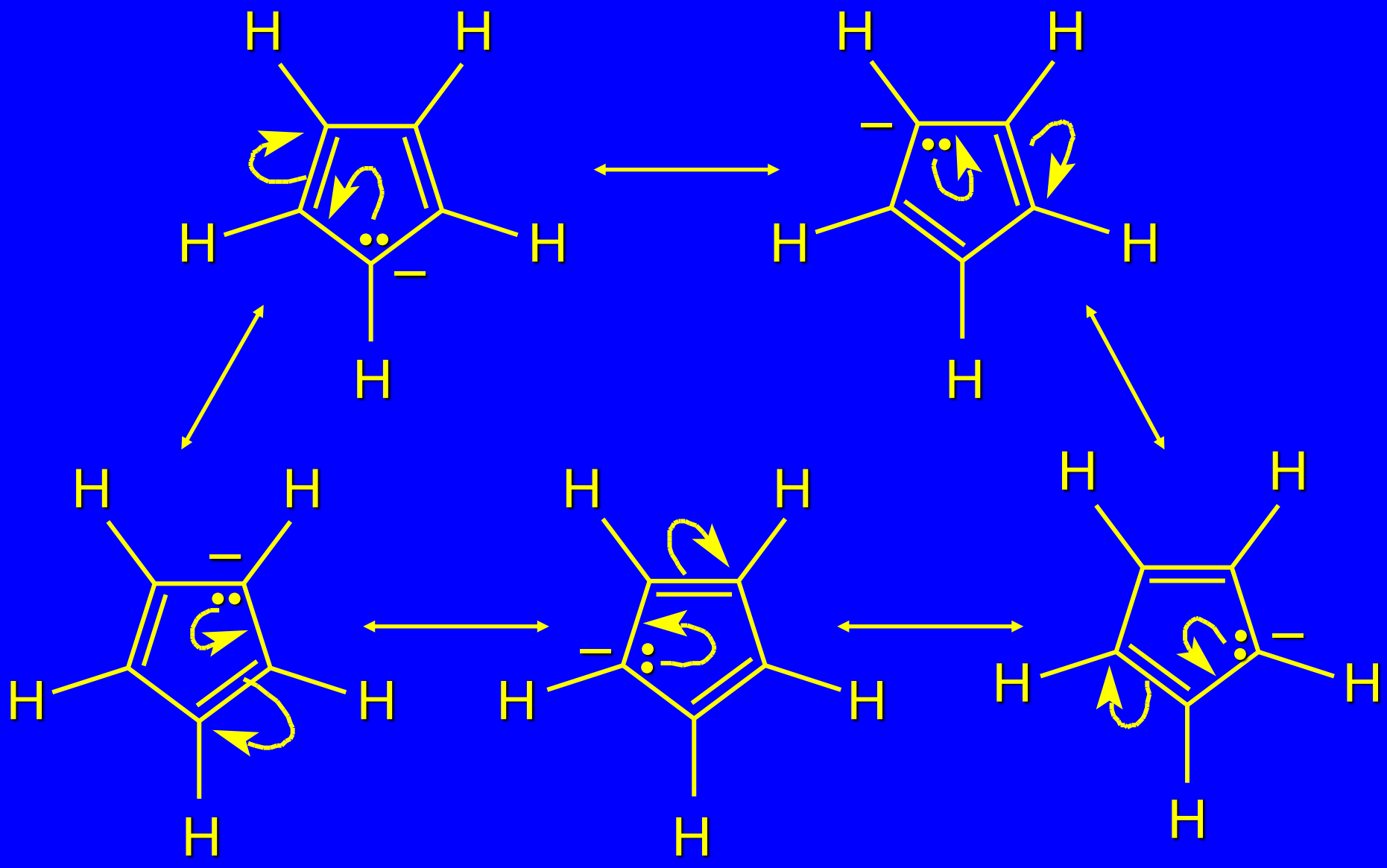
carga negativa dispersa sobre 5 carbonos

ânion estabilizado

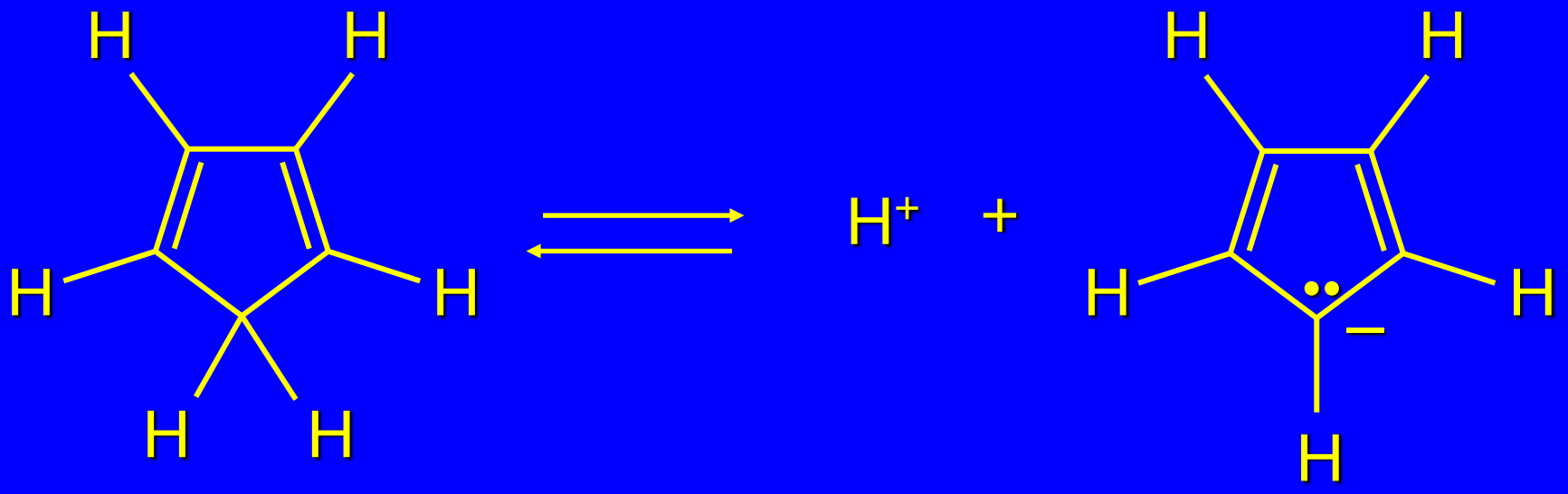
# *Ânion Ciclopentadieneto*



# *Deslocalização Eletrônica no Ânion Ciclopentadieneto*



# *Acidez de Ciclopentadieno*



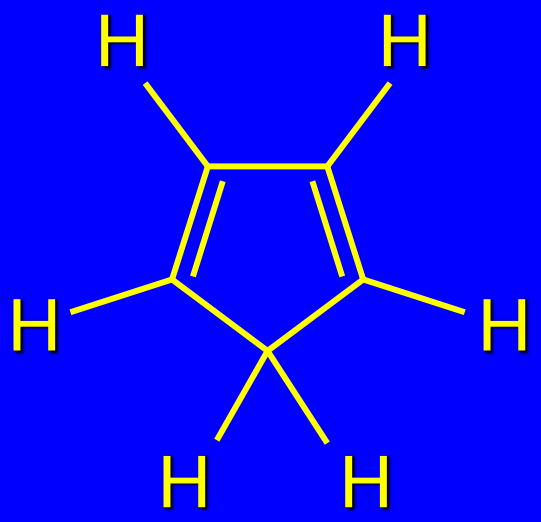

p$K_a$ = 16

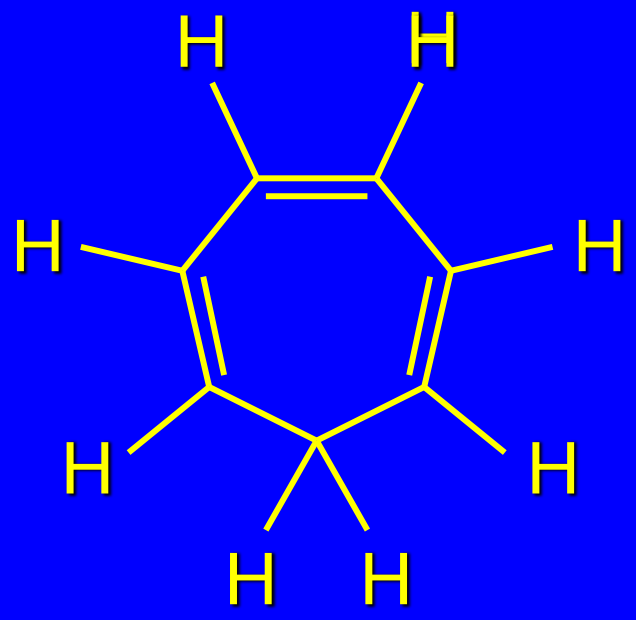
$K_a = 10^{-16}$

Ciclopentadieno é um hidrocarboneto cuja acidez é incomum.

Esse incremento na acidez deve-se à estabilidade do ânion ciclopentadieneto.

# *Comparando a Acidez de Ciclopentadieno e Ciclo-heptatrieno*



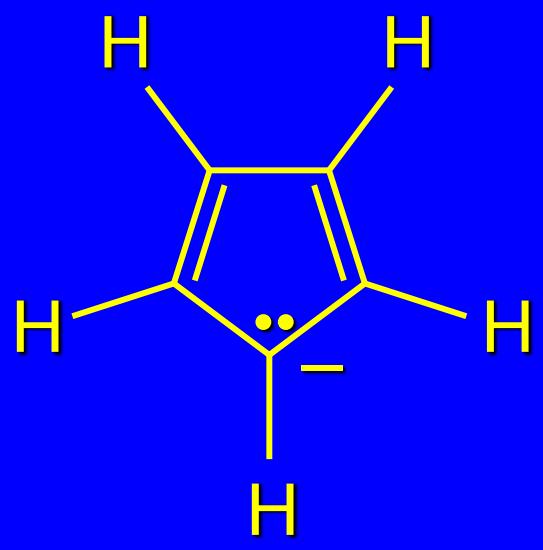

p$K_a$ = 16

$K_a = 10^{-16}$

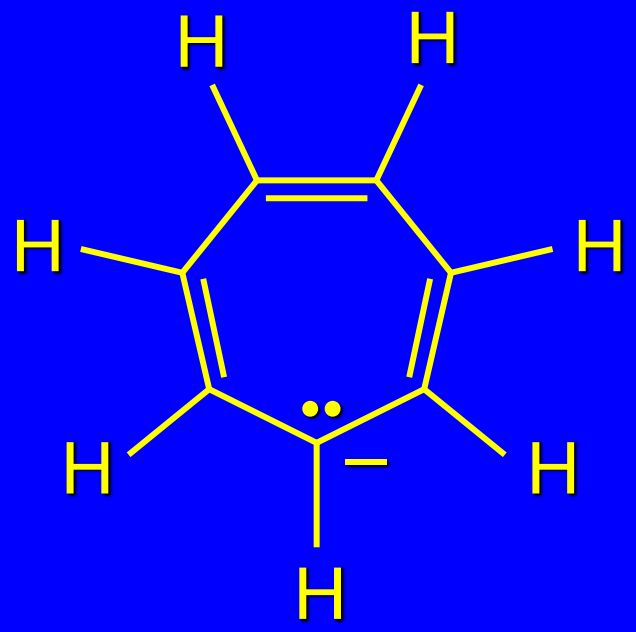
p$K_a$ = 36

$K_a = 10^{-36}$

# *Comparando a Acidez de Ciclopentadieno e Ciclo-heptatrieno*

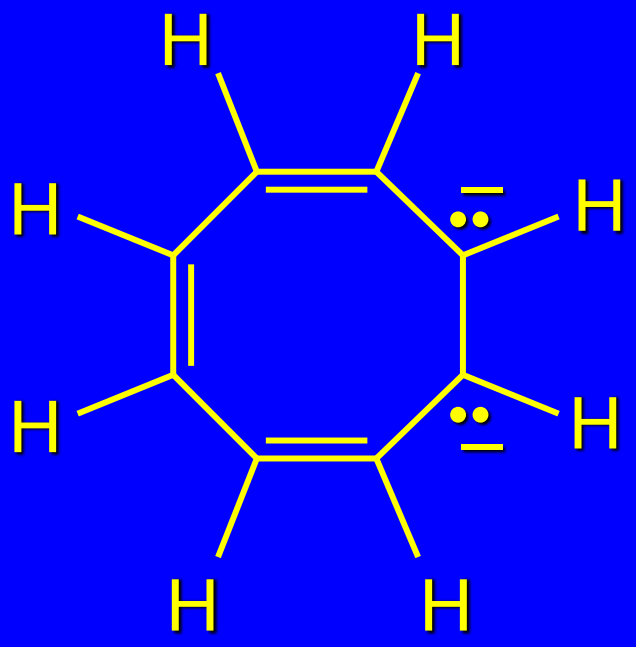



Ânion Aromático
6 elétrons π

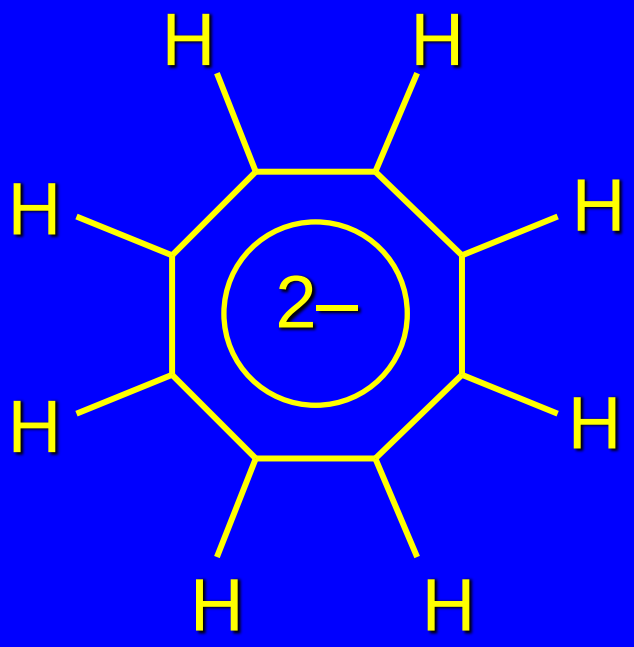



Ânion Antiaromático
8 elétrons π

# *Diânion Ciclooctatetraeneto*




**Também representado como**



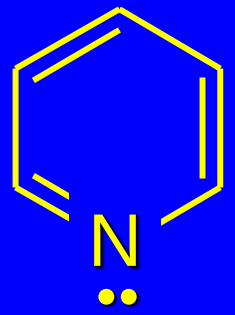

$n = 2$

$4n + 2 = 10$ elétrons $\pi$

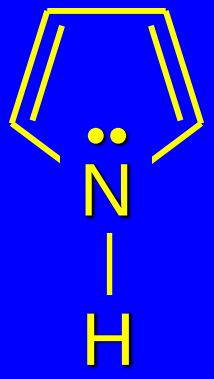
# 11.22

# Heterocyclic Aromatic Compounds

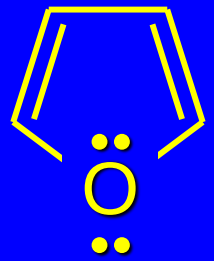
## *Examples*



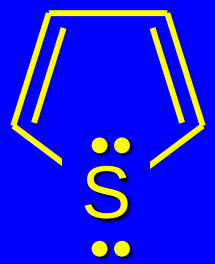

Pyridine




Pyrrole

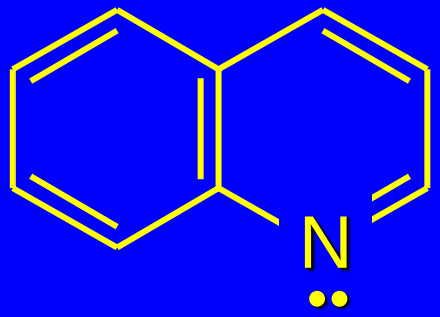



Furan

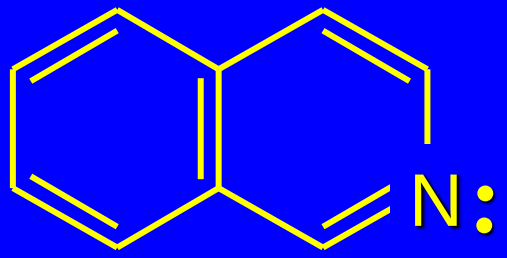



Thiophene

*Examples*



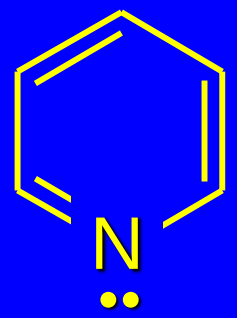

Quinoline




Isoquinoline

# 11.23
# Heterocyclic Aromatic Compounds
# and
# Hückel's Rule

# *Pyridine*

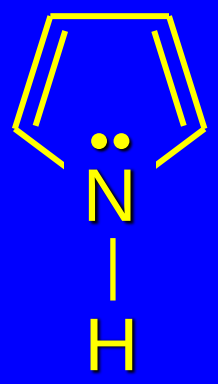



6 $\pi$ electrons in ring

lone pair on nitrogen is in an $sp^2$ hybridized orbital;

not part of $\pi$ system of ring

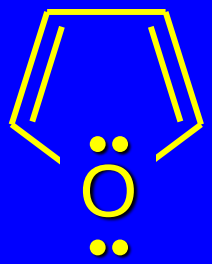
# *Pyrrole*




lone pair on nitrogen must be part of ring $\pi$ system if ring is to have 6 $\pi$ electrons

lone pair must be in a *p* orbital in order to overlap with ring $\pi$ system

# *Furan*

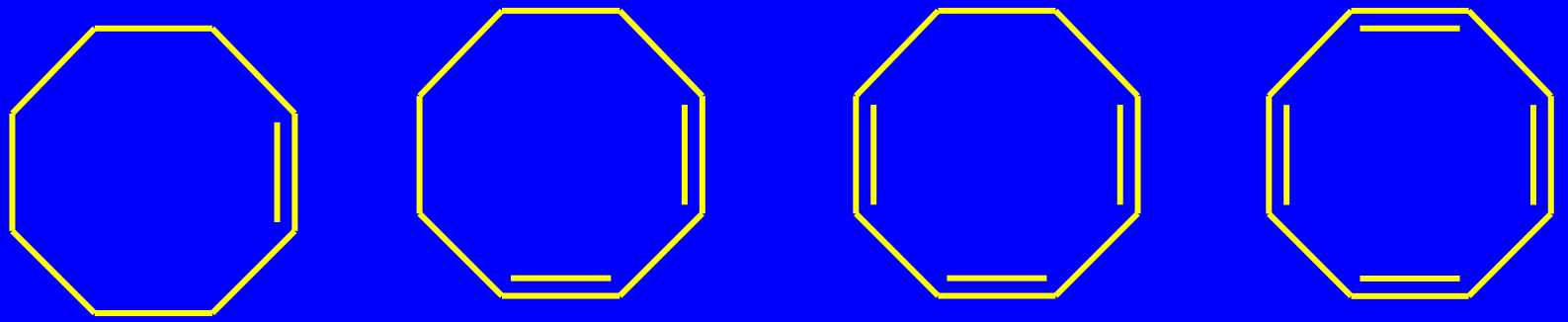


two lone pairs on oxygen

one pair is in a *p* orbital and is part of ring $\pi$ system; other is in an $sp^2$ hybridized orbital and is not part of ring $\pi$ system

# *Heats of Hydrogenation*

to give cyclooctane (kJ/mol)



97 205 303 410

heat of hydrogenation of cyclooctatetraene is more than 4 times heat of hydrogenation of cyclooctene