



Aromaticidade



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Aromático

QUAL A ORIGEM DO TERMO AROMÁTICO ?

História

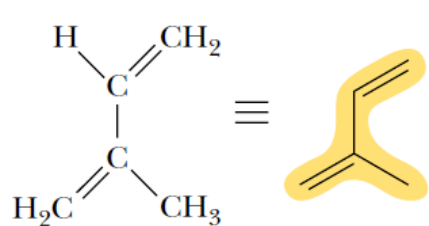
Hofmann foi o primeiro cientista a utilizar o palavra “aromático” como referência a compostos químicos contendo núcleo fenila em uma publicação científica de 1855. Porém, Hofmann também atribuiu o adjetivo aromático a certas substâncias as quais contém odor sendo que muitas dessas são terpenos e não tão somente compostos contendo o anel fenila.

No entanto, terpenos e benzenóides possuem a característica comum de possuir alto índice de insaturações.

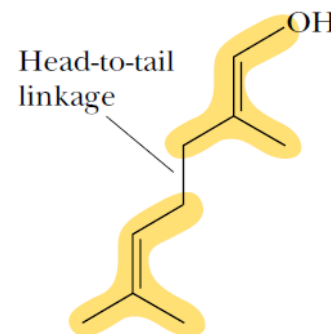
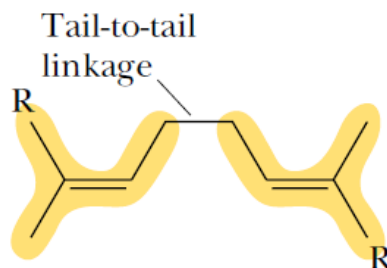
Assim, estaria Hofmann apto a reconhecer a diferença entre terpenos e benzenóides?

Terpenos

Terpenos são compostos os quais tem aroma bastante pronunciado e característico. Porém, não são compostos aromáticos!



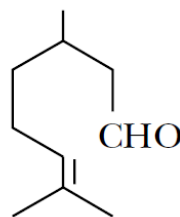
Isoprene



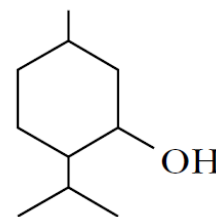
Geraniol



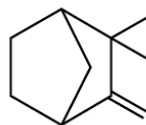
Limonene



Citronellal



Menthol

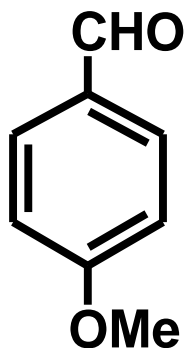


Camphene

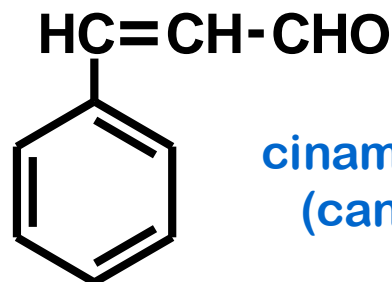


α -Pinene

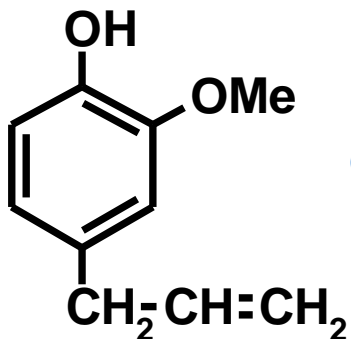
Todavia, muitos compostos de aroma agradável apresentam anéis aromáticos



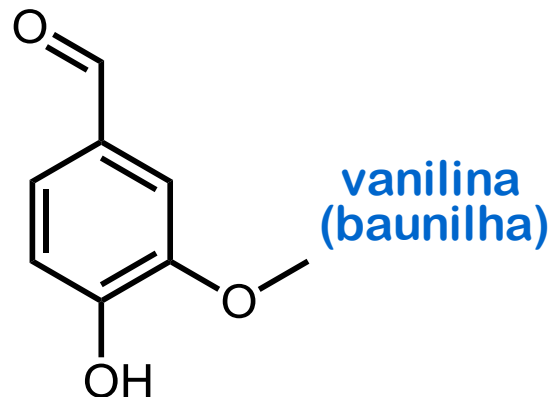
anisaldeído
(aníz)



cinamalaldeído
(canela)



eugenol
(cravo)

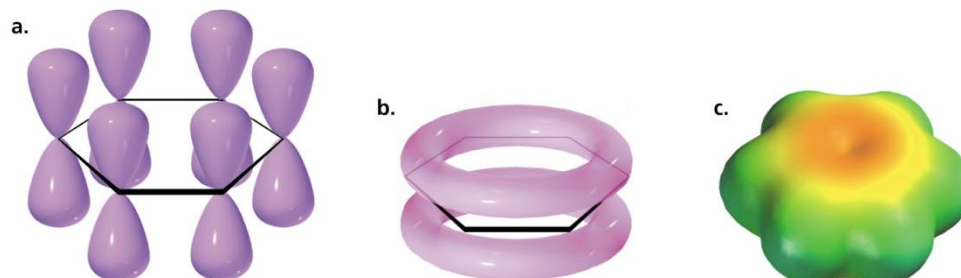
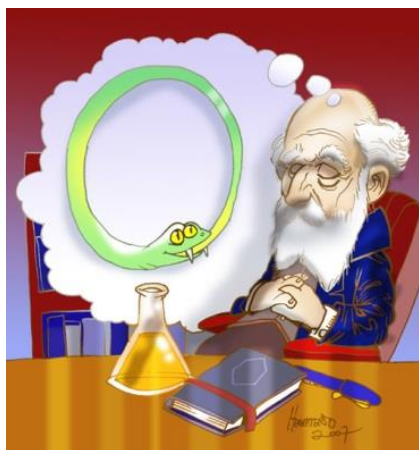


vanilina
(baunilha)

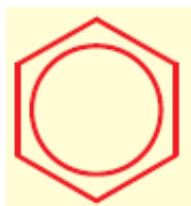
Benzeno

(Kekulé 1965)

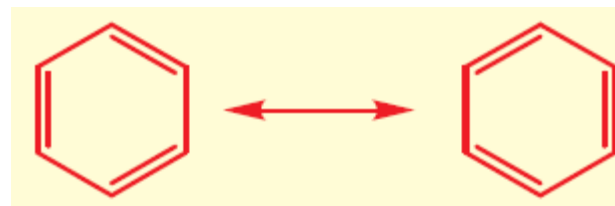
O benzeno é formado por ligações σ e π e os carbonos estão hibridizados na forma sp^2 .



Desenhando a molécula do benzeno



representação dos 6 π



Estrutura de Kekulé – setas curvas

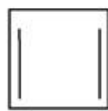
Critério de Aromaticidade

Exemplo, benzeno:

1. Um composto cíclico deve ter elétrons π conjugados acima e abaixo do plano da molécula.
2. O número de pares de elétrons π deve ser ímpar.
- 3 - Sistemas mono-cíclicos, planares e completamente conjugados são **aromáticos** quando possuem **$4n + 2$** elétrons π , sendo n um número natural.
- 4 - Os sistemas análogos com **$4n$** elétrons π são denominados **anti-aromáticos**.
- 5 - Os sistemas aromáticos possuem camada fechada de elétrons, todos em orbitais ligantes.

Anulenos

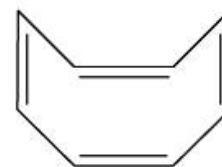
Anulenos são hidrocarbonetos monocíclicos com ligações simples e duplas alternadas.



cyclobutadiene
[4]-annulene

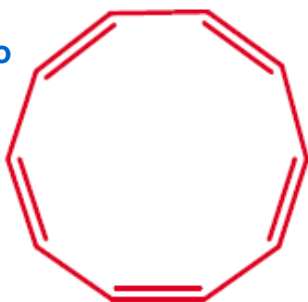


benzene
[6]-annulene



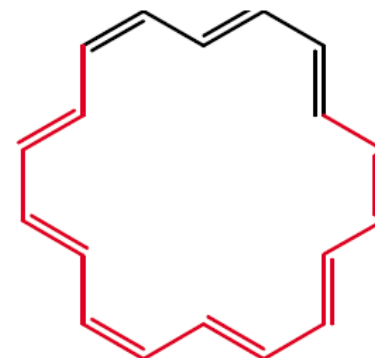
cyclooctatetraene
[8]-annulene

144°



all-cis-[10]annulene

Além de seguir a regra de Hückel, o anuleno precisa ser planar.

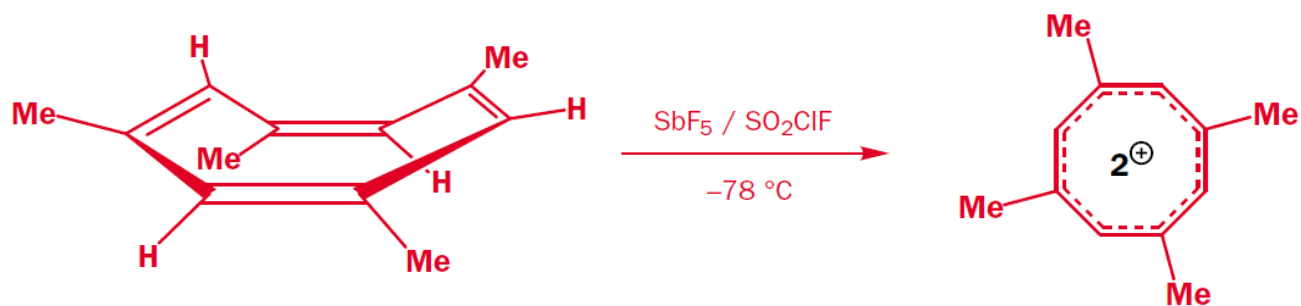


[18]-annulene

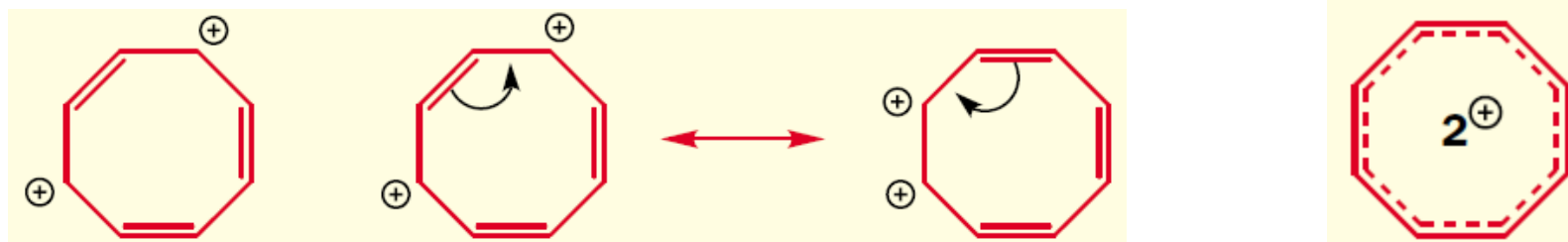
Quais os anulenos aromáticos e quais os anti-aromáticos?

COT: dicátion Aromático

Apesar do ciclooctatetreno (COT) não ser aromático, seu respectivo dicátion é:



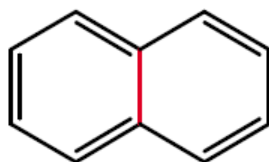
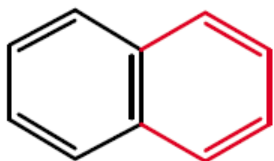
Portanto, o dicátion COT é planar



Aromaticidade

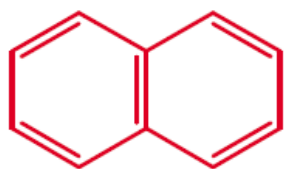
Como desenhar

Como contar os elétrons π ? Utilizando o naftaleno como exemplo:

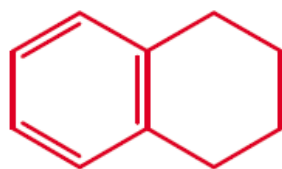


should we count naphthalene as two benzene rings or one large ring with 10 π electrons?

Naftaleno pode ser facilmente reduzido a tetralina o qual ainda possui um anel benzênico.

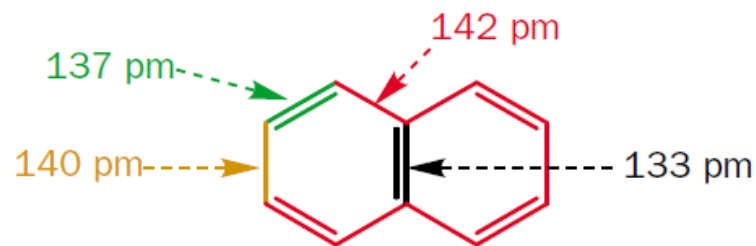


naphthalene

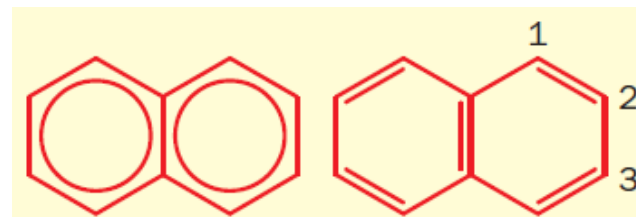


tetralin

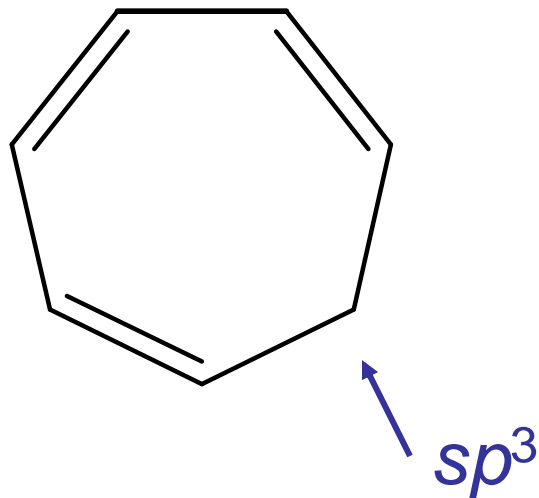
Apesar de aromático, as ligações no naftaleno não são iguais.



Formas de escrever o naftaleno

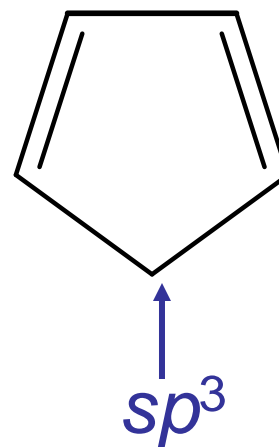


Nuvem Interrompida



cicloheptatriene

nuvem π interrompida:
não aromático



ciclopentadieno

2 pares de elétrons π :
não aromático

Derivados do Ciclopropano

Nem o ciclopropeno nem o ânion ciclopropenílico são aromáticos



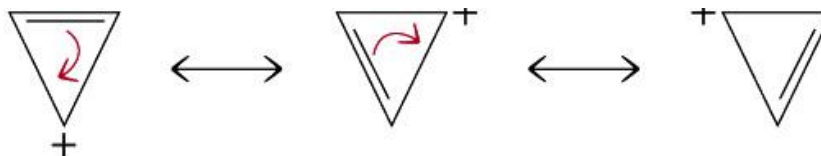
cyclopropene



cyclopropenyl cation

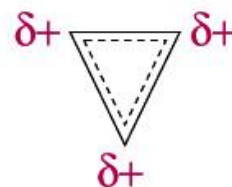


cyclopropenyl anion



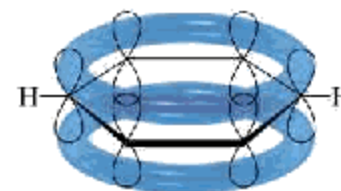
resonance contributors for the cyclopropenyl cation

O cátion ciclopropenílico é aromático

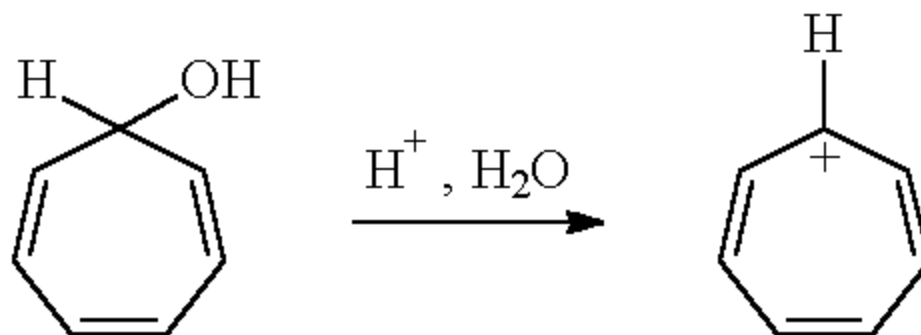


resonance hybrid

Íon Tropílio



- O cátion cicloheptatrienil tem 6 elétrons p e um orbital p vazio.
- Como $6=(4N+2)$ é Aromático
- O íon cíclico é extremamente mais estável do que o análogo de cadeia aberta

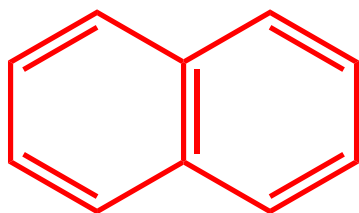


Exercício: Desenhar as estruturas (formas) canônicas do cátion cicloheptatrienila

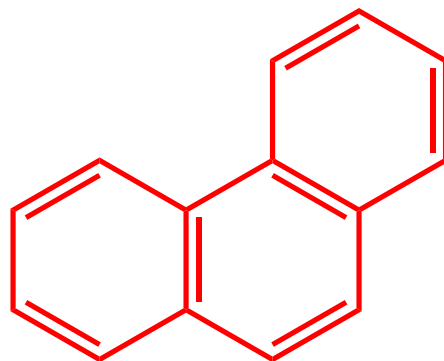
Orgânica. Aromáticos

34

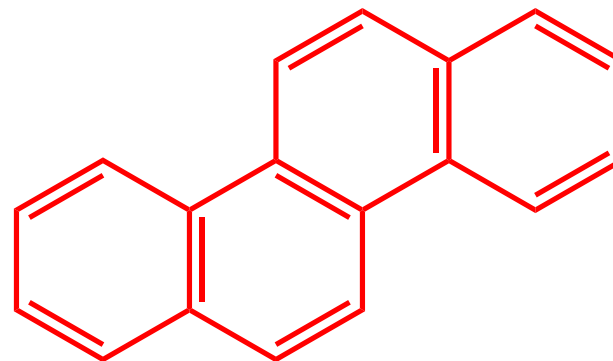
Exercício: Estes anulenos são aromáticos?



naphthalene

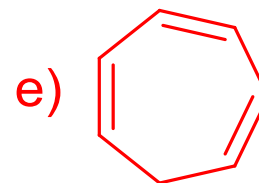
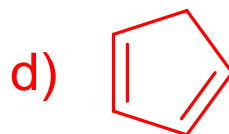
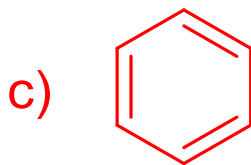


phenanthrene

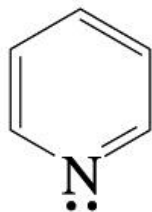


chrysene

Qual(is) composto(s) abaixo é(são) aromático(s) e Por que?



Heterocíclicos Aromáticos



pyridine



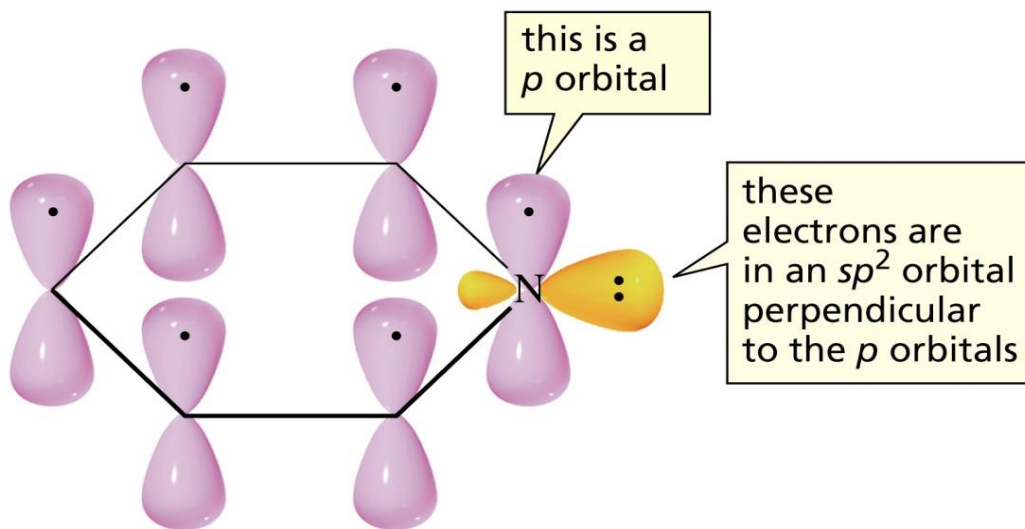
pyrrole



furan



thiophene

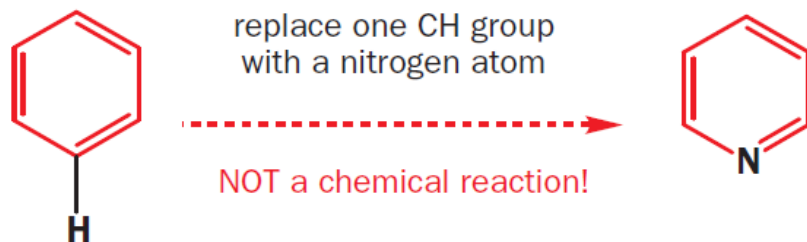


orbital structure of pyridine

Um composto heterocíclico é um composto cíclico que contém um ou mais átomos diferentes de carbono.

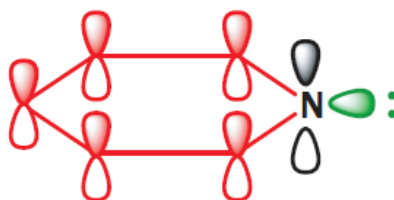
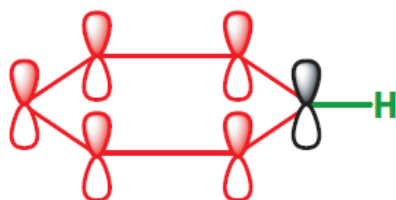
Heterociclos aromáticos

Piridina

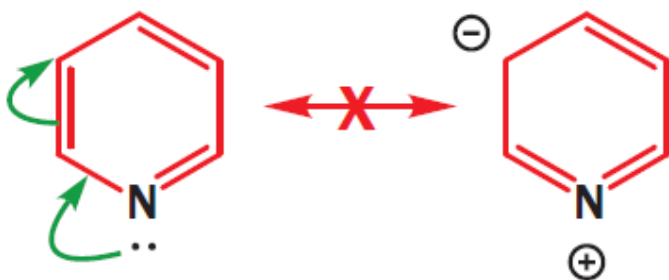


benzene

pyridine



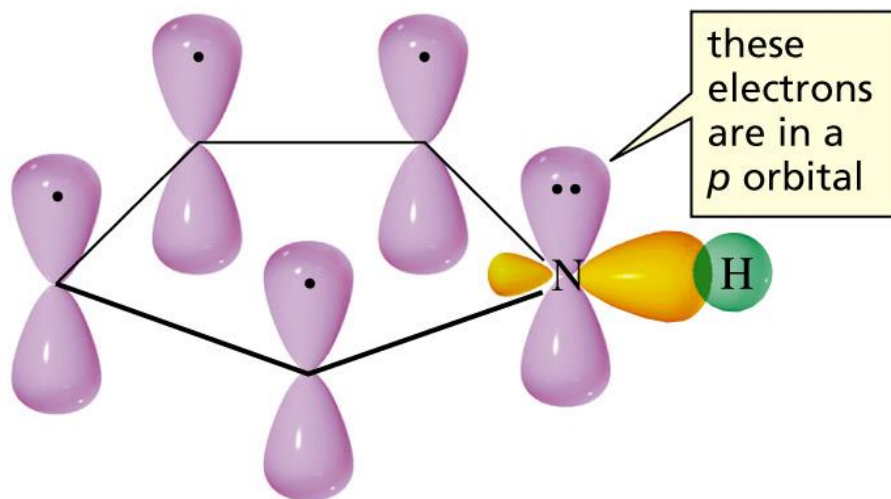
lone pair in sp^2 orbital at right angles to p orbitals in ring: no interaction between orthogonal orbitals



attempts to delocalize lone pair lead to ridiculous results

O par de elétrons sp^2 poderia ser deslocalizado no anel?

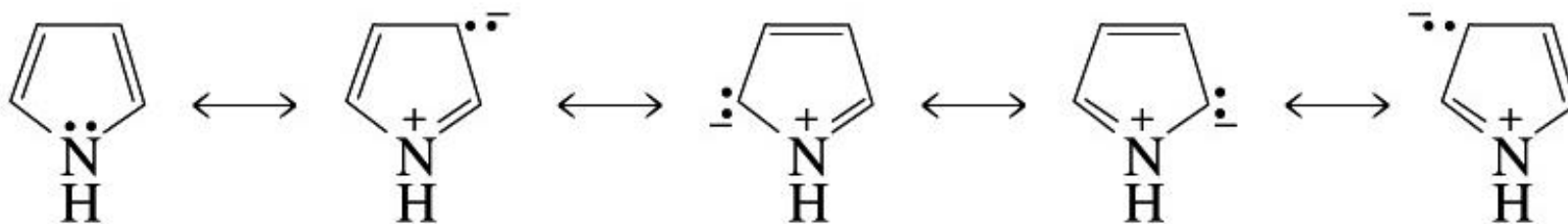
Pirrol



orbital structure of pyrrole

A adição eletrofílica pode ocorrer nas posições 2 e 3 do pirrol.

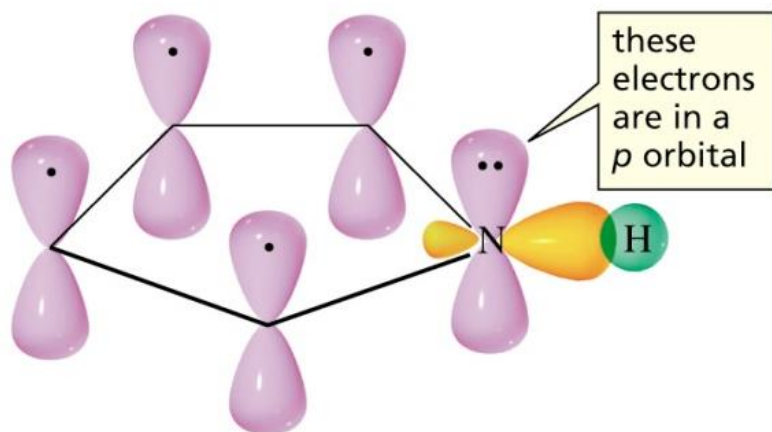
Percebe-se que o pirrol é aromático



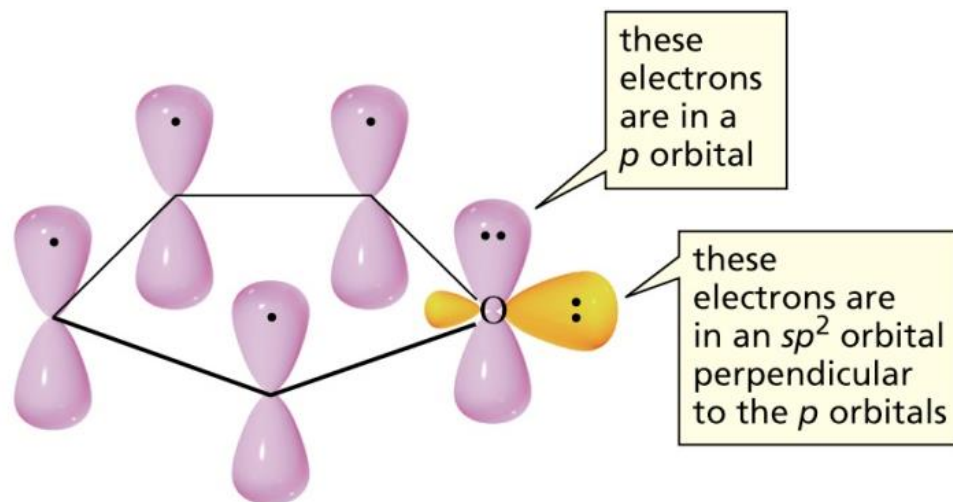
resonance contributors of pyrrole

Furano

De modo semelhante ao pirrol, o furano também pode sofrer substituições nas posições 2' e 3'. Um dos seus pares de elétrons está no orbital p.



orbital structure of pyrrole



orbital structure of furan

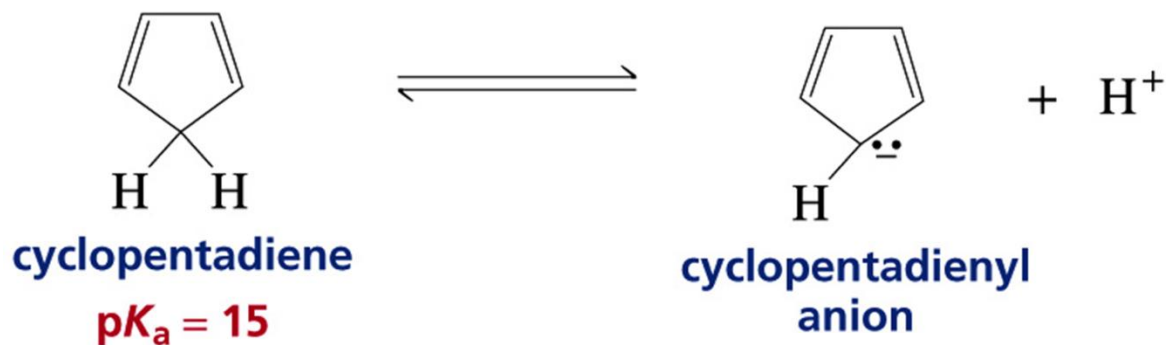
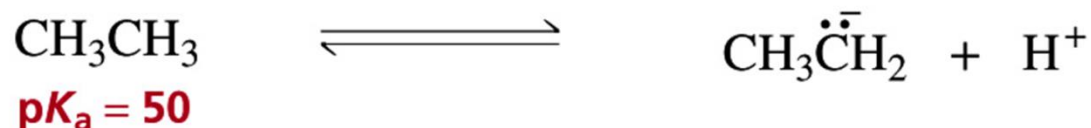


resonance contributors of furan

Exercício: O que você esperaria em termos de reatividade: furano, pirrol e tiofeno.

Efeito da Aromaticidade sobre o pK_a

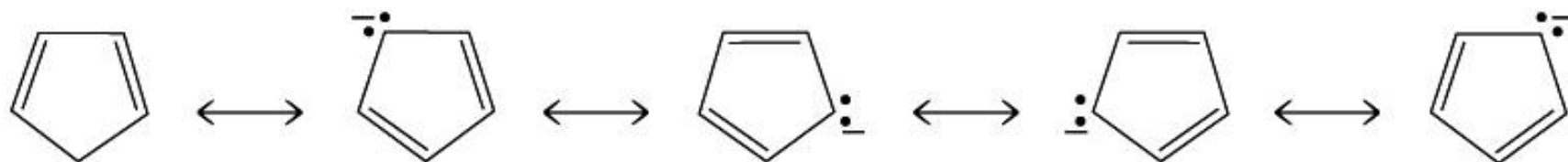
Como explica a diferença de pK_a entre esses hidrocarbonetos?



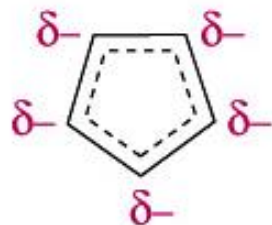
ânion ciclopentadienila:
6 elétrons π : aromático

Ânion ciclopentadienila

ânion ciclopentadienila: 6 elétrons π : aromático



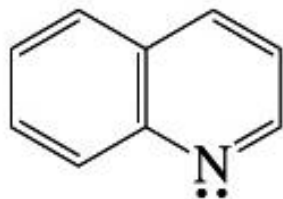
resonance contributors



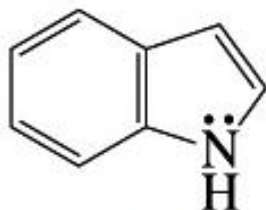
resonance hybrid

Exercício: prever os valores relativos de pK_a do ciclopentadieno e do cicloheptatrieno

Outros Compostos Heterocíclicos Aromáticos



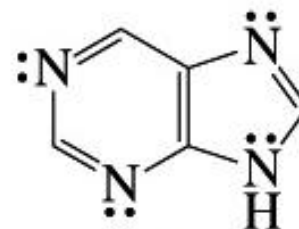
quinoline



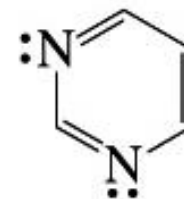
indole



imidazole



purine



pyrimidine