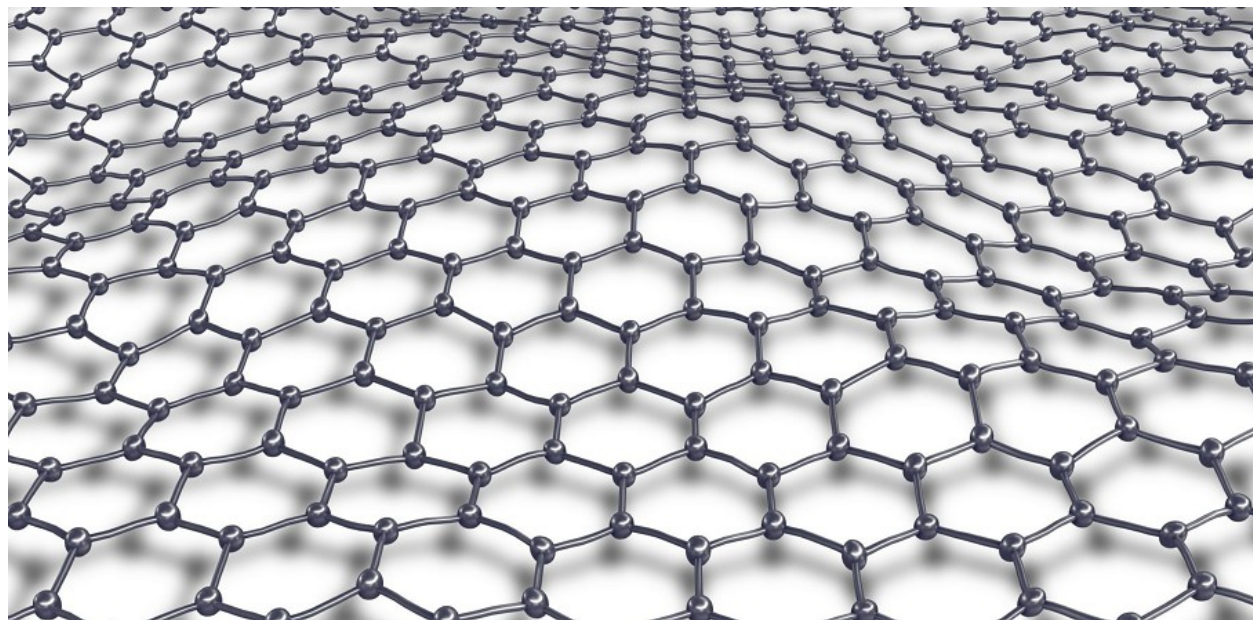


15

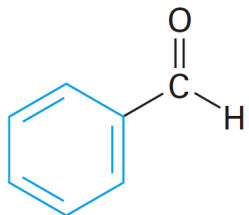
苯和芳香性



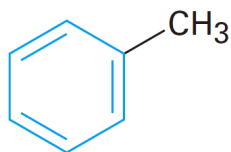
- 最早，芳香族一词用来描述诸如苯甲醛（樱桃，桃子和杏仁），甲苯（甲苯香脂）和苯（煤馏出物）之类的芳香物质。后来发现，这类物质的化学性质与大多数其他有机化合物不同。



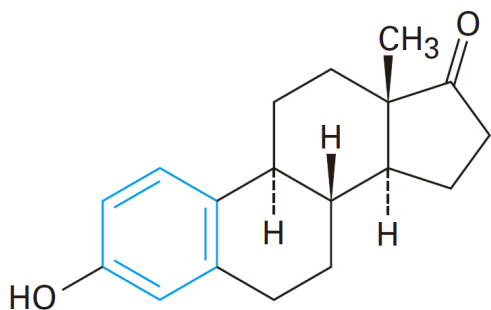
Benzene



Benzaldehyde

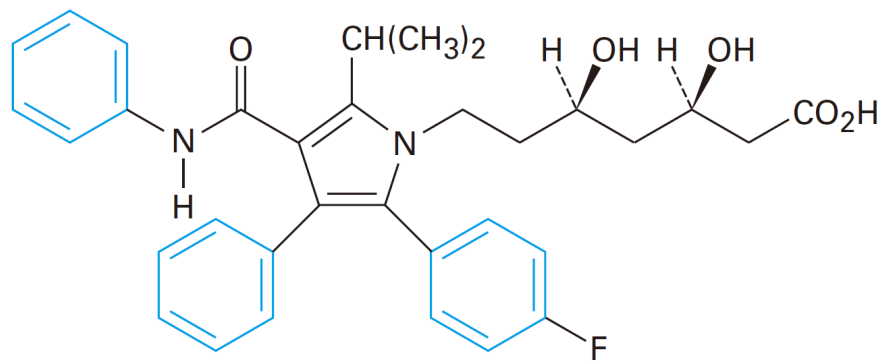


Toluene



Estrone

雌酮

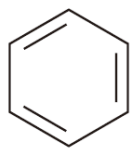


Atorvastatin
(Lipitor)

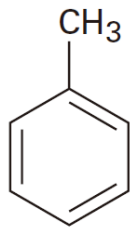
阿伐他汀

15.1 命名和来源

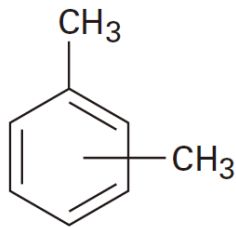
- 简单的芳烃是从煤和石油中提炼出来的



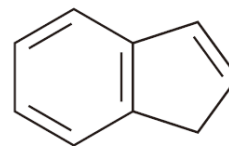
Benzene
(bp 80 °C)



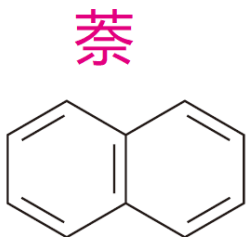
Toluene
(bp 111 °C)



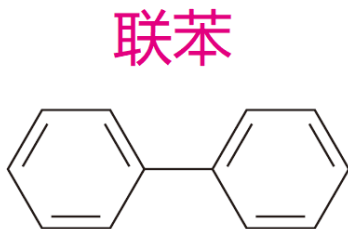
Xylene
(bp: ortho, 144 °C;
meta, 139 °C; para, 138 °C)



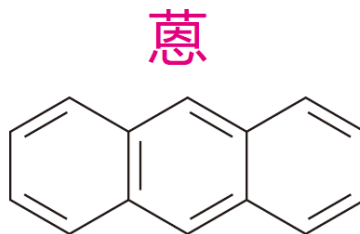
Indene 茚
(bp 182 °C)



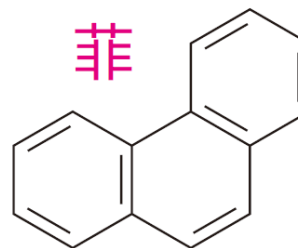
Naphthalene
(mp 80 °C)



Biphenyl
(mp 71 °C)



Anthracene
(mp 216 °C)



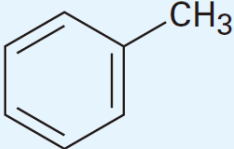
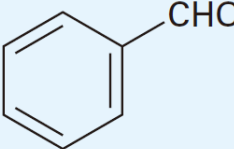
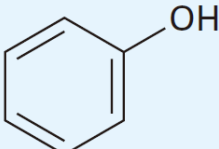
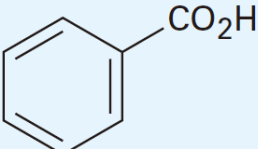
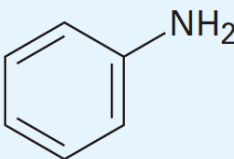
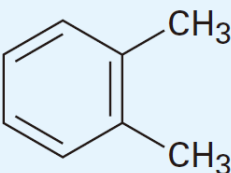
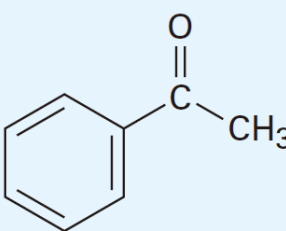
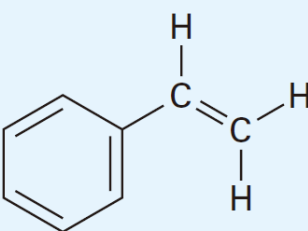
Phenanthrene
(mp 101 °C)

Figure 15.1 Some aromatic hydrocarbons found in coal tar.

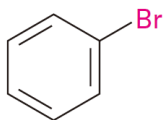
15.1 命名和来源

- 很多简单的芳香化合物有俗名

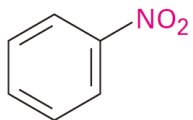
Table 15.1 Common Names of Some Aromatic Compounds

Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		ortho-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

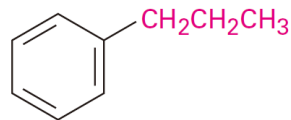
15.1 命名和来源



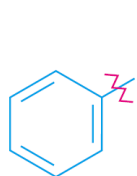
Bromobenzene



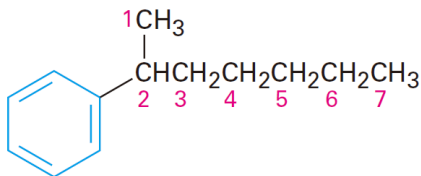
Nitrobenzene



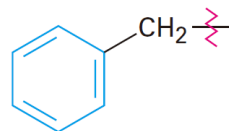
Propylbenzene



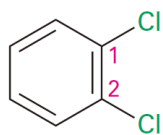
A phenyl group



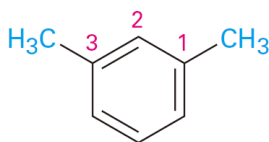
2-Phenylheptane



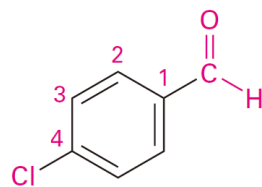
A benzyl group



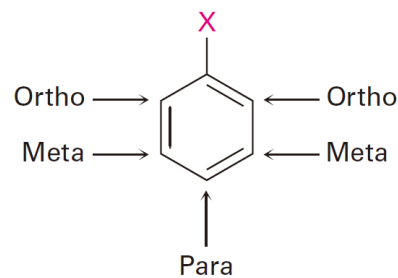
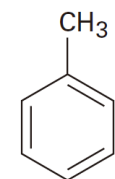
ortho-Dichlorobenzene
1,2 disubstituted



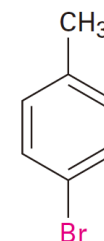
meta-Dimethylbenzene
(*meta*-xylene)
1,3 disubstituted



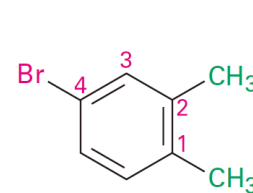
para-Chlorobenzaldehyde
1,4 disubstituted



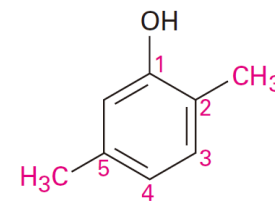
Toluene



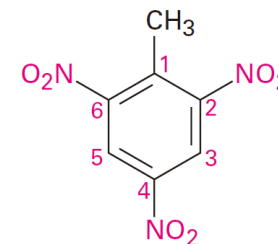
p-Bromotoluene



4-Bromo-1,2-dimethylbenzene

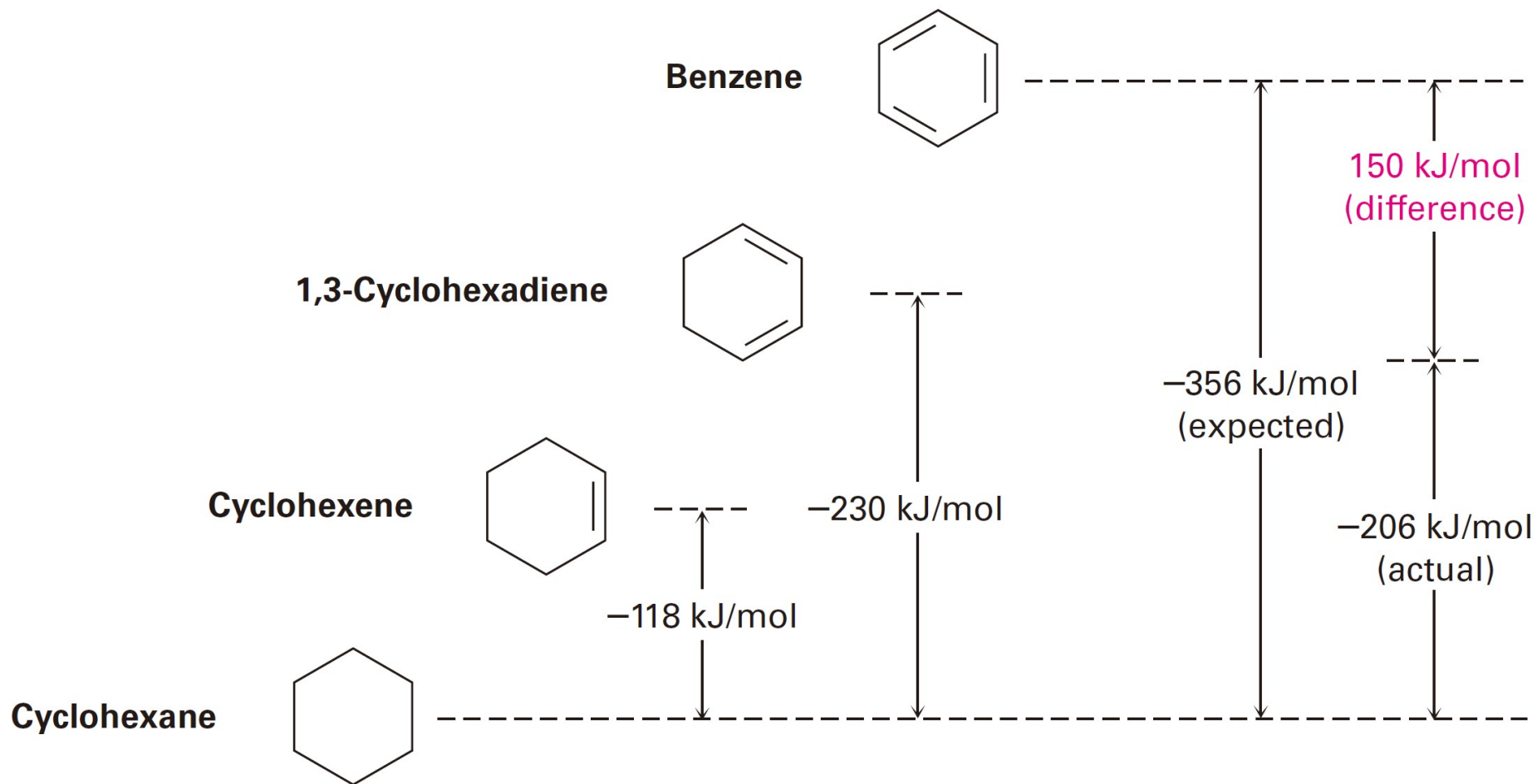


2,5-Dimethylphenol



2,4,6-Trinitrotoluene (TNT)

15.2 结构和稳定性



15.2 结构和稳定性

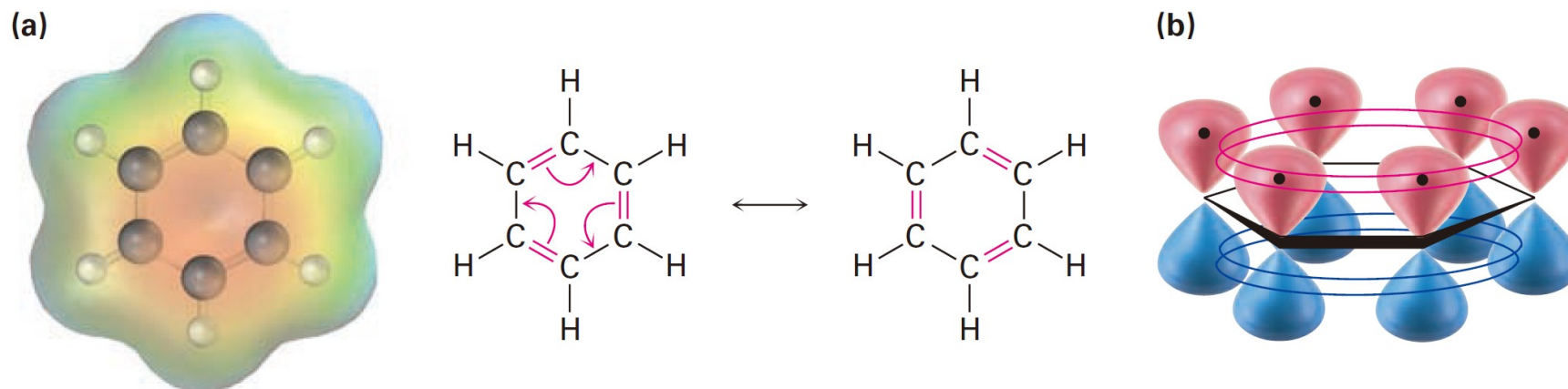
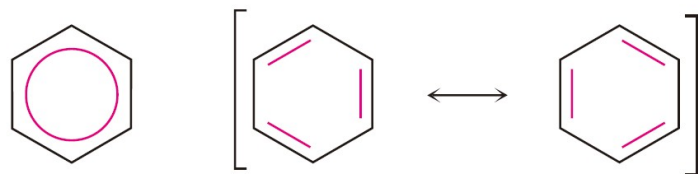


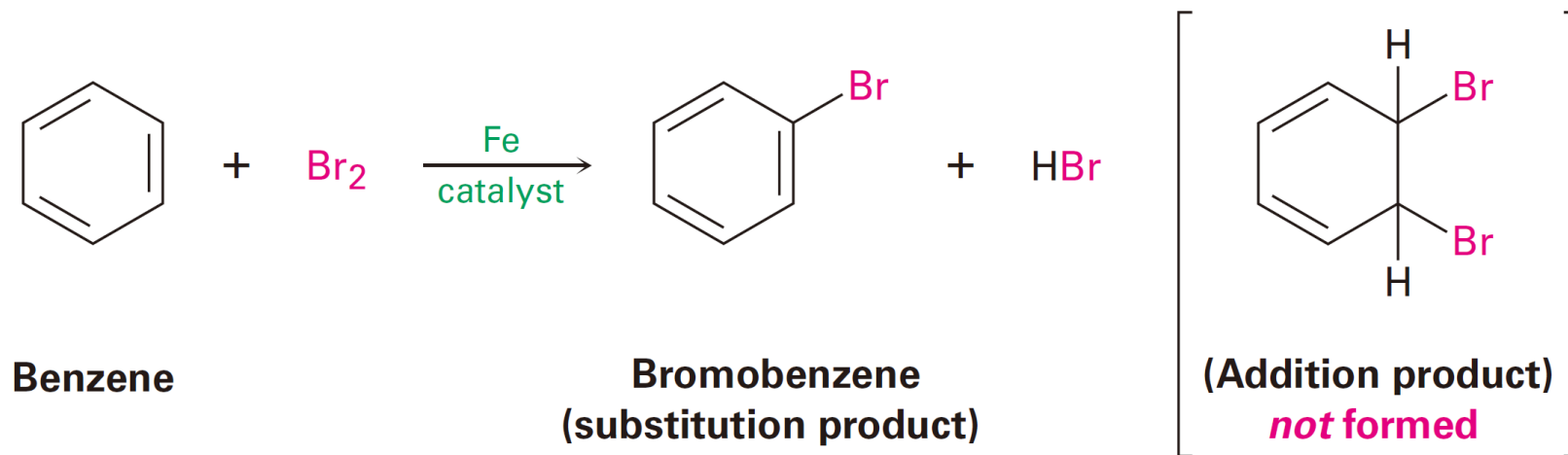
Figure 15.3 (a) An electrostatic potential map of benzene and (b) an orbital picture. Each of the six carbon atoms has a p orbital that can overlap equally well with neighboring p orbitals on both sides. As a result, all C—C bonds are equivalent and benzene must be represented as a hybrid of two resonance forms.



Alternative representations of benzene. The "circle" representation must be used carefully since it doesn't indicate the number of π electrons in the ring.

15.2 结构和稳定性

- 因为苯的实际结构并不是三个独立共轭的双键，因此化学性质上和烯烃差别很大，容易发生取代反应（没有破坏苯的结构），不容易发生加成反应（破坏苯的结构）



15.3 芳香性和休克尔规则

- 关于苯的结构和性质的描述

- Benzene is cyclic and conjugated.
- Benzene is unusually stable, having a heat of hydrogenation 150 kJ/mol less negative than we might expect for a conjugated cyclic triene.
- Benzene is planar and has the shape of a regular hexagon. All bond angles are 120° , all carbon atoms are sp^2 -hybridized, and all carbon-carbon bond lengths are 139 pm.
- Benzene undergoes substitution reactions that retain the cyclic conjugation rather than electrophilic addition reactions that would destroy the conjugation.
- Benzene can be described as a resonance hybrid whose structure is intermediate between two line-bond structures.



15.3 芳香性和休克尔规则

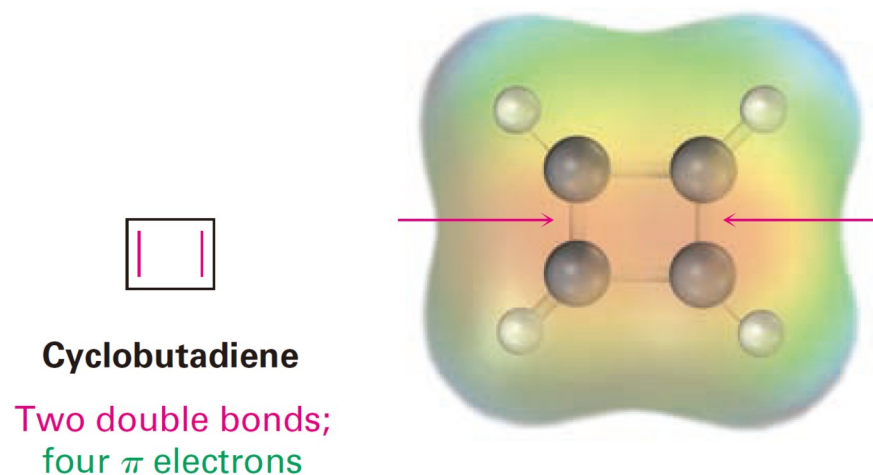
- 休克尔规则是有机化学的经验规则。它是指当闭合环状平面型的共轭多烯（轮烯） π 电子数为 $4n+2$ 时，具有芳香性。
- 反芳香性是指具有 $4n$ 个 π 电子而又具近似平面结构的环状化合物，如环丁二烯。
- 非芳香性是指环状多烯的稳定性与开链多烯相近。环辛四烯具有典型的非芳香性，它有 $4n$ 个 π 电子，但不是反芳香性的。因为其中的碳原子不在同一平面内， π 电子不能离域。



15.3 芳香性和休克尔规则

- 环丁二烯

- Cyclobutadiene has four π electrons and is antiaromatic. The π electrons are localized in two double bonds rather than delocalized around the ring, as indicated by an electrostatic potential map.

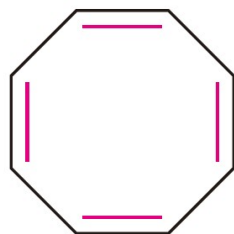


Cyclobutadiene is highly reactive and shows none of the properties associated with aromaticity. In fact, it was not even prepared until 1965, when Rowland Pettit of the University of Texas was able to make it at low temperature. Even at $-78\text{ }^{\circ}\text{C}$, however, cyclobutadiene is so reactive that it dimerizes by a Diels–Alder reaction. One molecule behaves as a diene and the other as a dienophile.

15.3 芳香性和休克尔规则

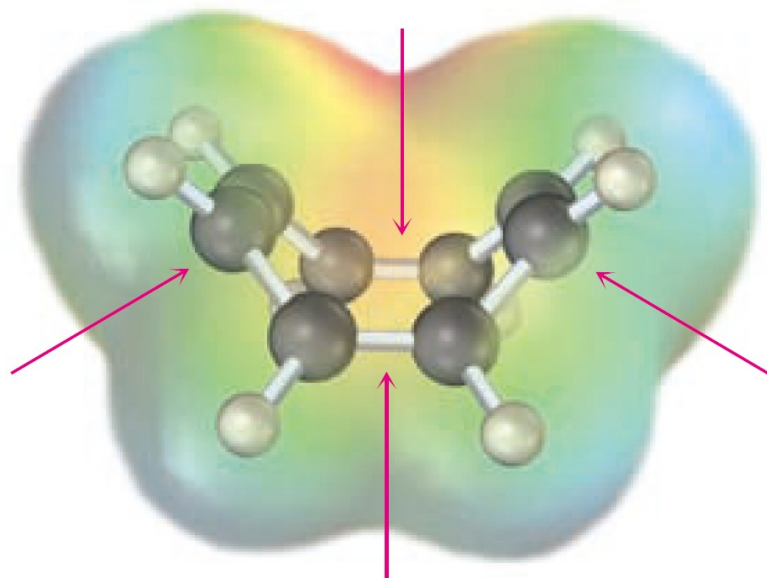
- 环辛四烯

- Cyclooctatetraene** has eight π electrons and is not aromatic. The π electrons are localized into four double bonds rather than delocalized around the ring, and the molecule is tub-shaped rather than planar.



Cyclooctatetraene

Four double bonds;
eight π electrons

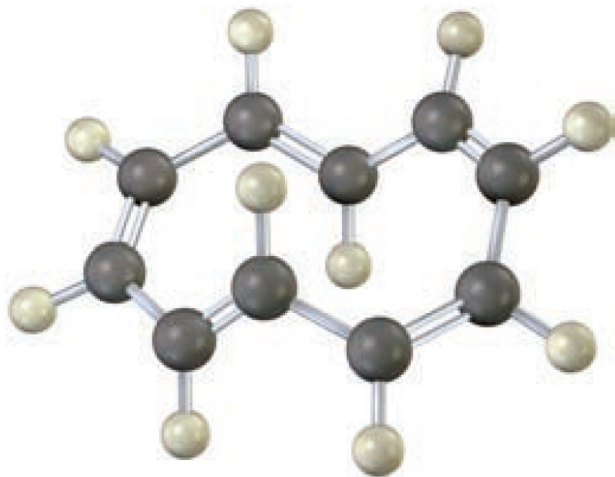


15.3 芳香性和休克尔规则

- 课堂练习

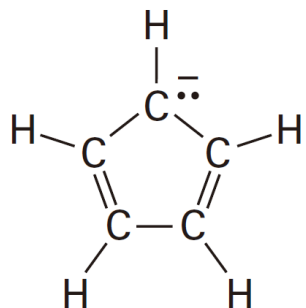
Problem 15.5

To be aromatic, a molecule must have $4n + 2 \pi$ electrons and must have cyclic conjugation. 1,3,5,7,9-Cyclodecapentaene fulfills one of these criteria but not the other and has resisted all attempts at synthesis. Explain.

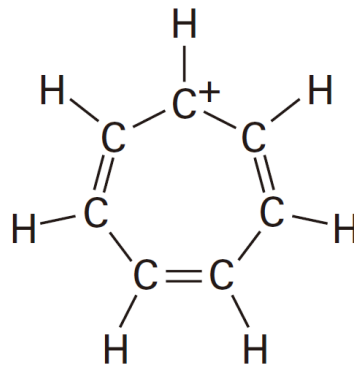


15.4 芳香性的离子化合物

According to the Hückel criteria for aromaticity, a molecule must be cyclic, conjugated (nearly planar with a p orbital on each atom), and have $4n + 2 \pi$ electrons. Nothing in this definition says that the number of π electrons must be the same as the number of atoms in the ring or that the substance must be neutral. In fact, the numbers can be different and the substance can be an ion. Thus, both the cyclopentadienyl anion and the cycloheptatrienyl cation are aromatic even though both are ions and neither contains a six-membered ring.



Cyclopentadienyl anion



Cycloheptatrienyl cation

Six π electrons; aromatic ions

15.4 芳香性的离子化合物

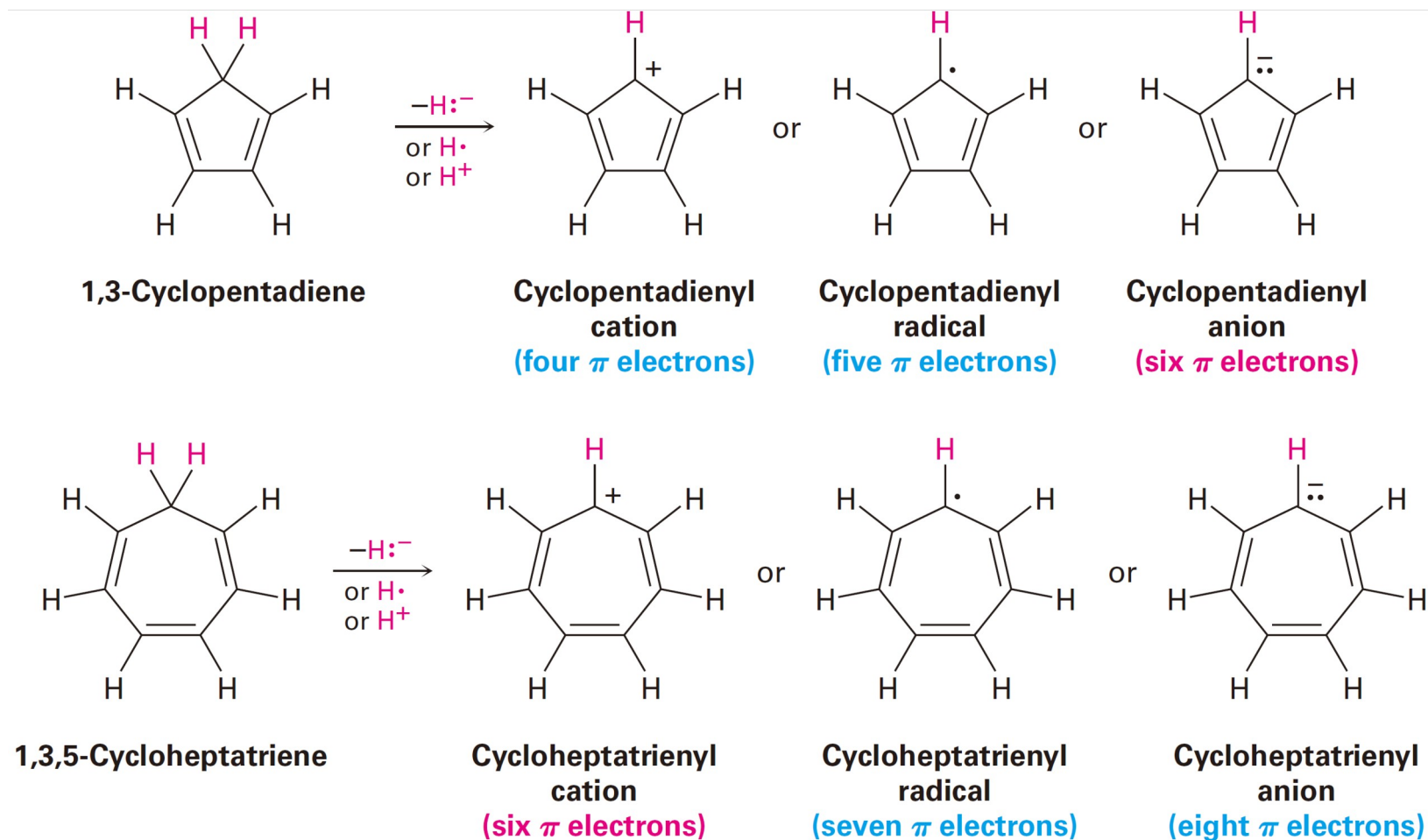
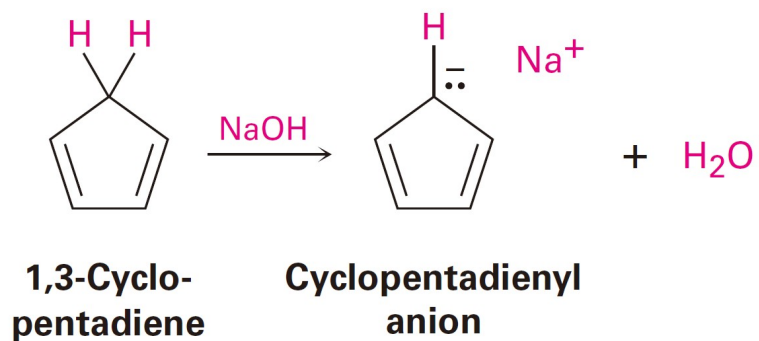
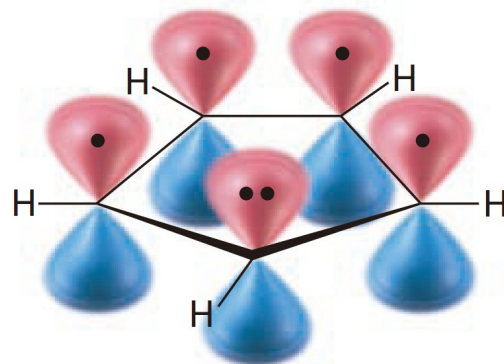


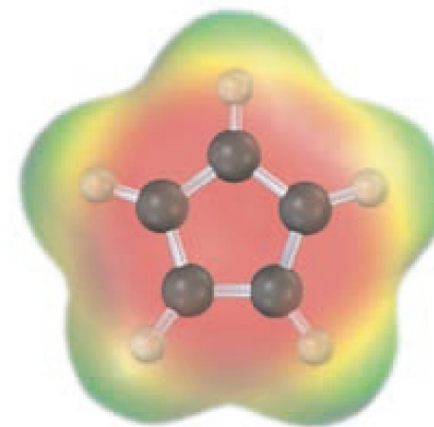
Figure 15.6 The aromatic six- π -electron cyclopentadienyl anion can be formed by removing a hydrogen ion (H^+) from the CH_2 group of 1,3-cyclopentadiene. Similarly, the aromatic six- π -electron cycloheptatrienyl cation can be generated by removing a hydride ion (H^-) from the CH_2 group of 1,3,5-cycloheptatriene.

15.4 芳香性的离子化合物

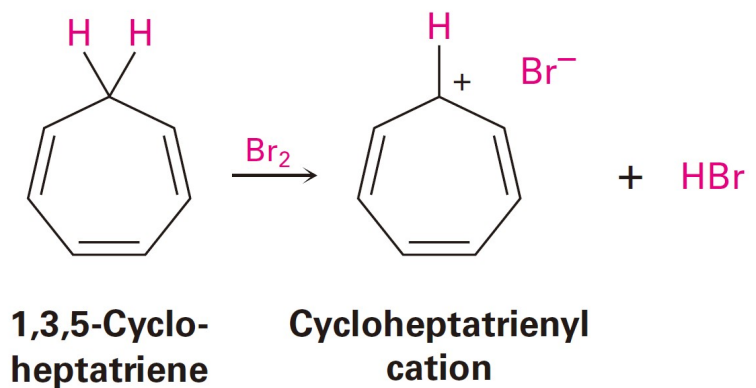
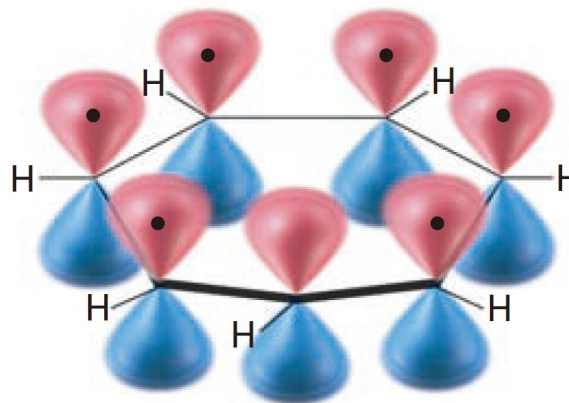
(a)



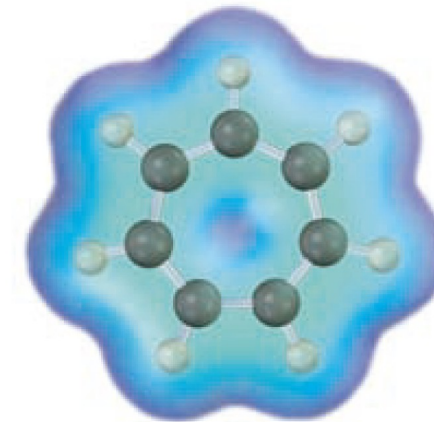
Aromatic cyclopentadienyl anion
with six π electrons



(b)



Cycloheptatrienyl cation
six π electrons



15.4 芳香性的离子化合物

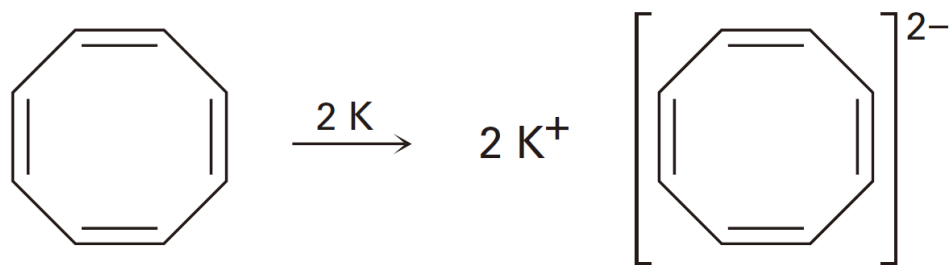
- 课堂练习

Problem 15.6

Draw the five resonance structures of the cyclopentadienyl anion. Are all carbon-carbon bonds equivalent? How many absorption lines would you expect to see in the ^1H NMR and ^{13}C NMR spectra of the anion?

Problem 15.7

Cyclooctatetraene readily reacts with potassium metal to form the stable cyclooctatetraene dianion, $\text{C}_8\text{H}_8^{2-}$. Why do you suppose this reaction occurs so easily? What geometry do you expect for the cyclooctatetraene dianion?



15.5 芳香杂环化合物：吡啶和吡咯

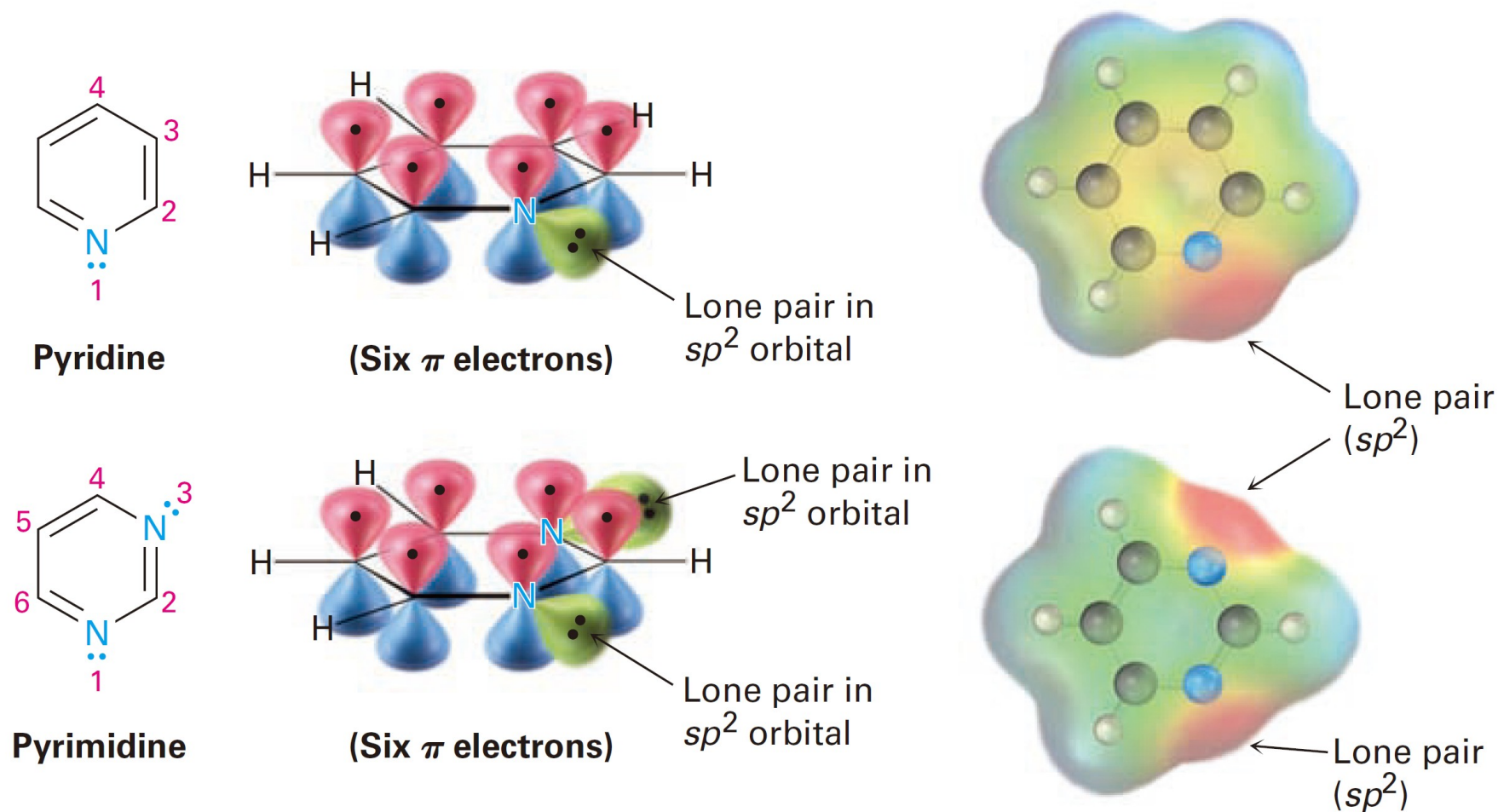
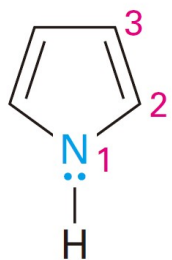
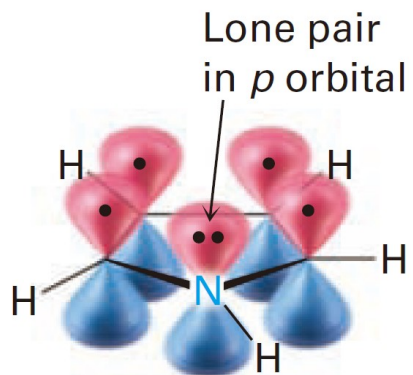


Figure 15.8 Pyridine and pyrimidine are nitrogen-containing aromatic heterocycles with π electron arrangements like that of benzene. Both have a lone pair of electrons on nitrogen in an sp^2 orbital in the plane of the ring.

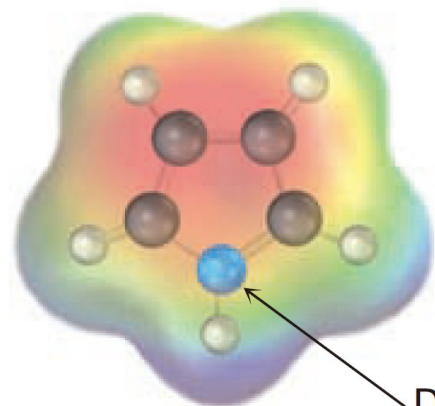
15.5 芳香杂环化合物：吡啶和吡咯



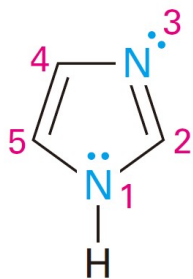
Pyrrole



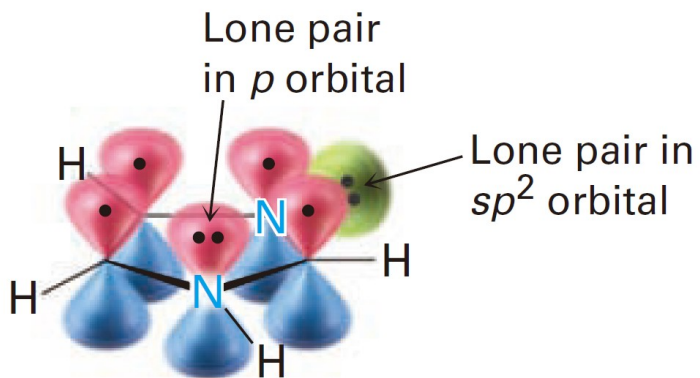
(Six π electrons)



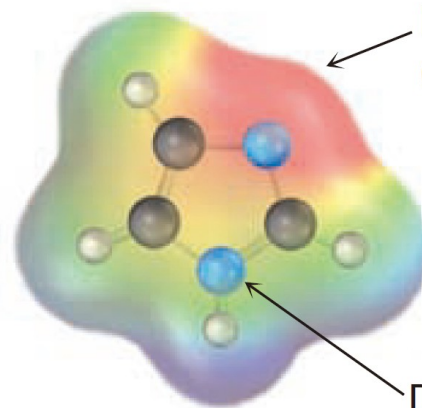
Delocalized lone pair (p)



Imidazole



(Six π electrons)

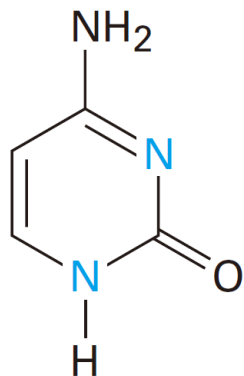


Lone pair (sp^2)

Delocalized lone pair (p)

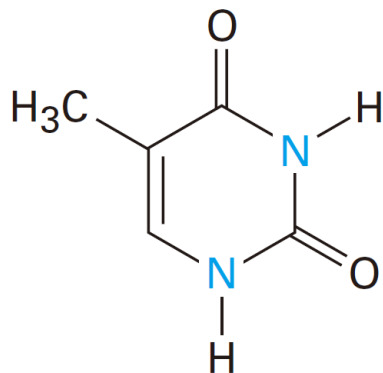
15.5 芳香杂环化合物：吡啶和吡咯

Pyrimidine and imidazole rings are particularly important in biological chemistry. Pyrimidine, for instance, is the parent ring system in cytosine, thymine, and uracil, three of the five heterocyclic amine bases found in nucleic acids. An aromatic imidazole ring is present in histidine, one of the twenty amino acids found in proteins.



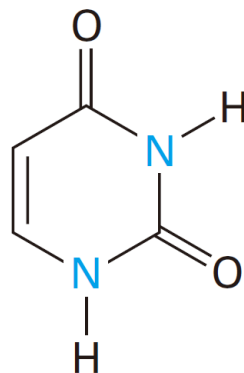
Cytosine
(in DNA and RNA)

胞嘧啶



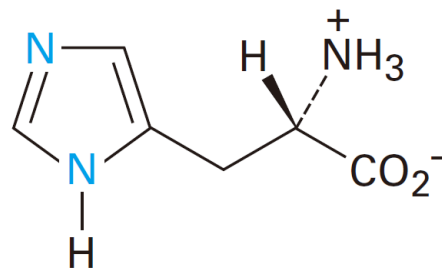
Thymine
(in DNA)

胸腺嘧啶



Uracil
(in RNA)

尿嘧啶



Histidine
(an amino acid)

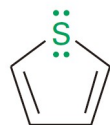
组胺酸

15.5 芳香杂环化合物：吡啶和吡咯

Worked Example 15.1

Accounting for the Aromaticity of a Heterocycle

Thiophene, a sulfur-containing heterocycle, undergoes typical aromatic substitution reactions rather than addition reactions. Why is thiophene aromatic?



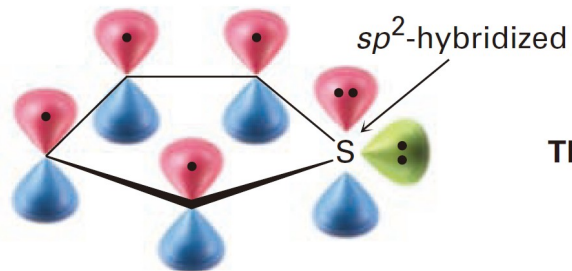
Thiophene

Strategy

Recall the requirements for aromaticity—a planar, cyclic, conjugated molecule with $4n + 2 \pi$ electrons—and see how these requirements apply to thiophene.

Solution

Thiophene is the sulfur analog of pyrrole. The sulfur atom is sp^2 -hybridized and has a lone pair of electrons in a p orbital perpendicular to the plane of the ring. Sulfur also has a second lone pair of electrons in the ring plane.

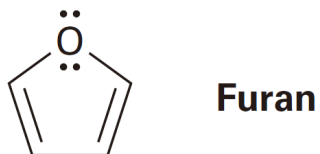


Thiophene

15.5 芳香杂环化合物：吡啶和吡咯

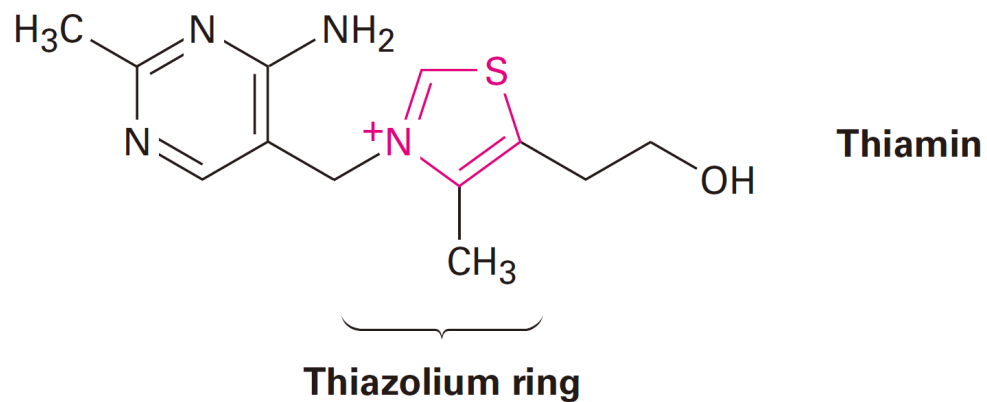
Problem 15.9

Draw an orbital picture of furan to show how the molecule is aromatic.



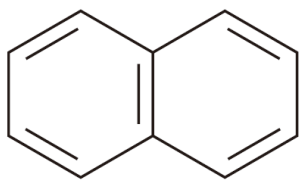
Problem 15.10

Thiamin, or vitamin B₁, contains a positively charged five-membered nitrogen–sulfur heterocycle called a *thiazolium* ring. Explain why the thiazolium ring is aromatic.



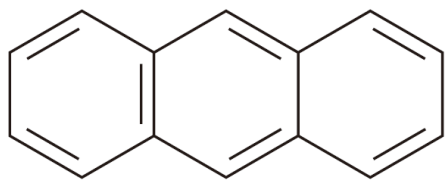
15.6 多环芳香化合物

萘



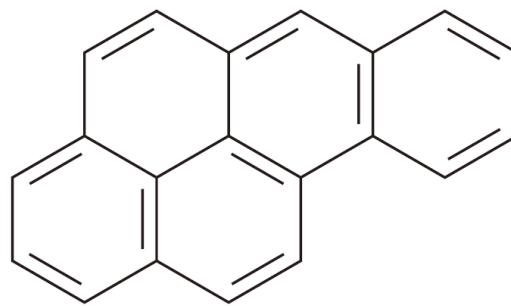
Naphthalene

蒽

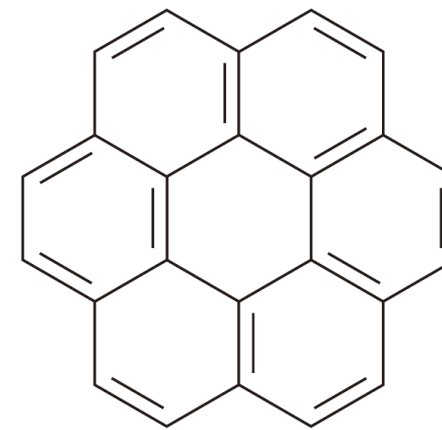


Anthracene

苯并芘

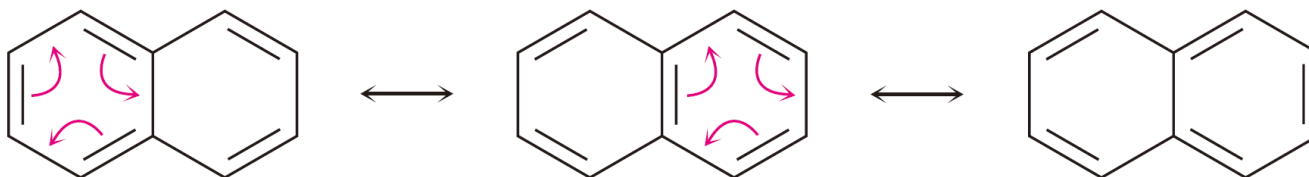


Benzo[a]pyrene



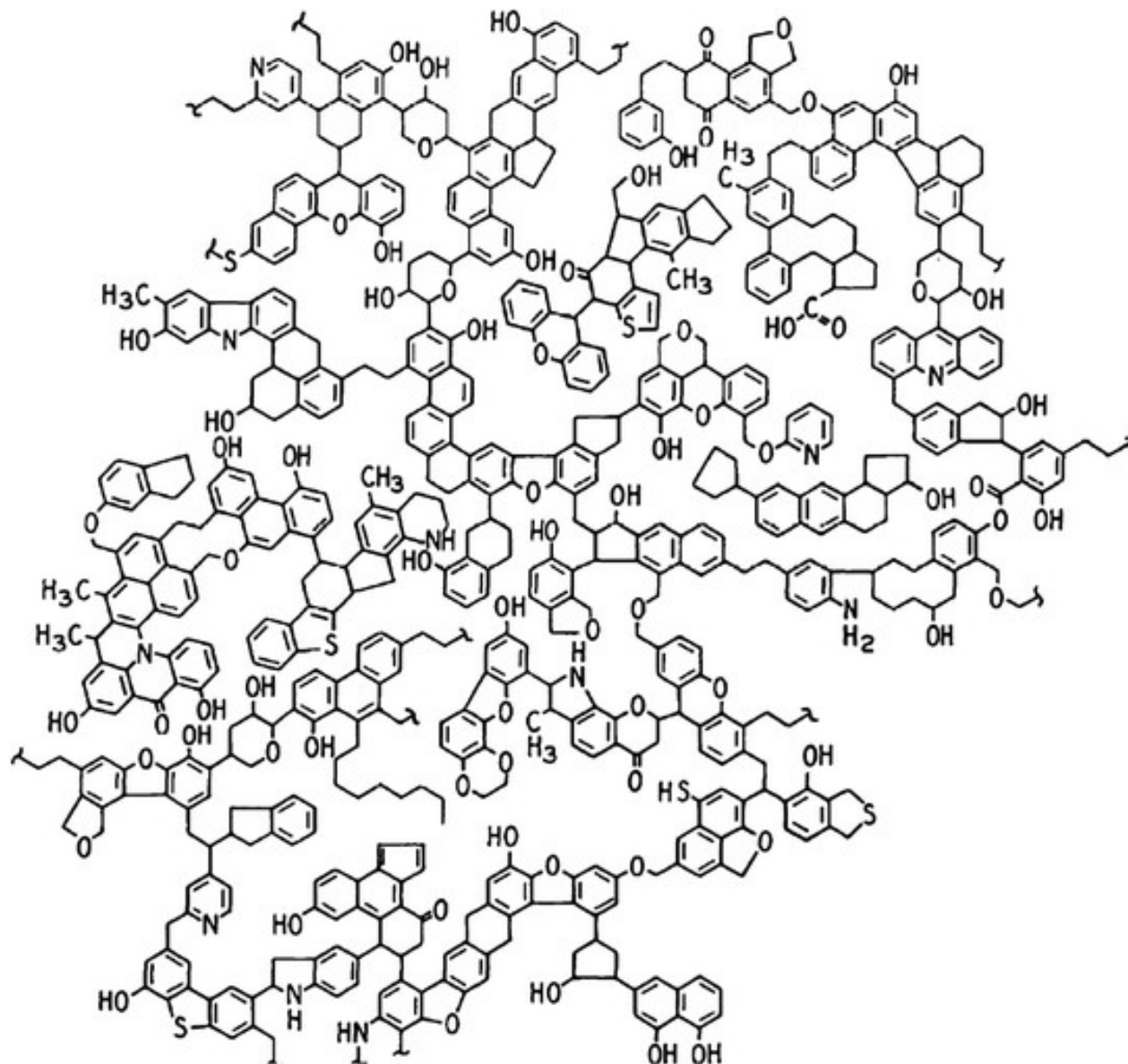
Coronene 蔻

All polycyclic aromatic hydrocarbons can be represented by a number of different resonance forms. Naphthalene, for instance, has three.



15.6 多环芳香化合物

- 煤的结构片段



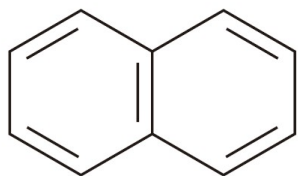
✓ 扩展资料：煤，干酪根和
沥青质化学

✓ [https://
link.springer.com/
chapter/10.1007/978-3-
319-49634-4_3](https://link.springer.com/chapter/10.1007/978-3-319-49634-4_3)

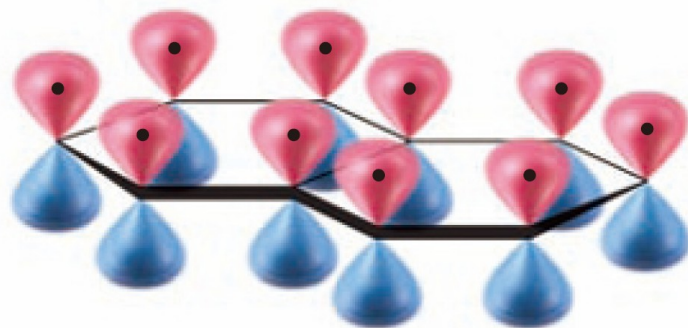
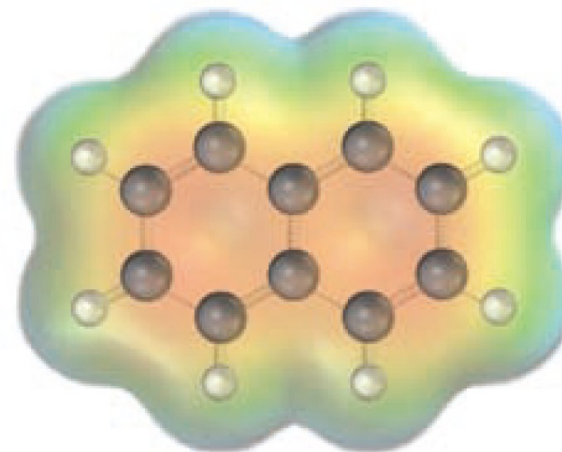
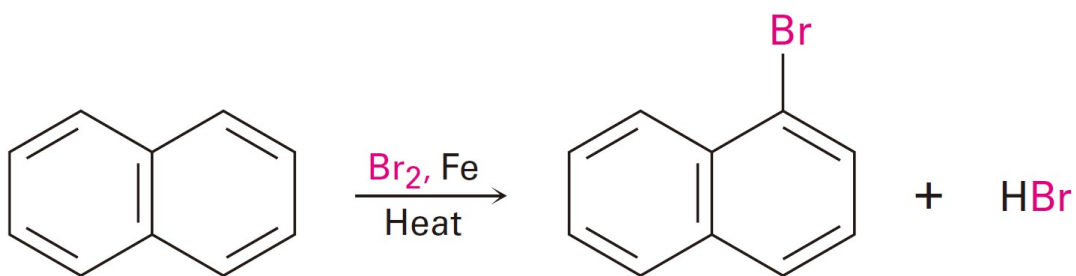


15.6 多环芳香化合物

- 芳香性，易发生取代反应，不易发生加成反应。



Naphthalene



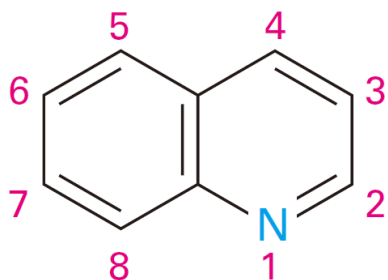
Naphthalene

1-Bromonaphthalene (75%)

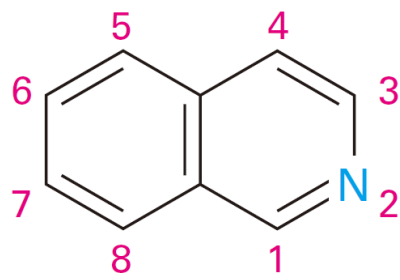
15.6 多环芳香化合物

- 常见的含有杂原子（主要是 N）的多环芳烃

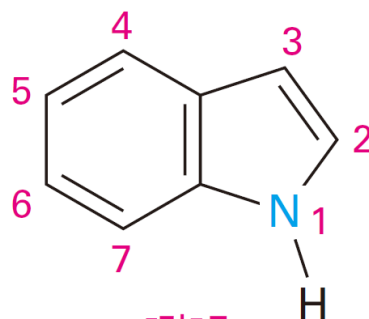
Just as there are heterocyclic analogs of benzene, there are also many heterocyclic analogs of naphthalene. Among the most common are quinoline, isoquinoline, indole, and purine. Quinoline, isoquinoline, and purine all contain pyridine-like nitrogens that are part of a double bond and contribute one electron to the aromatic π system. Indole and purine both contain pyrrole-like nitrogens that contribute two π electrons.



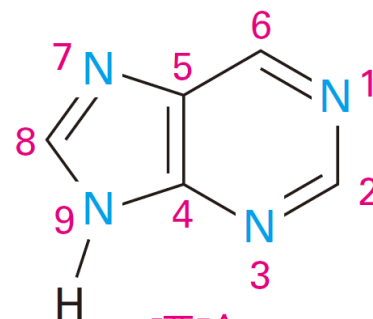
喹啉
Quinoline



异喹啉
Isoquinoline



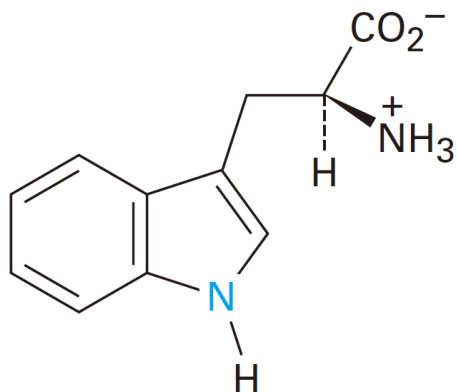
吲哚
Indole



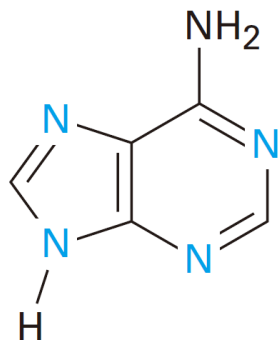
嘌呤
Purine

15.6 多环芳香化合物

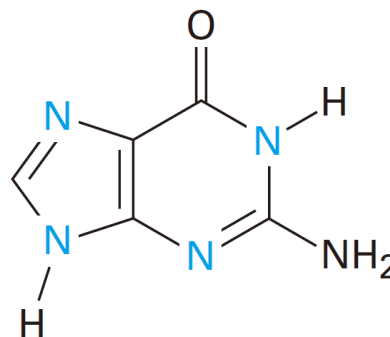
- 生物活性分子中的杂环芳烃



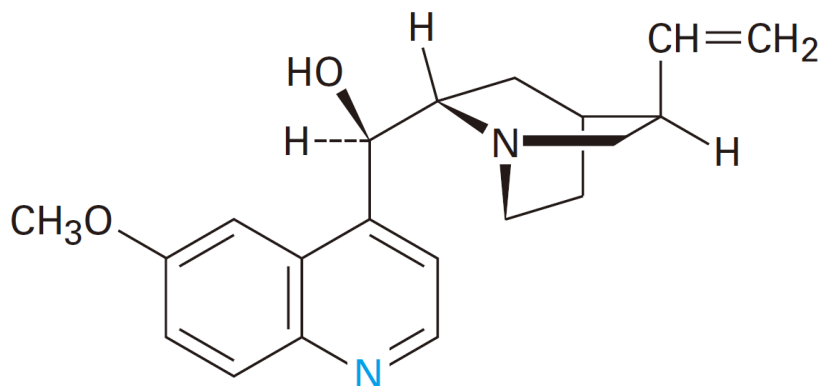
色氨酸
Tryptophan
(an amino acid)



腺嘌呤
Adenine
(in DNA and RNA)

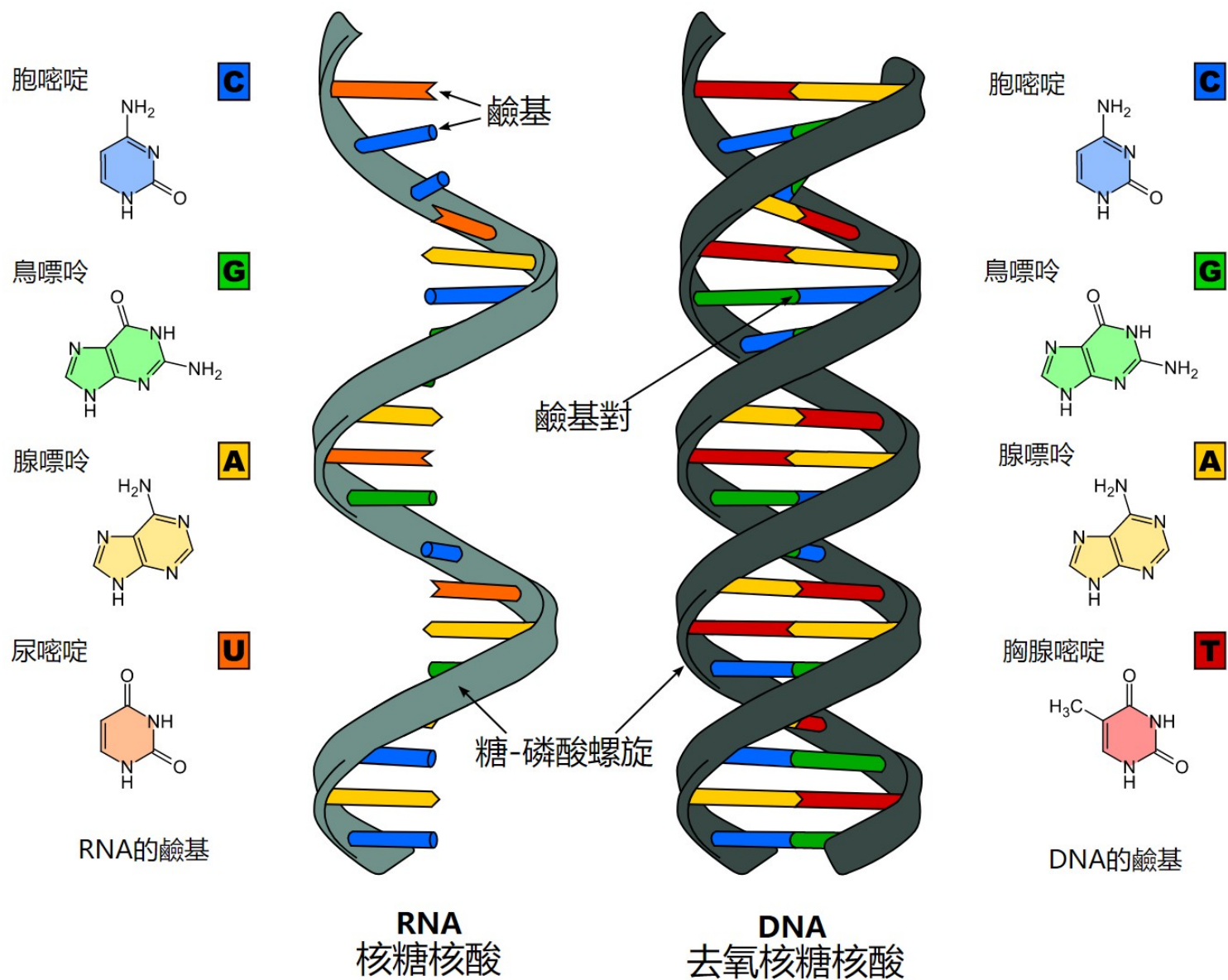


鸟嘌呤
Guanine
(in DNA and RNA)



奎宁
Quinine
(an antimalarial agent)

15.6 多环芳香化合物

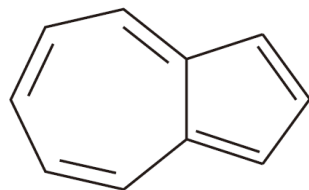


15.6 多环芳香化合物

- 课堂练习

Problem 15.11

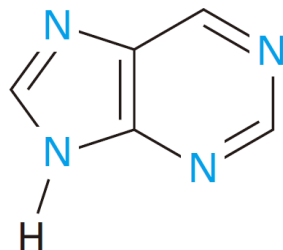
Azulene, a beautiful blue hydrocarbon, is an isomer of naphthalene. Is azulene aromatic? Draw a second resonance form of azulene in addition to that shown.



Azulene

Problem 15.12

How many electrons does each of the four nitrogen atoms in purine contribute to the aromatic π system?



Purine



The blue color of the mushroom *Lactarius indigo* is due to the azulene derivative (7-isopropenyl-4-methylazulen-1-yl)methyl stearate.^[3]

15.7 芳香化合物的光谱分析

- 红外

Monosubstituted:	690–710 cm^{-1}	<i>m</i>-Disubstituted:	690–710 cm^{-1}
	730–770 cm^{-1}		810–850 cm^{-1}
<i>o</i>-Disubstituted:	735–770 cm^{-1}	<i>p</i>-Disubstituted:	810–840 cm^{-1}

The IR spectrum of toluene in **Figure 15.11** shows these characteristic absorptions.

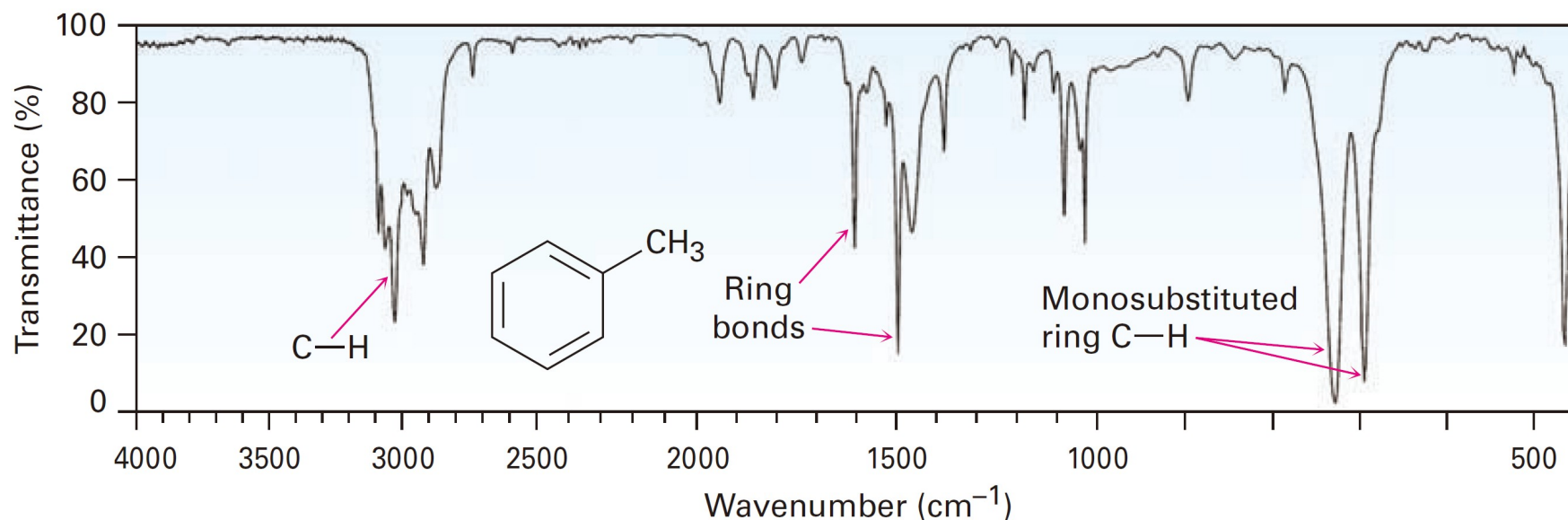


Figure 15.11 The infrared spectrum of toluene.

15.7 芳香化合物的光谱分析

- 紫外

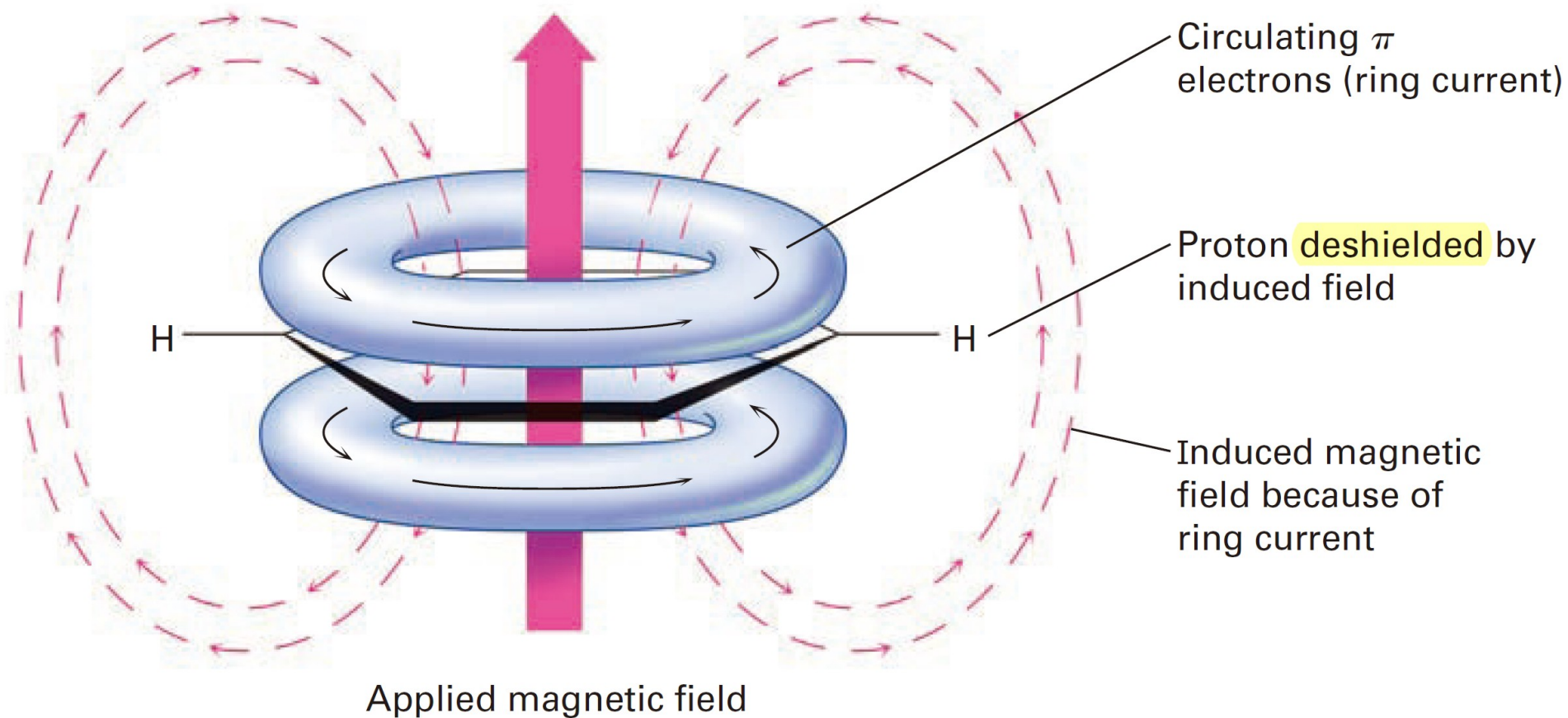
Ultraviolet Spectroscopy

Aromatic rings are detectable by ultraviolet spectroscopy because they contain a conjugated π electron system. In general, aromatic compounds show a series of bands, with a fairly intense absorption near 205 nm and a less intense absorption in the 255 to 275 nm range. The presence of these bands in the ultraviolet spectrum of a molecule is a sure indication of an aromatic ring.

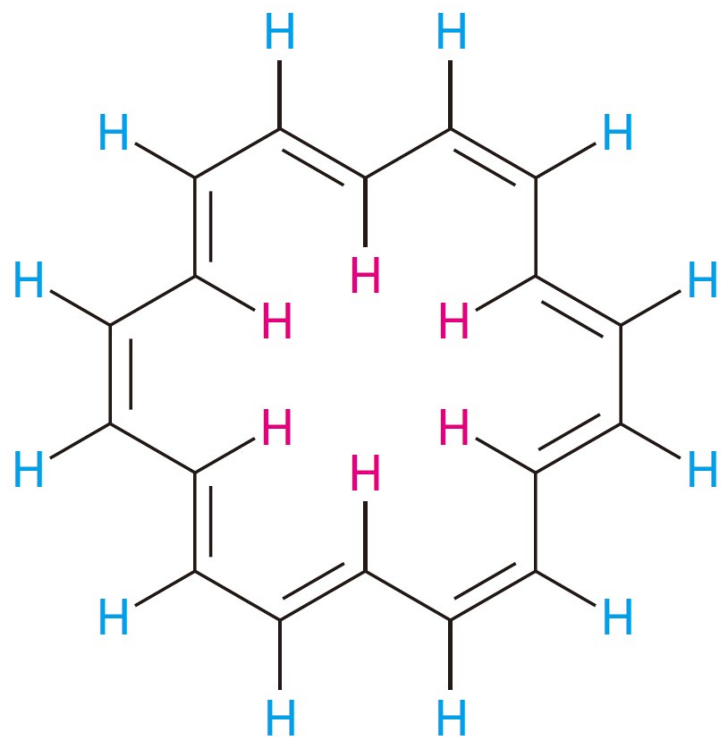


15.7 芳香化合物的光谱分析

- 核磁：屏蔽作用和去屏蔽作用



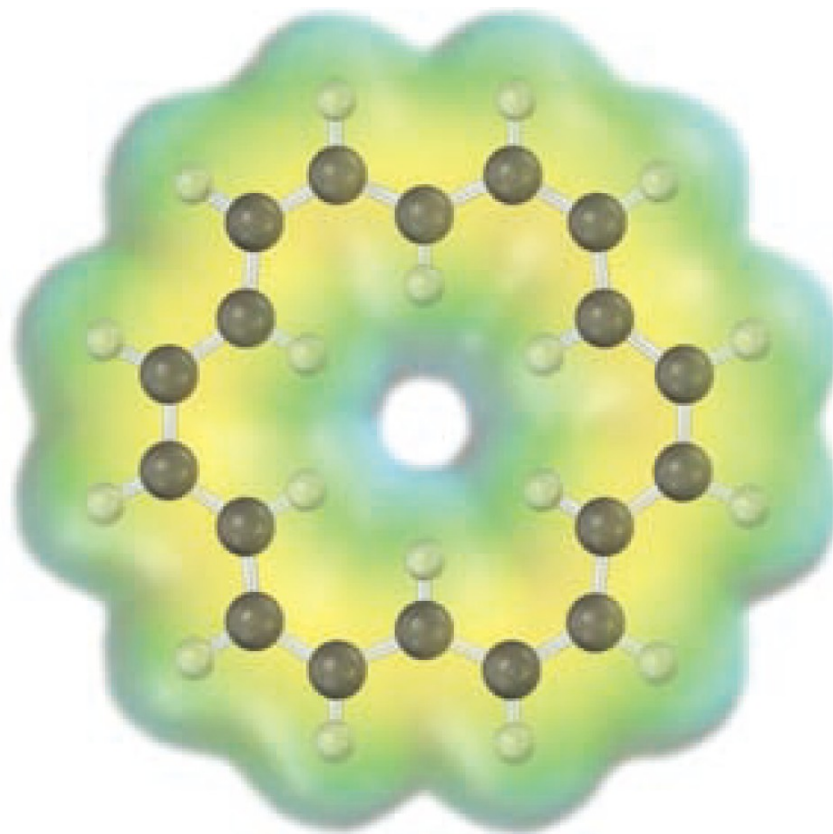
15.7 芳香化合物的光谱分析



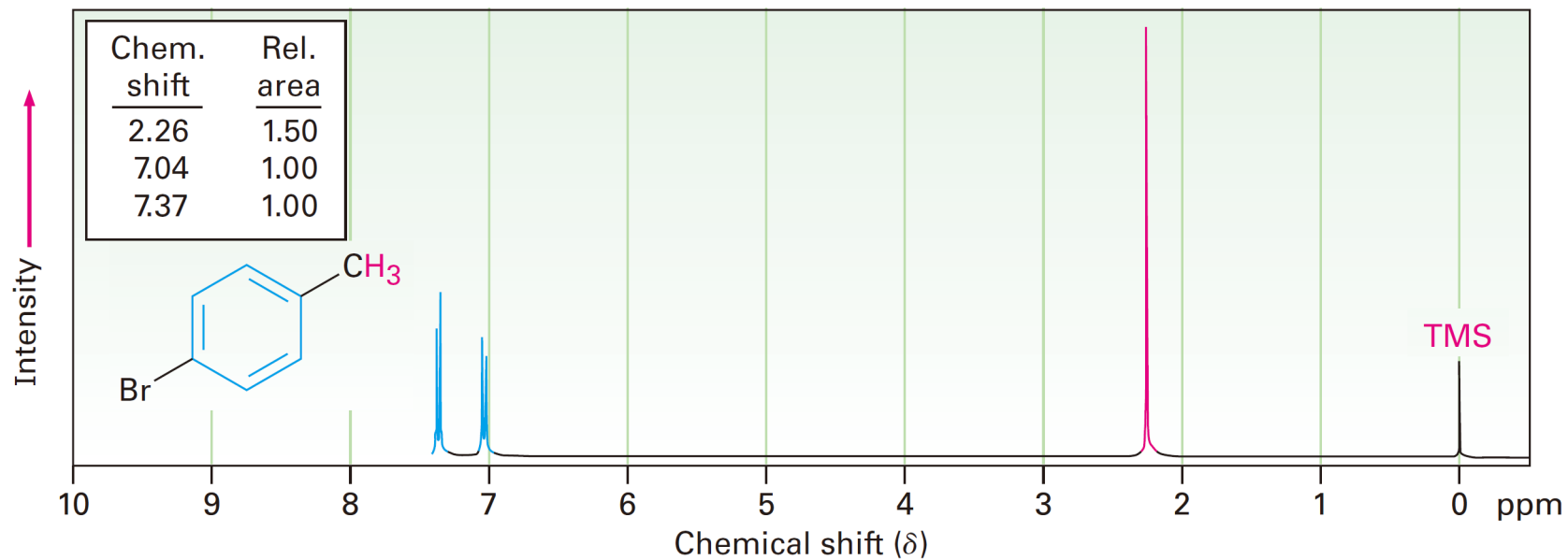
[18]Annulene

Inside H: -3.0δ

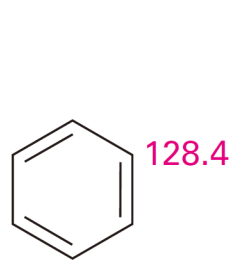
Outside H: 9.3δ



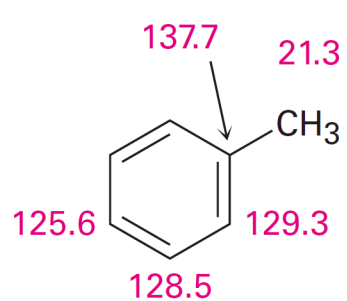
15.7 芳香化合物的光谱分析



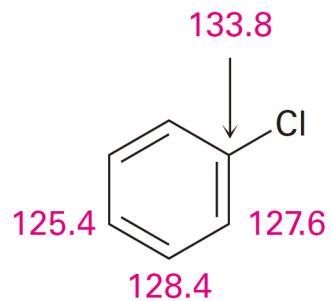
碳谱



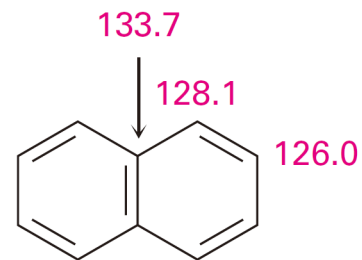
Benzene



Toluene



Chlorobenzene



Naphthalene

作业

- 15. 42-50

