Benzene and Aromaticity

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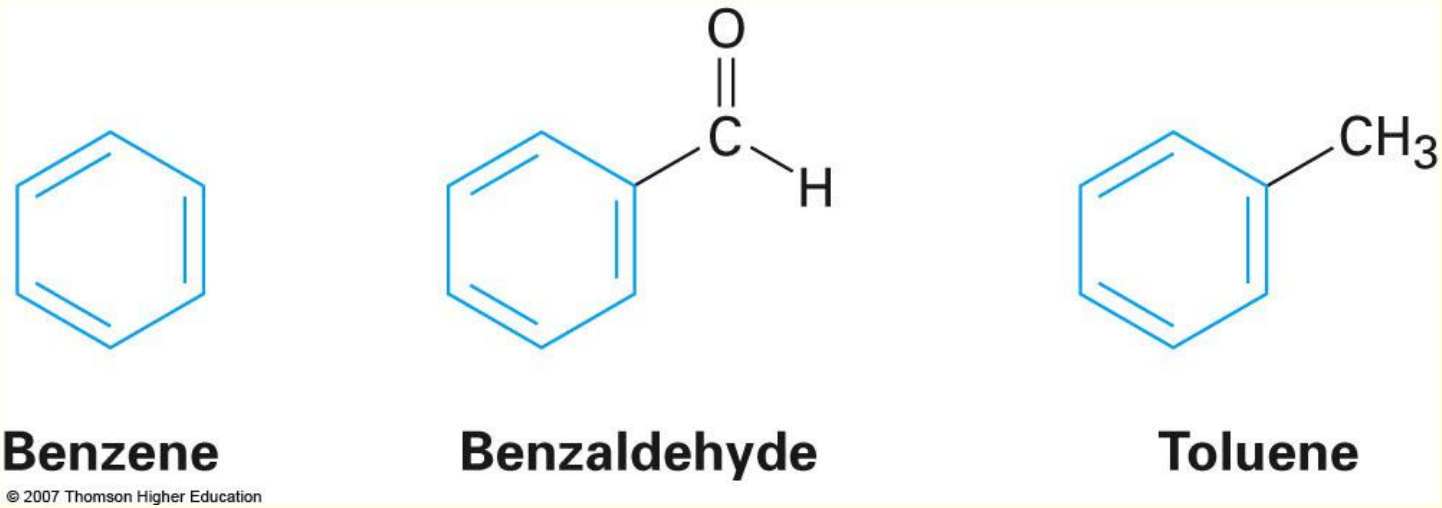
Aromatic Compounds

- *Aromatic* was used to described some fragrant compounds in early 19th century
  - Not correct now: later they are grouped by chemical behavior (unsaturated compounds that undergo substitution rather than addition)
- Current: distinguished from *aliphatic* compounds by electronic configuration

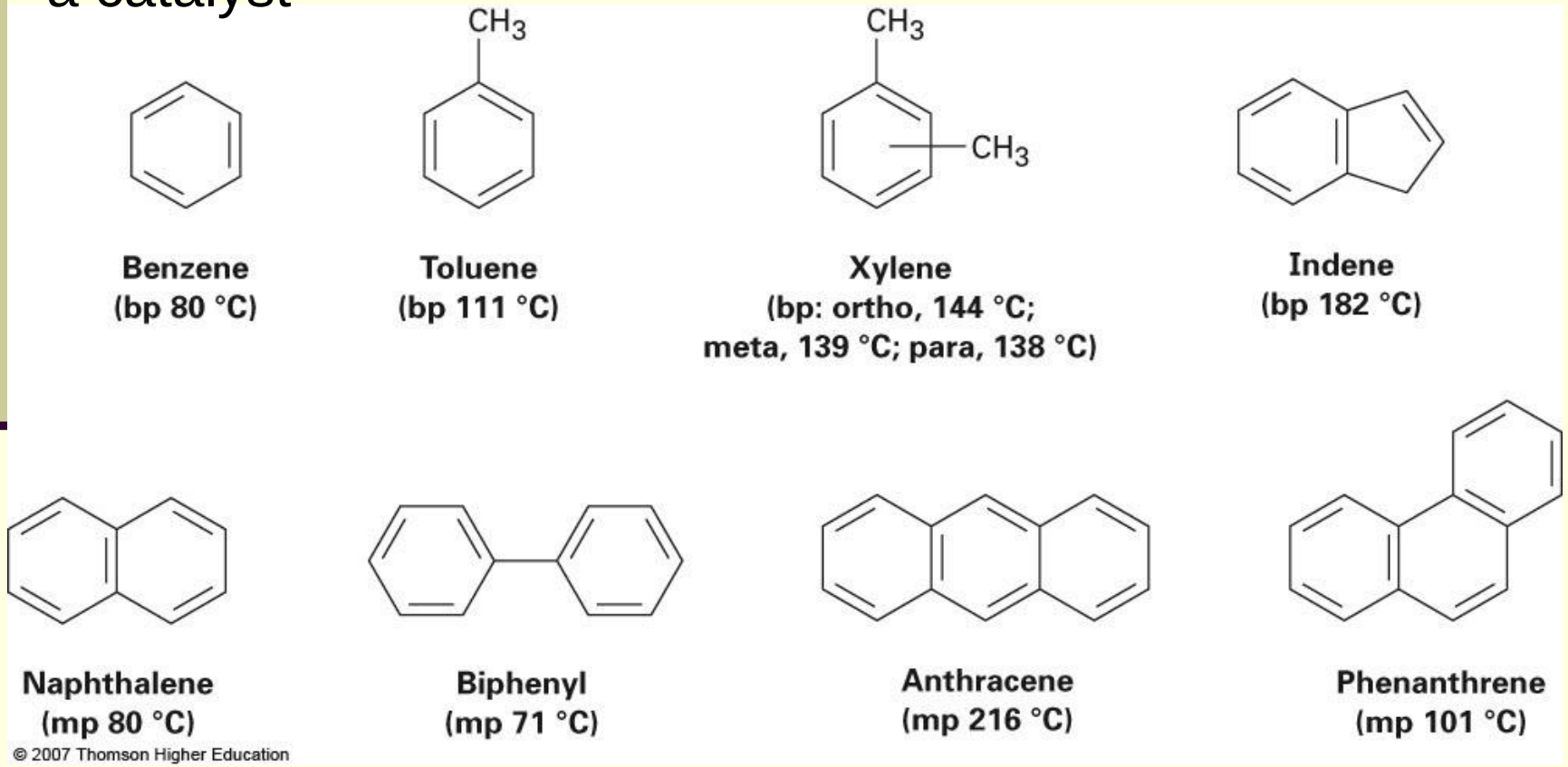


Why this Chapter?

- Reactivity of substituted aromatic compounds is tied to their structure
- Aromatic compounds provide a sensitive probe for studying relationship between structure and reactivity

15.1 Sources and Names of Aromatic Hydrocarbons

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



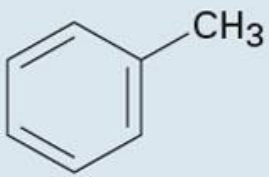
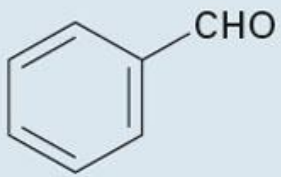
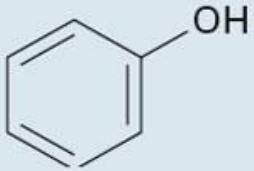
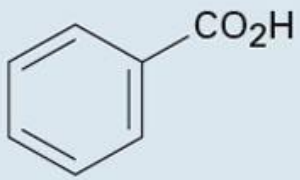
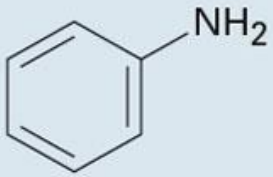
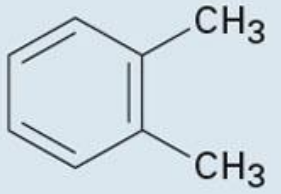
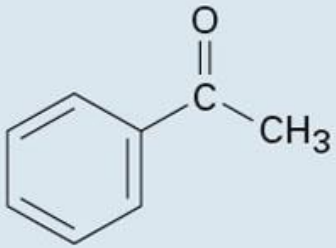
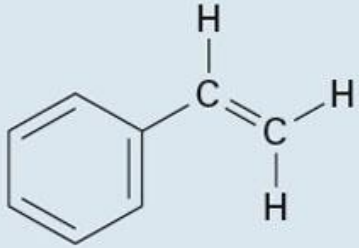
Naming Aromatic Compounds

- Many common names

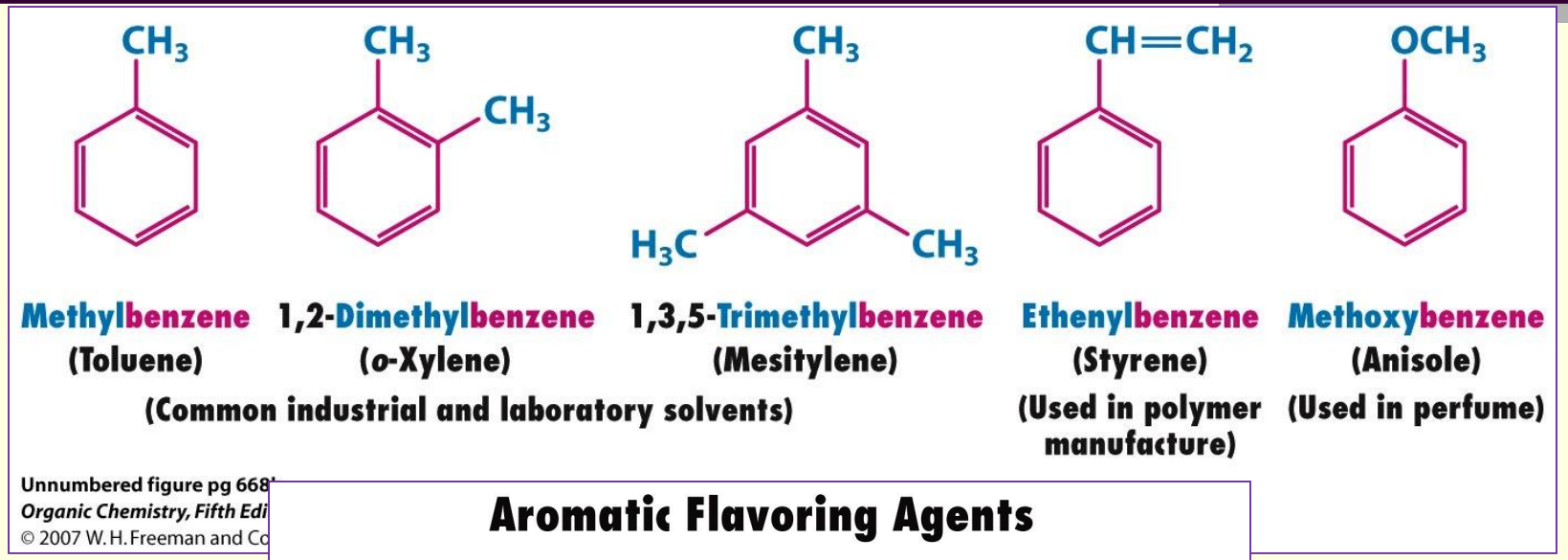
  (toluene = methylbenzene; aniline = aminobenzene)
- Monosubstituted benzenes systematic names as hydrocarbons with *–benzene*
  - C_6H_5Br = bromobenzene
  - $C_6H_5NO_2$ = nitrobenzene, and
  - $C_6H_5CH_2CH_2CH_3$ is propylbenzene

Naming Aromatic Compounds

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)

More examples:



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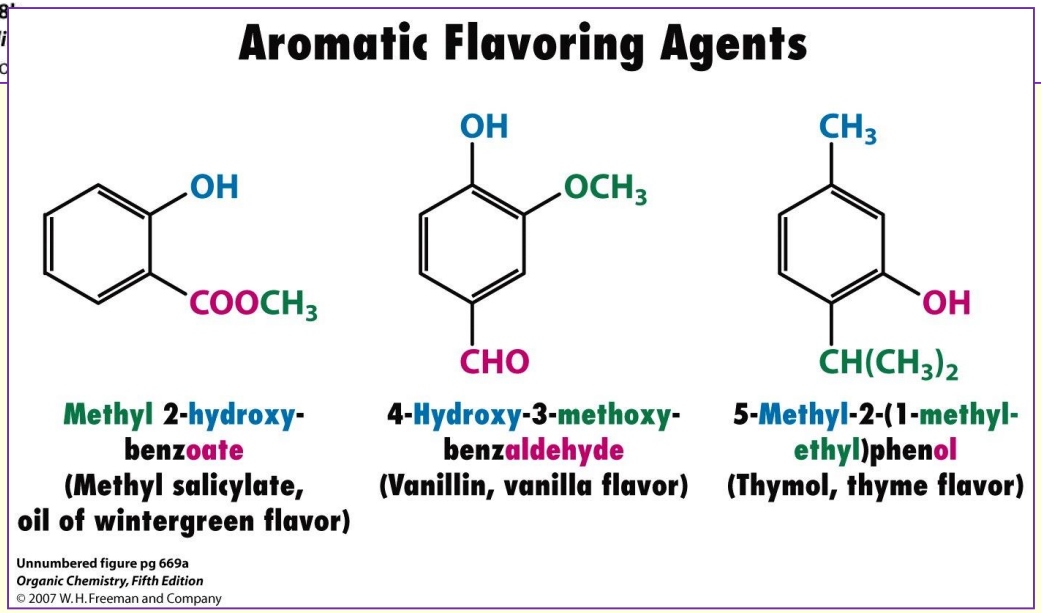
Organic Chemistry, Fifth Edi



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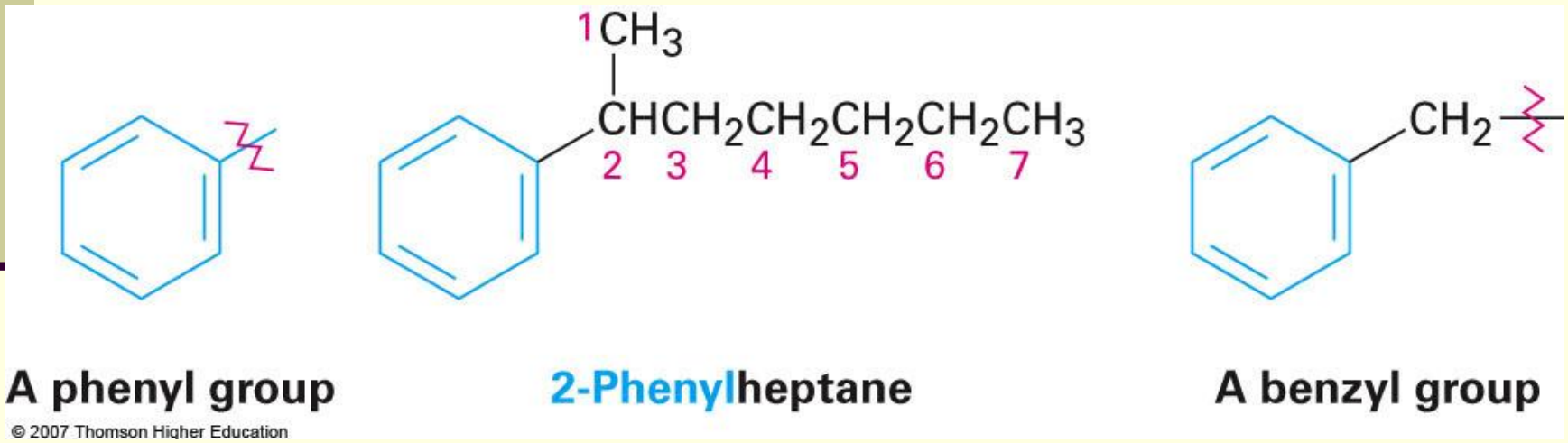
Organic Chemistry, Fifth Edition

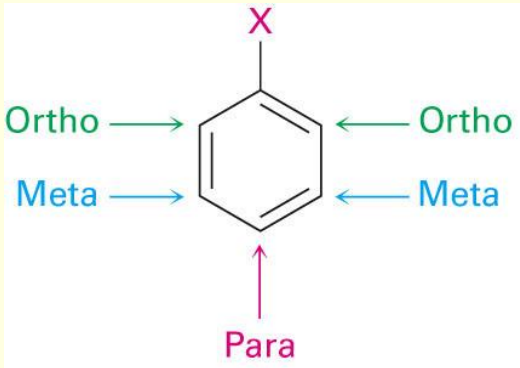
The Phenyl Group

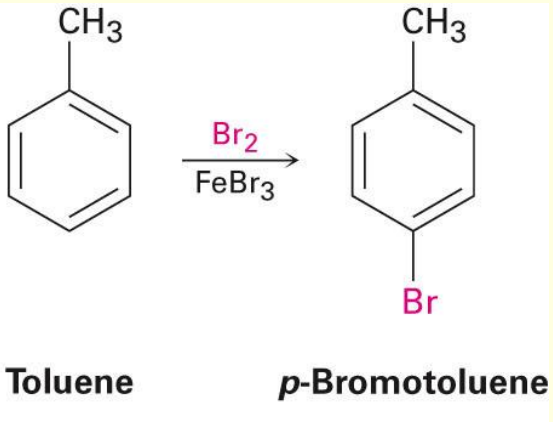
- When a benzene ring is a substituent, the term **phenyl** is used (for C_6H_5)
  - You may also see "Ph" or "ϕ" in place of "C_6H_5"
- "**Benzyl**" refers to "$C_6H_5CH_2$"

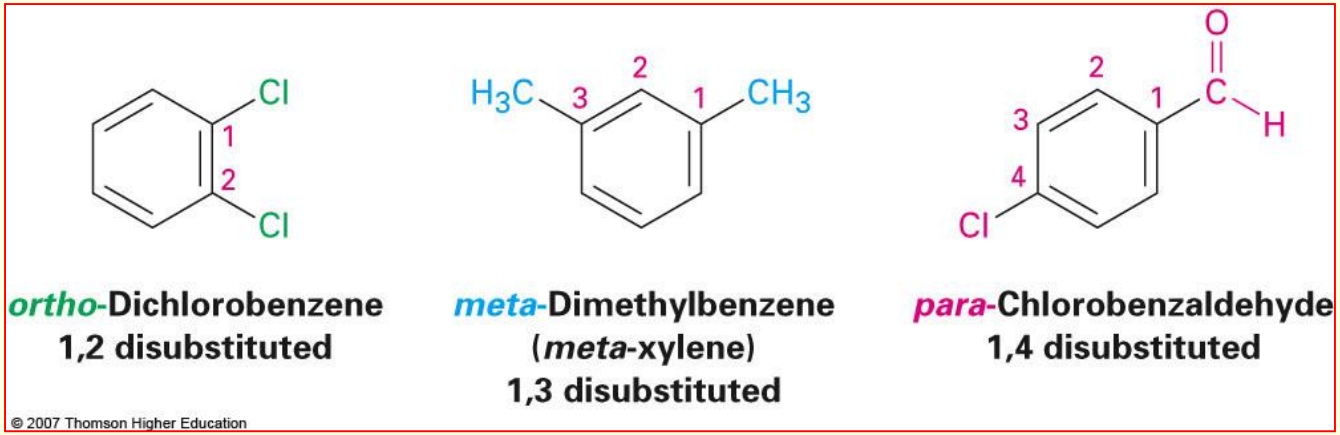


Disubstituted Benzenes

- 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)

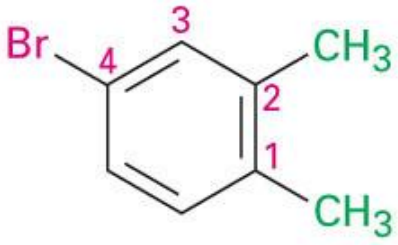




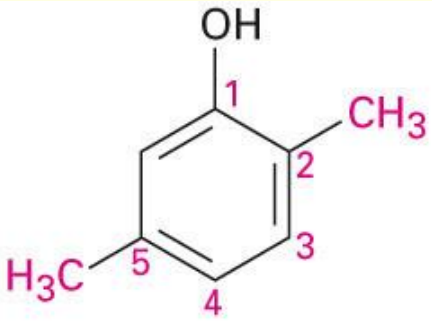


Naming Benzenes With More Than Two Substituents

- Choose numbers to get lowest possible values
- List substituents alphabetically with hyphenated numbers
- Common names, such as “toluene” can serve as root name (as in TNT)



4-bromo-1,2-dimethylbenzene

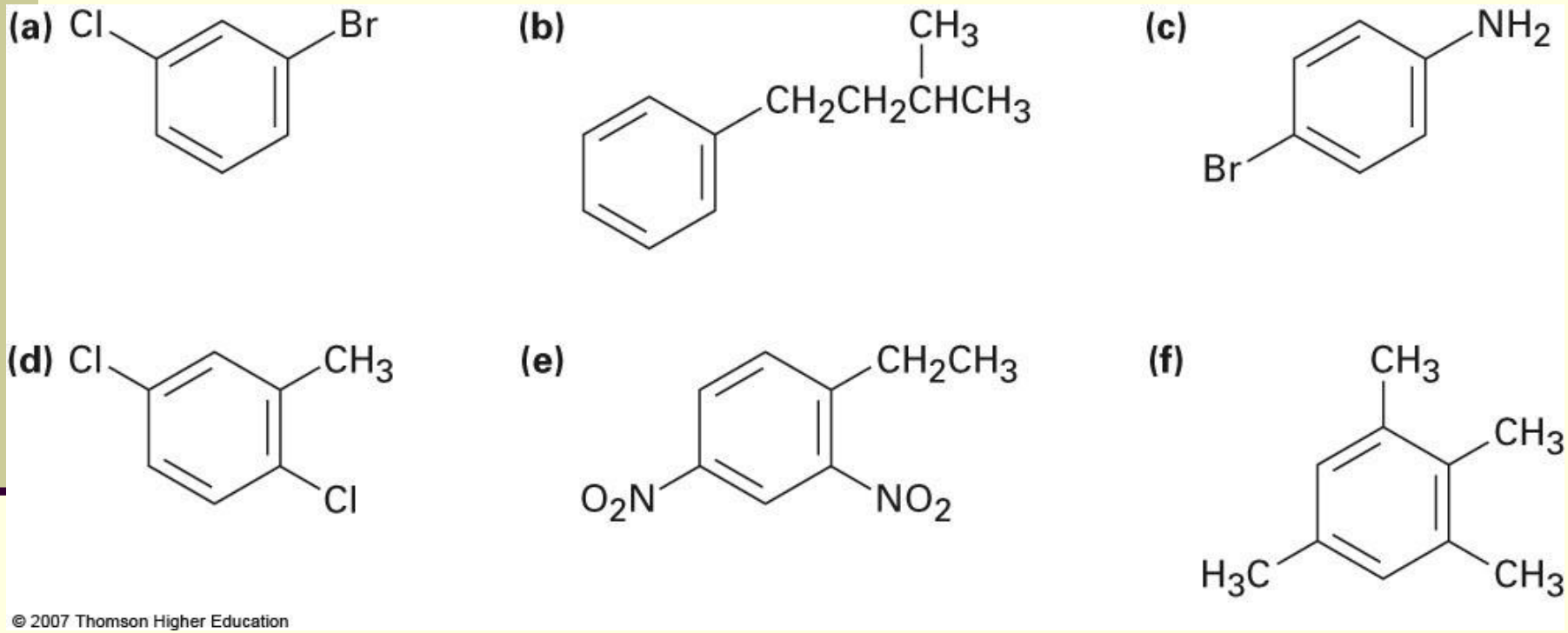


2,5-Dimethylphenol

2,4,6-Trinitrotoluene (TNT)

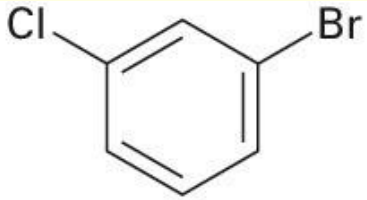
Learning Check:

- Give IUPAC names for the following:

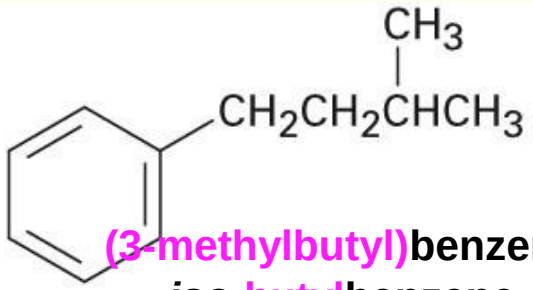


Solution:

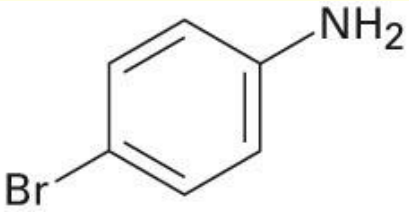
- Give IUPAC names for the following:

(a) 

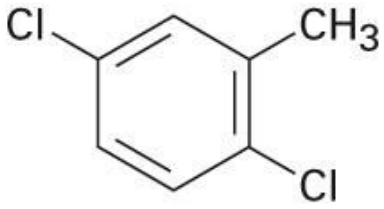
1-bromo-3-chlorobenzene
m-bromochlorobenzene

(b) 

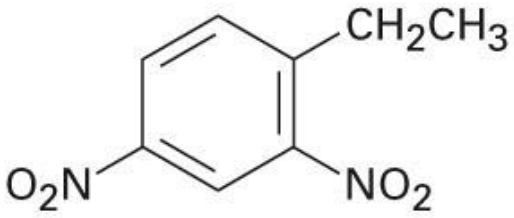
(3-methylbutyl)benzene
iso-butylbenzene

(c) 

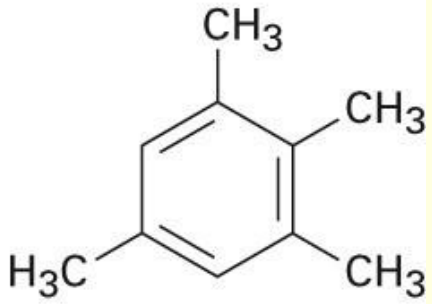
4-bromoaniline
p-bromoaniline

(d) 

2,5-dichlorotoluene
1,4-dichloro-2-methylbenzene

(e) 

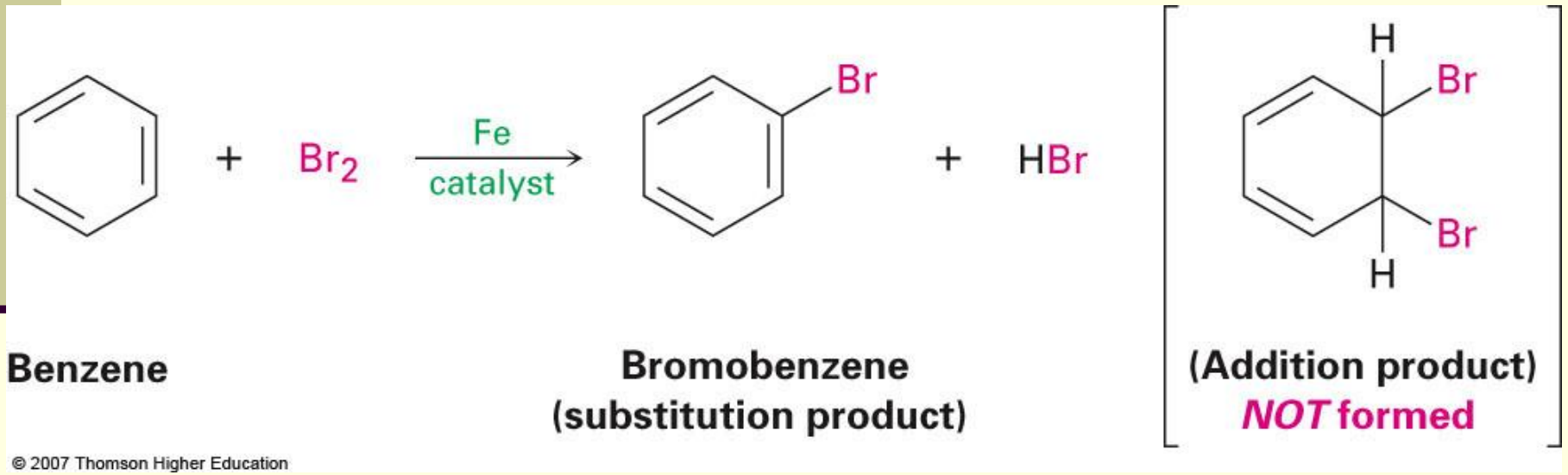
1-ethyl-2,4-dinitrobenzene

(f) 

1,2,3,5-tetramethylbenzene

15.2 Structure and Stability of Benzene: Molecular Orbital Theory

- Benzene reacts slowly with Br_2 to give bromobenzene (Br replaces H)
- This is substitution rather than the rapid addition reaction common to compounds with C=C, suggesting that in benzene there is a higher barrier

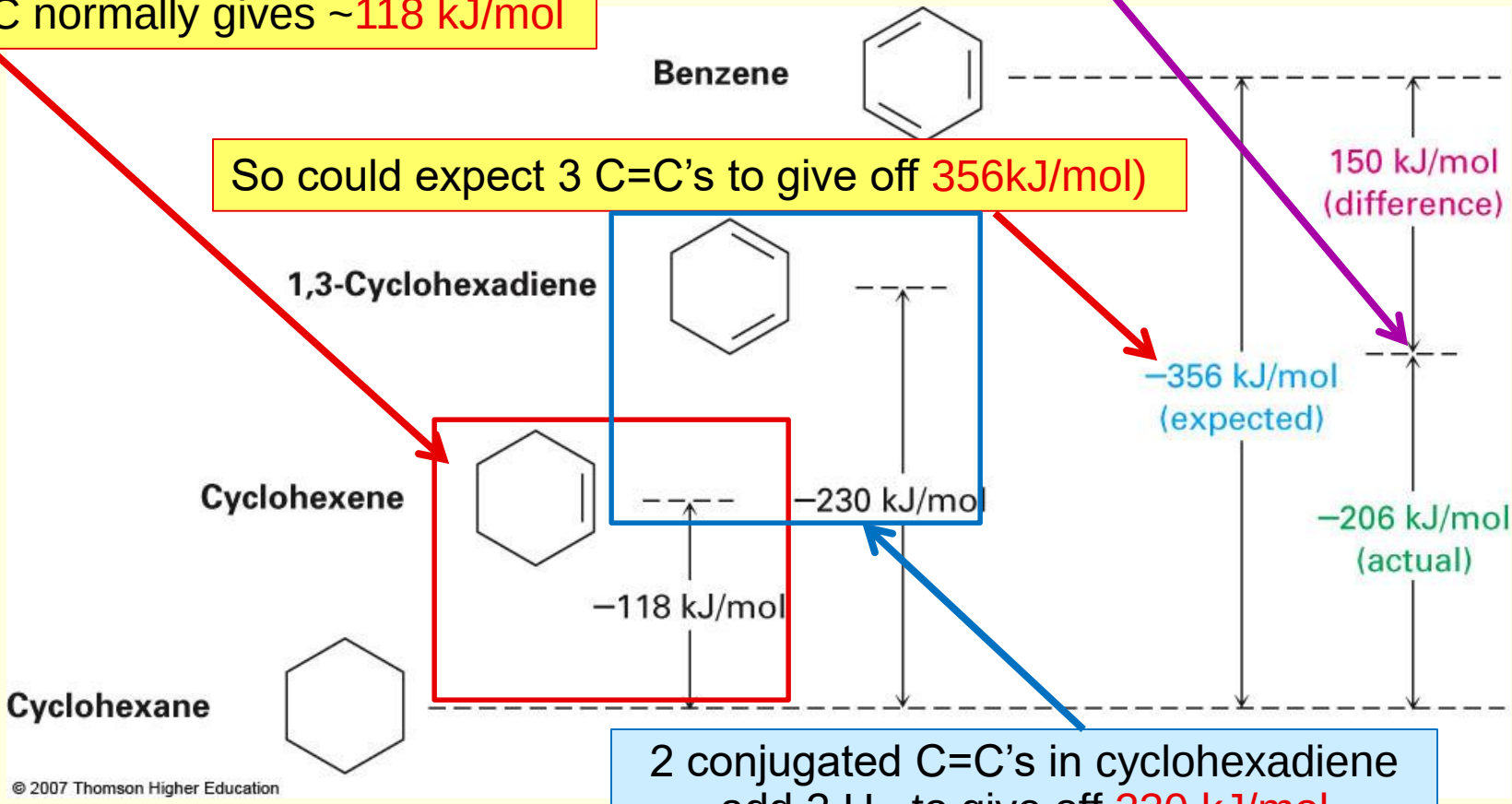


Heats of Hydrogenation as Indicators of Stability

Benzene has 3 unsaturation sites but gives off only 206 kJ/mol on reacting with 3 H_2 molecules

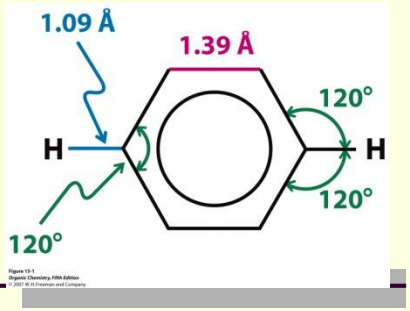
Therefore has ~ **150 kJ more "stability"** than an isolated set of three double bonds

H_2 + C=C normally gives ~118 kJ/mol

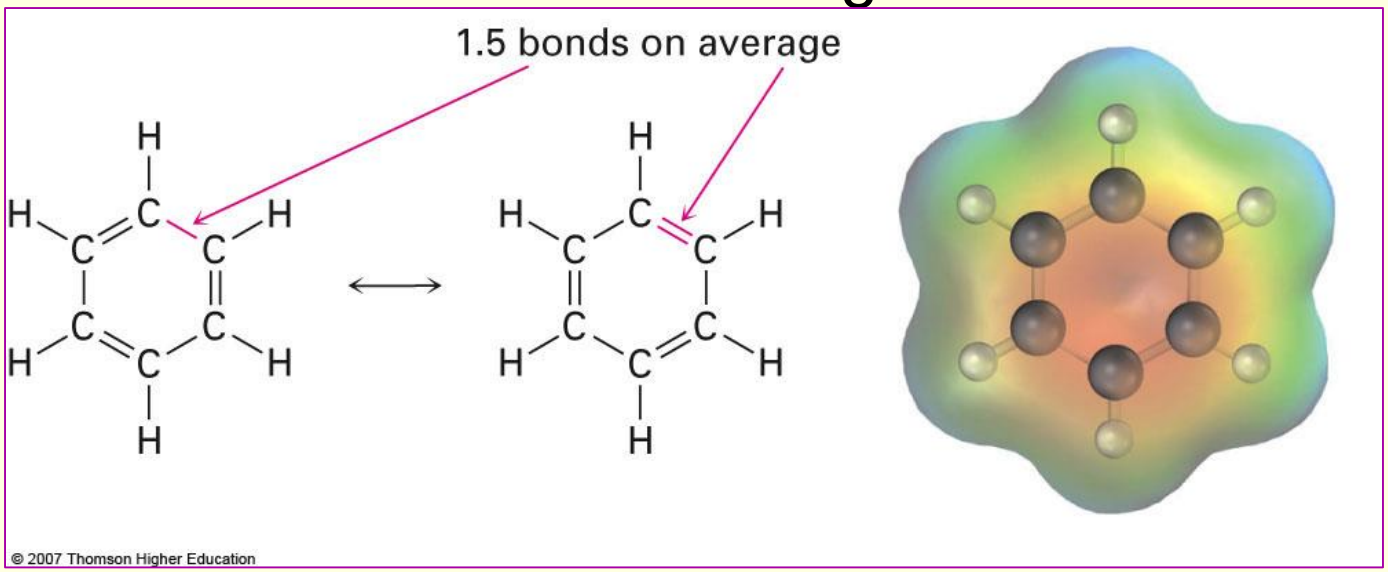


2 conjugated C=C's in cyclohexadiene add 2 H_2 to give off 230 kJ/mol

Benzene's Unusual Structure

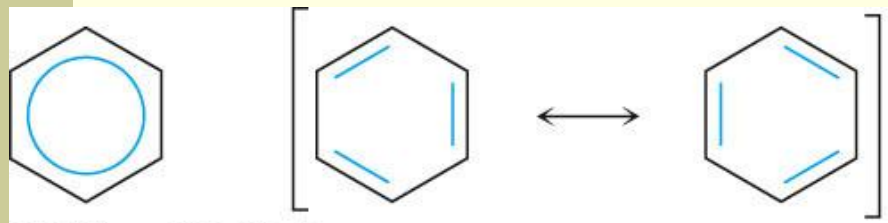


- **All its C-C bonds are the same length: 139 pm** — between single (154 pm) and double (134 pm) bonds
- Electron density in all six C-C bonds is identical
- Structure is **planar, hexagonal**
- **C–C–C bond angles 120°**
- Each C is sp^2 and has a *p* orbital perpendicular to the plane of the six-membered ring



Drawing Benzene and Its Derivatives

- The two benzene resonance forms can be represented by a single structure with a circle in the center to indicate the equivalence of the carbon–carbon bonds
- Circle doesn't indicate the number of π electrons in the ring but does reminds us of the delocalized structure

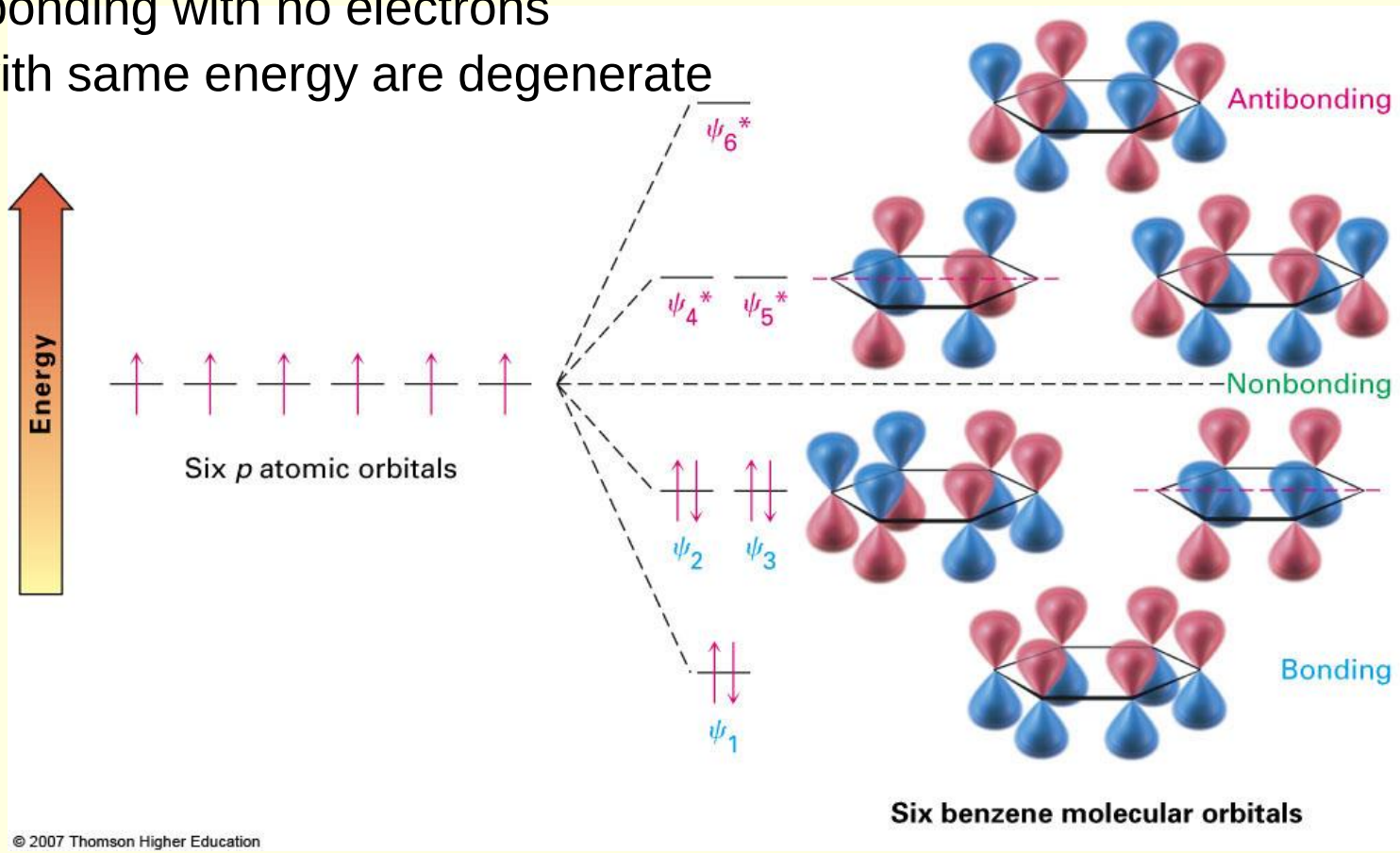


Alternative representations of benzene. The "circle" representation must be used carefully since it doesn't indicate the number of π electrons in the ring.

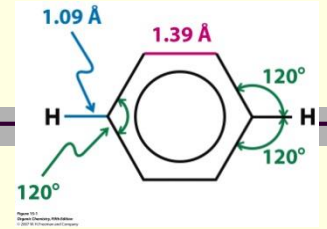
We use one resonance structure to represent benzene for ease in keeping track of bonding changes in reactions

Molecular Orbital Description of Benzene

- The 6 p-orbitals combine to give
  - 3 bonding orbitals with 6 π e-s,
  - 3 antibonding with no electrons
- Orbitals with same energy are degenerate



15.3 Aromaticity and the Hückel 4n+2 Rule



- In Summary **Benzene is**:
  - Unusually stable - heat of hydrogenation 150 kJ/mol less negative than a cyclic triene
  - Planar: bond angles are 120°, carbon–carbon bond lengths 139 pm
  - Undergoes substitution rather than electrophilic addition
  - Resonance hybrid with structure between two line-bond structures

Qualities similar for all Aromatic (4n+2) Compounds

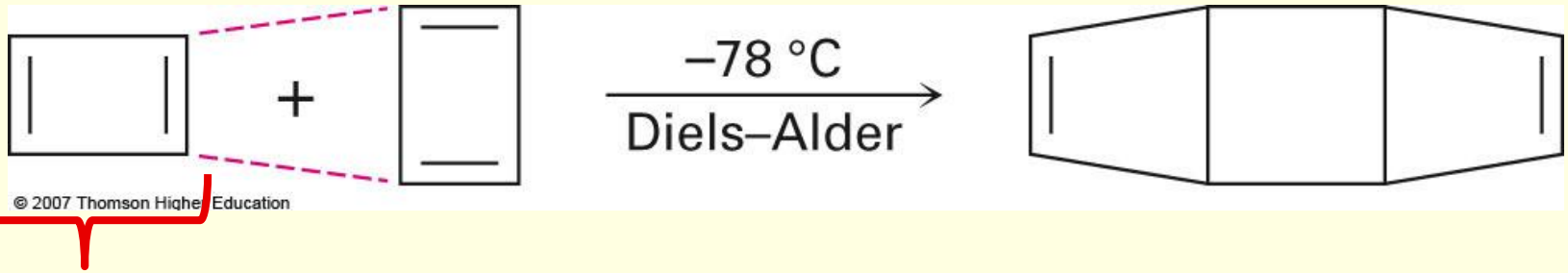
Aromaticity and the 4*n* + 2 Rule

- **Huckel's rule**, based on calculations – a compound is **aromatic** if it is a
  - **planar**
  - **cyclic** molecule with
  - alternating double and single bonds and has
  - ***4n+ 2*** *π electrons* (*n is 0,1,2,3,4*)
- For n=1: 4n+2 = 6; **benzene** is stable and the electrons are delocalized

Compounds With 4n π Electrons Are Not Aromatic (May be Antiaromatic)

- Planar, cyclic molecules with ***4 n*** π electrons are much *less* stable than expected (antiaromatic)
- They will distort out of plane and behave like ordinary alkenes

Cyclobutadiene is so unstable that it dimerizes by a self-Diels-Alder reaction at low temperature



Anti-Aromatic (unstable)

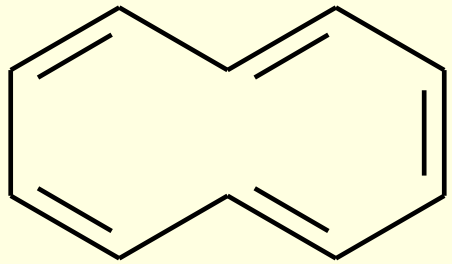
Non-aromatic

- Cyclooctatetraene has four double bonds, reacting with Br_2, $KMnO_4$, and HCl as if it were four alkenes
- Distorts out of plane so C=C's behave like ordinary alkenes

The molecular structure of cyclooctatetraene is non-planar and tub shaped. The double bonds are nearly orthogonal and are not conjugated.

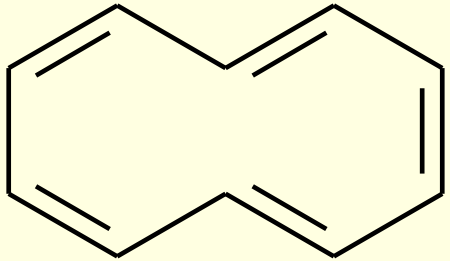
Learning Check:

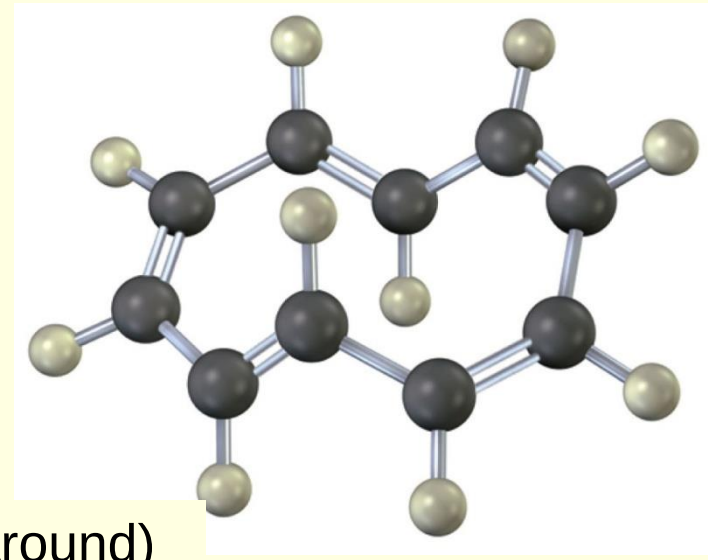
- Is cyclodecapentaene aromatic? Why or why not?



Solution:

- Is cyclodecapentaene aromatic? Why or why not?





✓Is cyclic

✓Is conjugated (dbl single dbl all around)

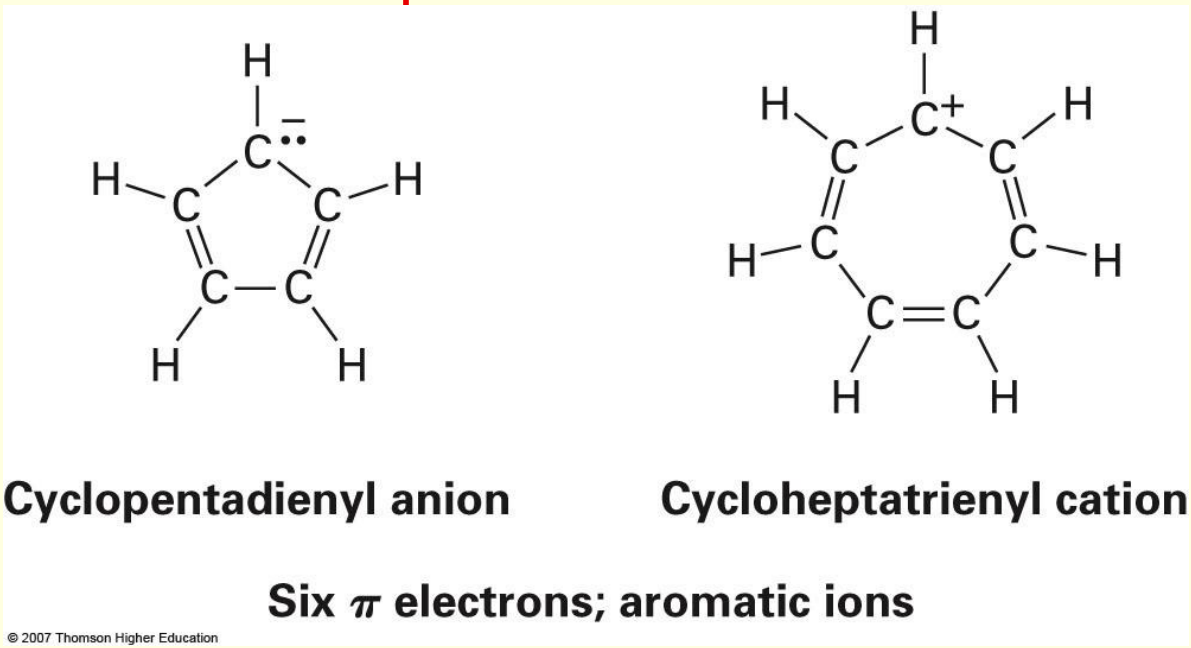
✓Has 4n + 2 = 10 π e-'s

☹Is ~~**planar**~~

No, Not planar so non-aromatic;
H's crowd so distort out of plane

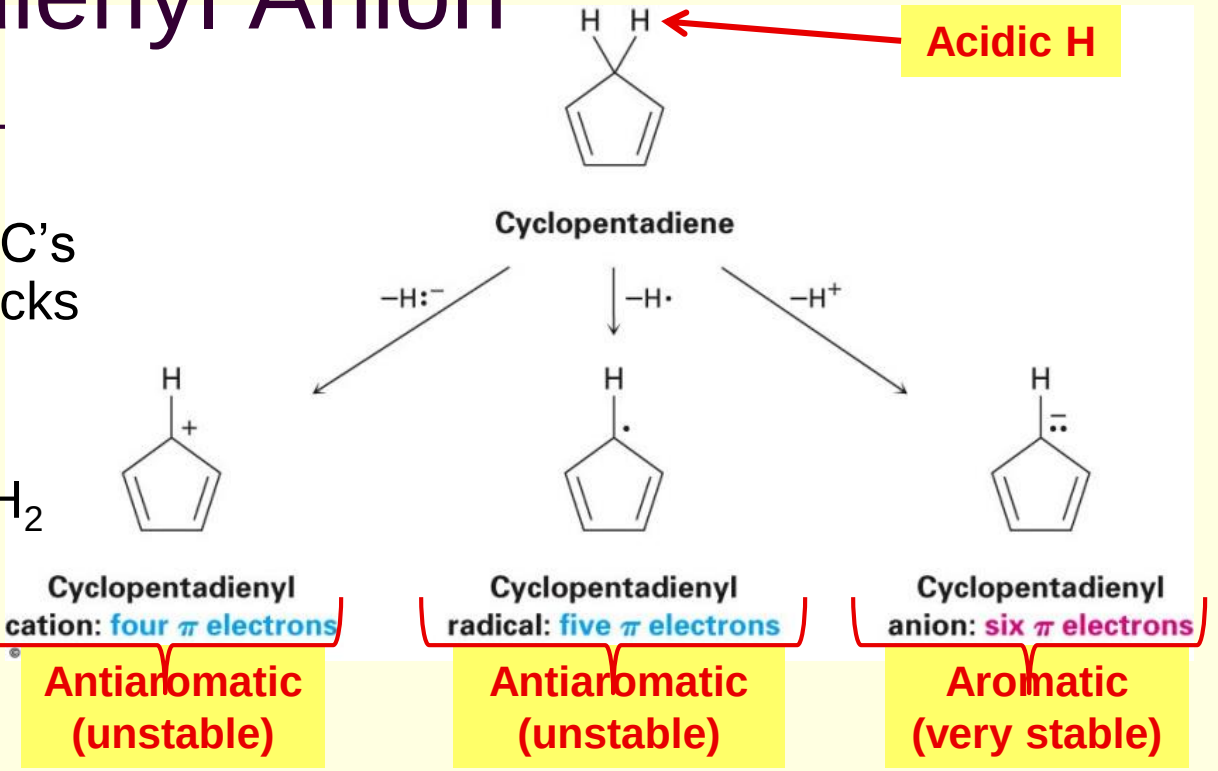
15.4 Aromatic Ions

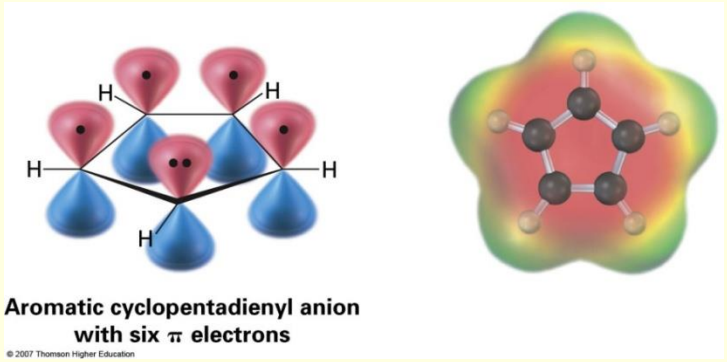
- The $4n + 2$ rule applies to ions as well as neutral species
- Both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic
- The key feature of both is that they contain 6 π electrons in a ring of continuous p orbitals



Cyclopentadienyl Anion

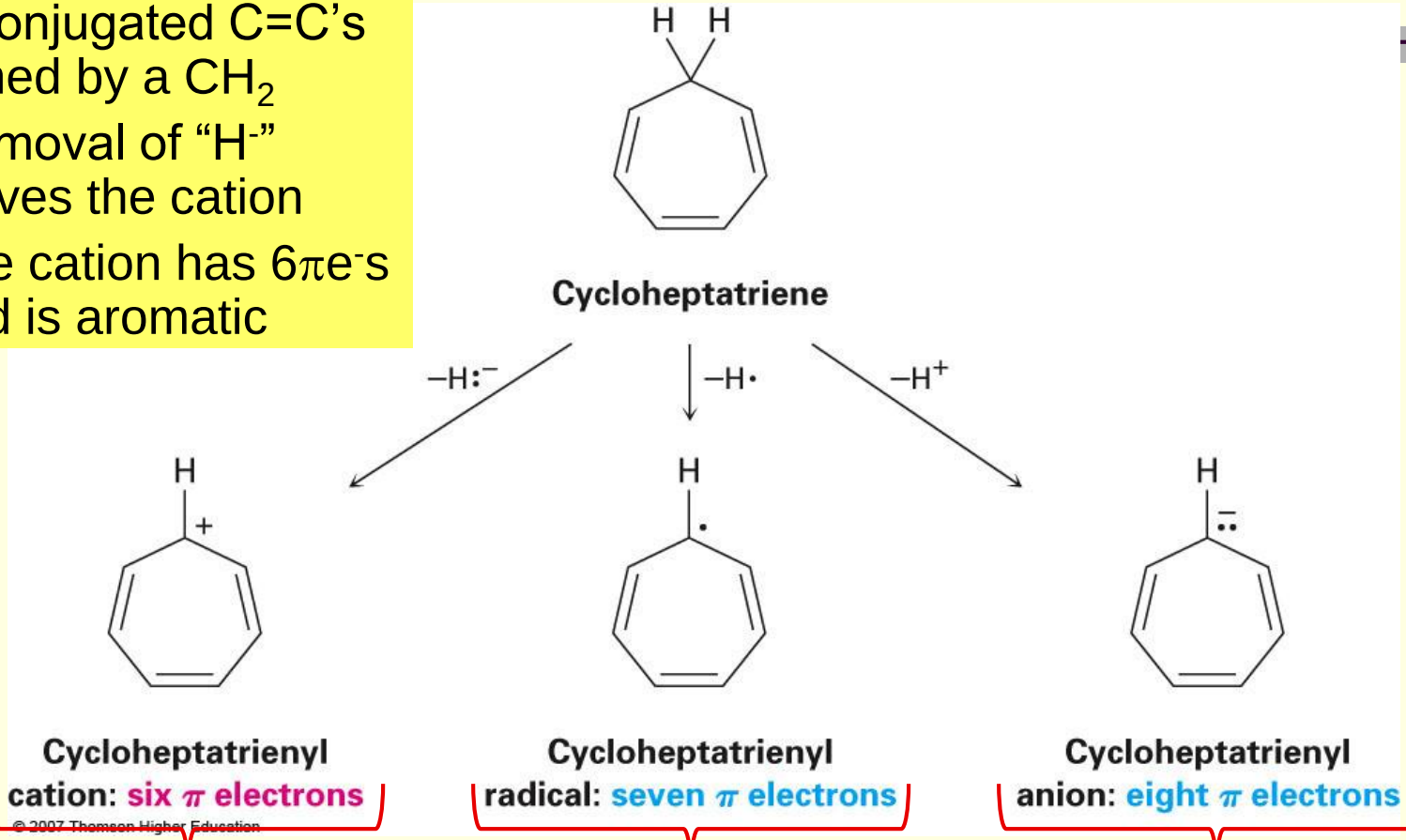
- 1,3-Cyclopentadiene contains conjugated C=C's joined by a CH_2 that blocks delocalization
- Removal of H^+ at the CH_2 produces a cyclic 6 π e^- system, which is stable
- Removal of H^- or H• generate nonaromatic 4 and 5 electron systems
- Relatively acidic (p*K*a = 16) because the anion is stable





Cycloheptatrienyl Cation

- ✓ 3 conjugated C=C's joined by a CH_2
- ✓ Removal of "H^-" leaves the cation
- ✓ The cation has 6πe^-s and is aromatic



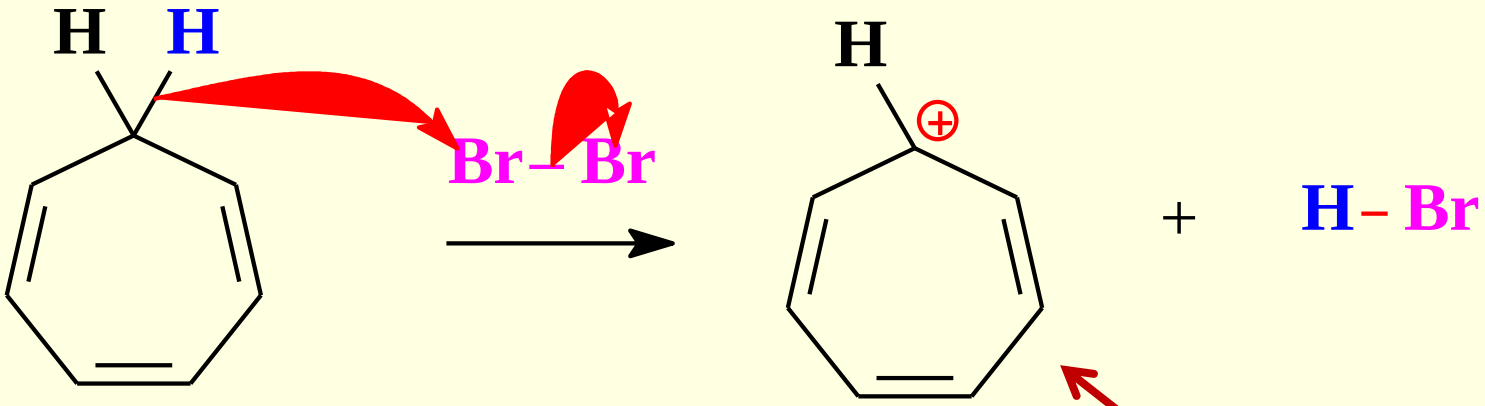
Aromatic (stable)

Antiaromatic (unstable)

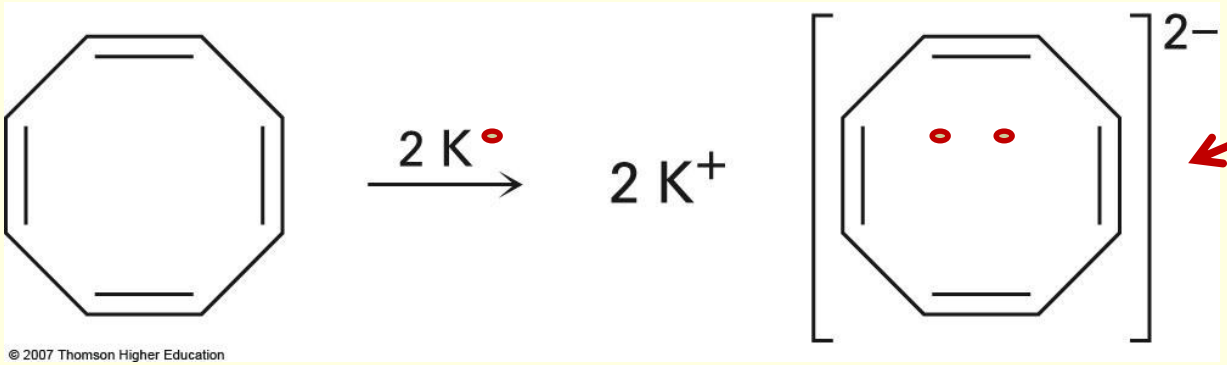
Antiaromatic (very unstable)

Reactivity Examples:

- Cycloheptatriene reacts easily to lose "H^-"



- Cyclooctatetraene reacts easily to gain "2e⁻'s"



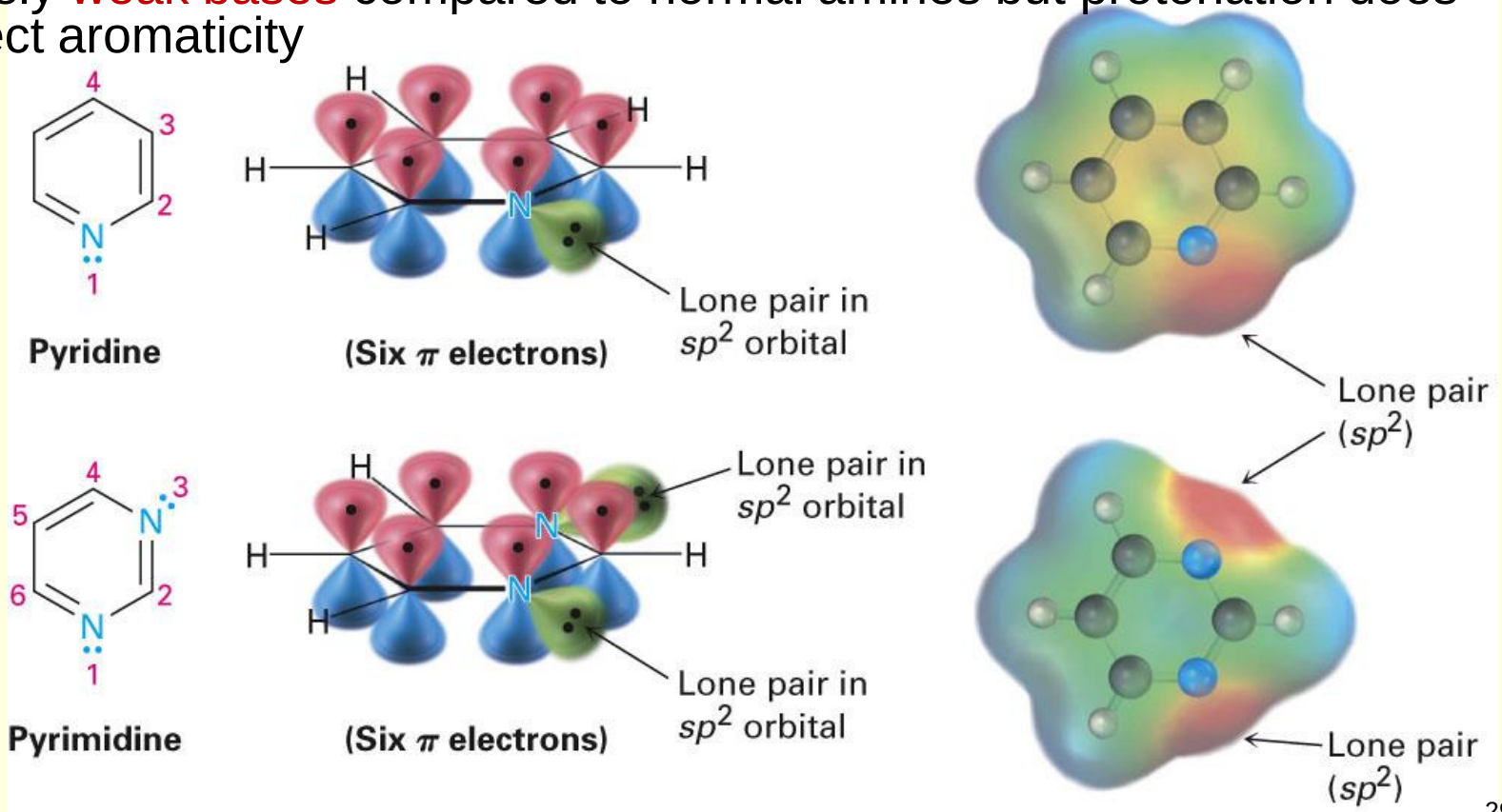
Aromatic (stable)

15.5 Aromatic Heterocycles:

- **Heterocyclic** compounds contain elements other than carbon in a ring, such as N,S,O,P
- Aromatic compounds can have **elements other than C** in the ring
- There are many heterocyclic aromatic compounds and many are very common
- Cyclic compounds that contain only carbon are called carbocycles (not homocycles)
- Nomenclature is specialized

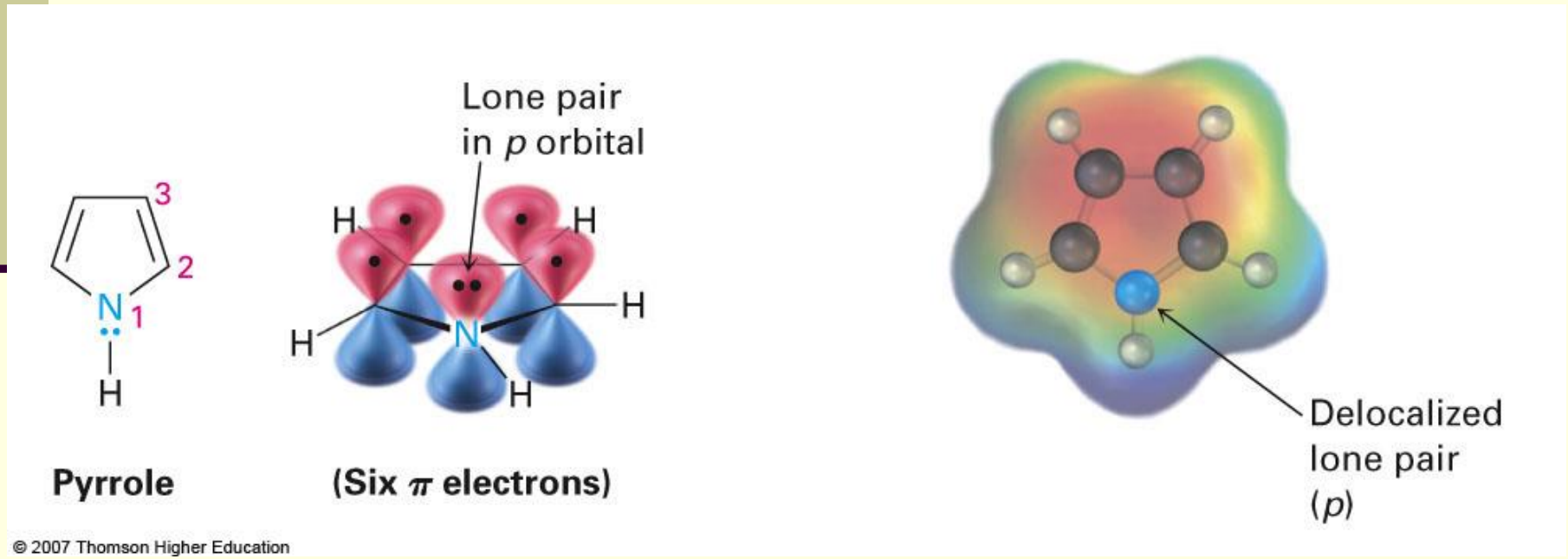
Pyridine & Pyrimidine

- **6** membered heterocycle with 1 **N** (pyridine) and 2 N's (in pyrimidine)
- 4n+2 π e's resembles benzene (6 electrons)
- The **N** lone pair e-s not part of aromatic system (perpendicular orbital)
- Relatively weak bases compared to normal amines but protonation does not affect aromaticity



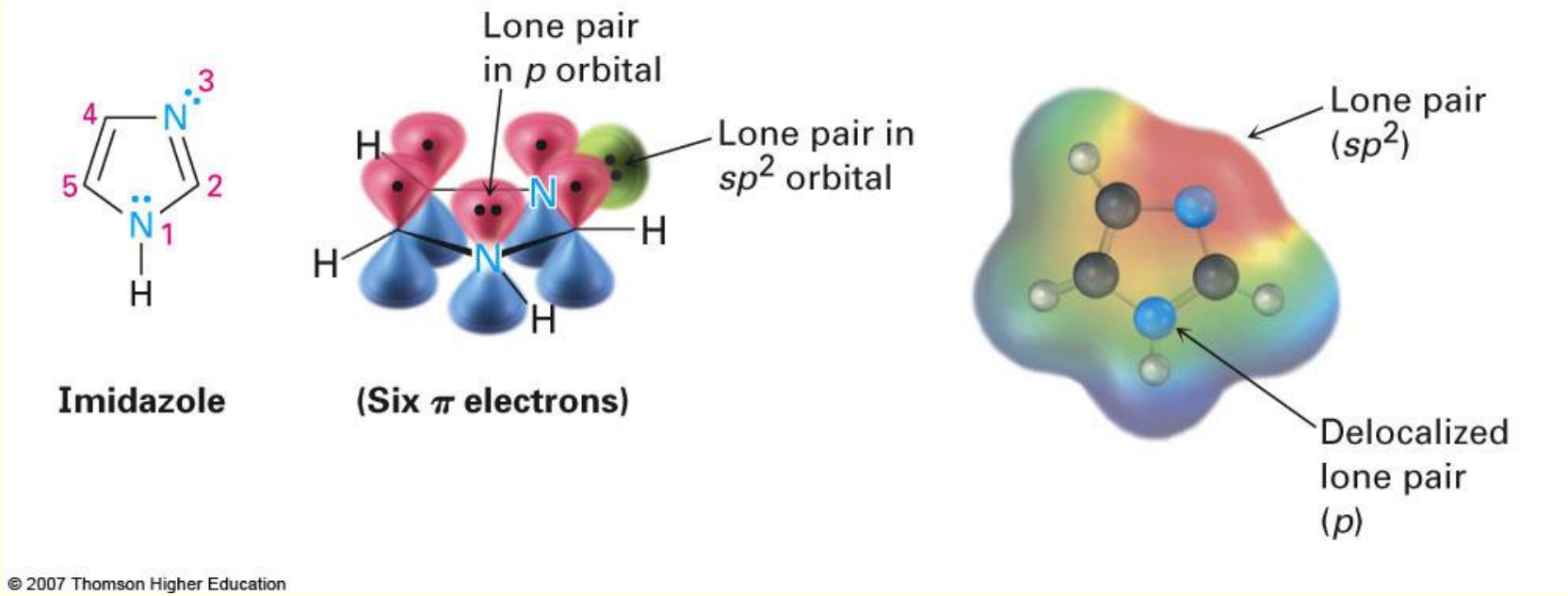
Pyrrole

- A 5-membered heterocycle with one **N**
- 4n+2 π e's resembles that of cyclopentadienyl anion
- Four sp^2-hybridized C's with 4 *p* orbitals perpendicular to ring and 4 p e-'s
- **N** atom is sp^2-hybridized, and lone pair e-s occupies a *p* orbital (6 π e-s)
- Since lone pair electrons are in the aromatic ring, protonation destroys aromaticity, making pyrrole a very weak base



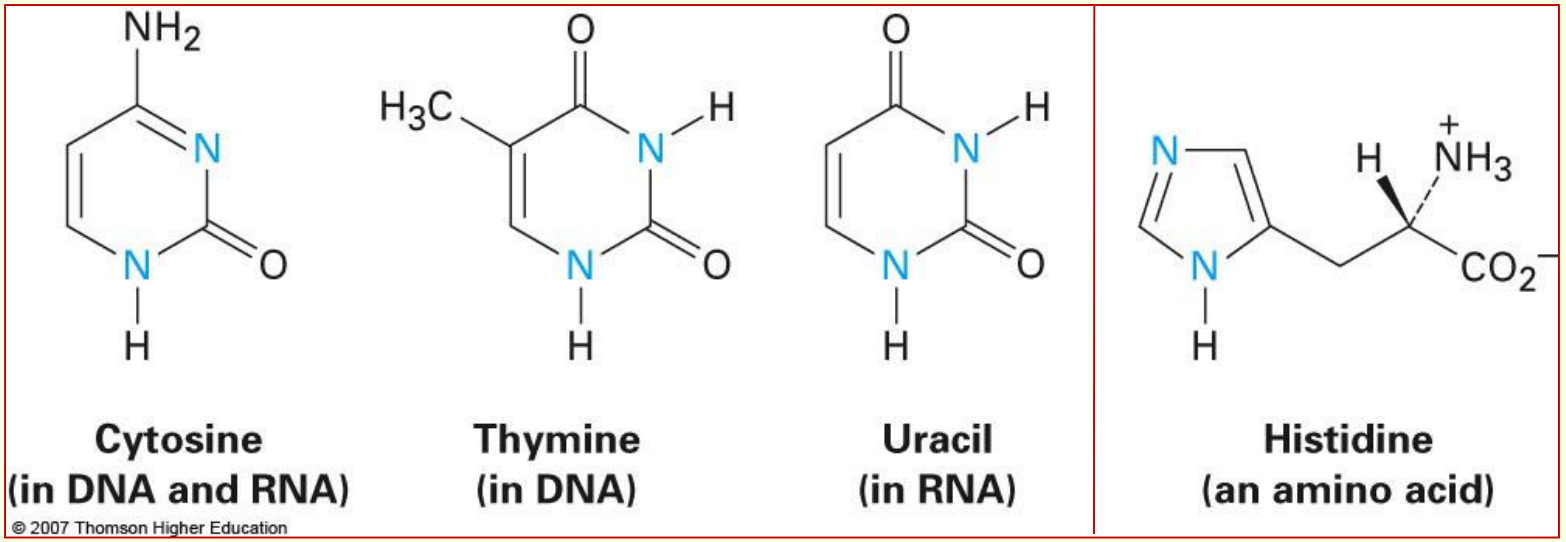
Imidazole

- A 5-membered heterocycle with 2 **N's**
- 4n+2 π e's resembles that of cyclopentadienyl anion
- Four *sp*^{2}-hybridized C's with 4 *p* orbitals perpendicular to ring and 4 p e-'s
- **N** atoms *sp*^{2}-hybridized, and 1 lone pair e-s occupies a *p* orbital (6 π e-s)
- One lone pair electrons are in the aromatic ring, second lone pair perpendicular to ring so can be protonated without destroying aromaticity



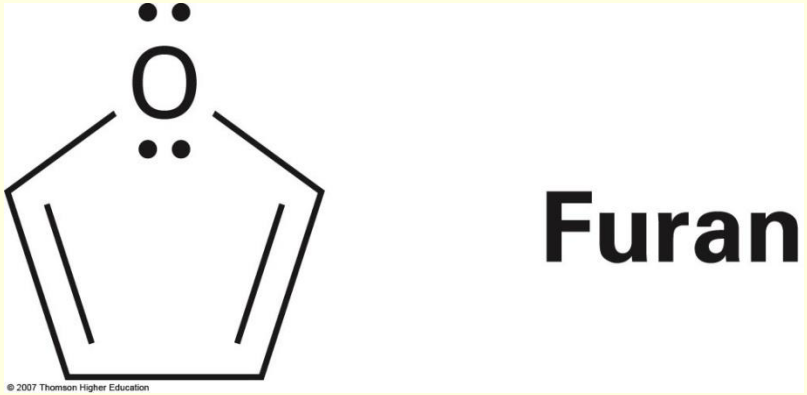
N Heteroaromatics in Biochemistry

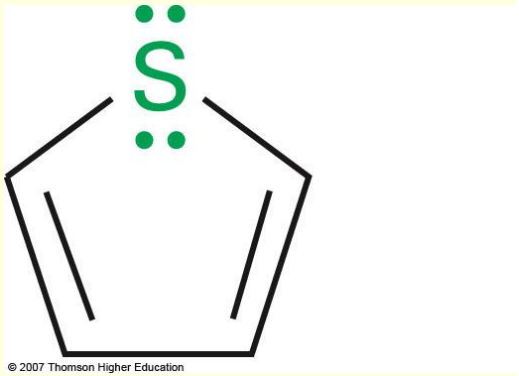
Pyrimidines:

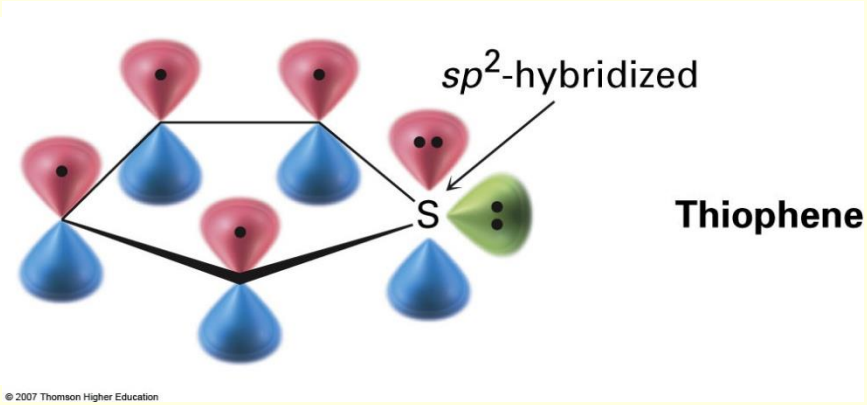


An Imidazole Amino Acid:

Other Aromatic Heterocycles

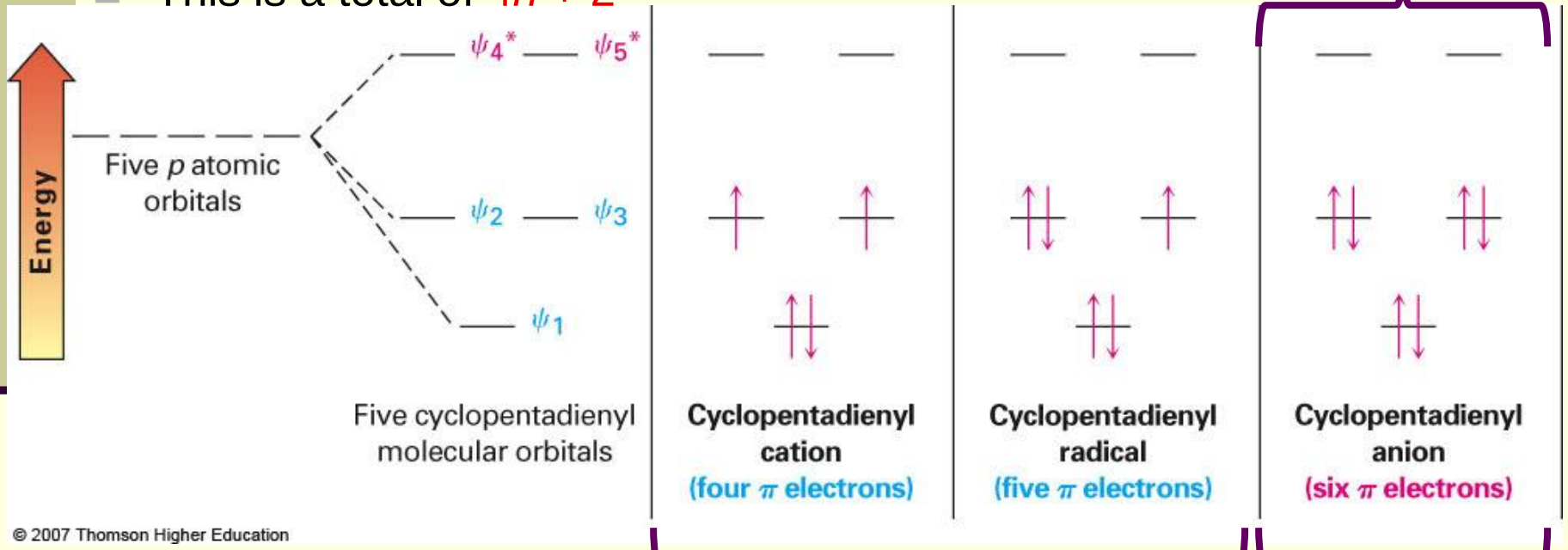






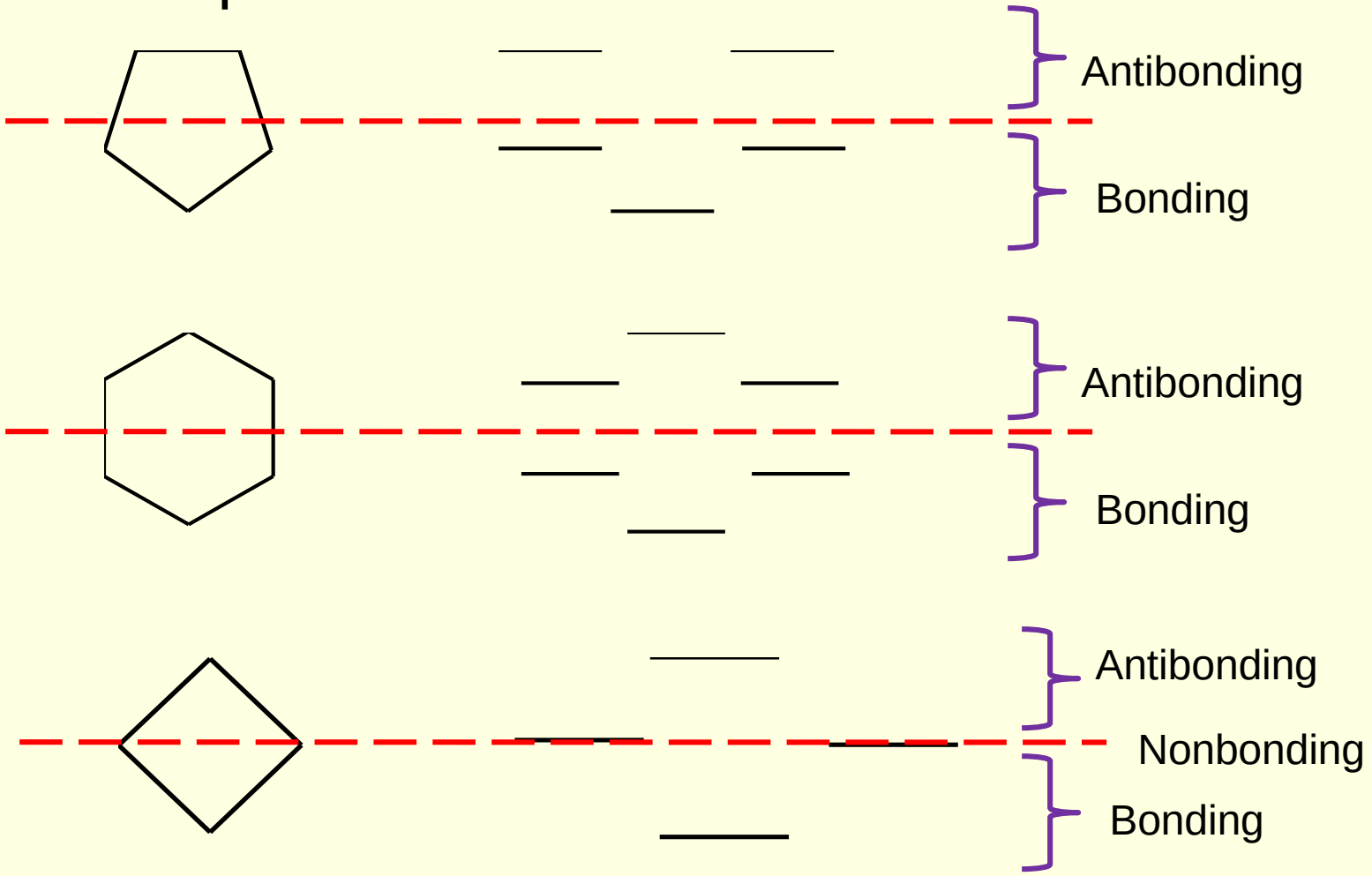
15.6 Why 4n +2?

- When electrons fill the various molecular orbitals, it takes two electrons (one pair) to fill the lowest-lying orbital and four electrons (two pairs) to fill each of *n* succeeding energy levels
- This is a total of *4n + 2*

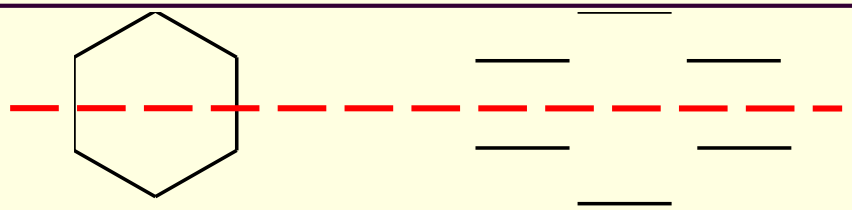


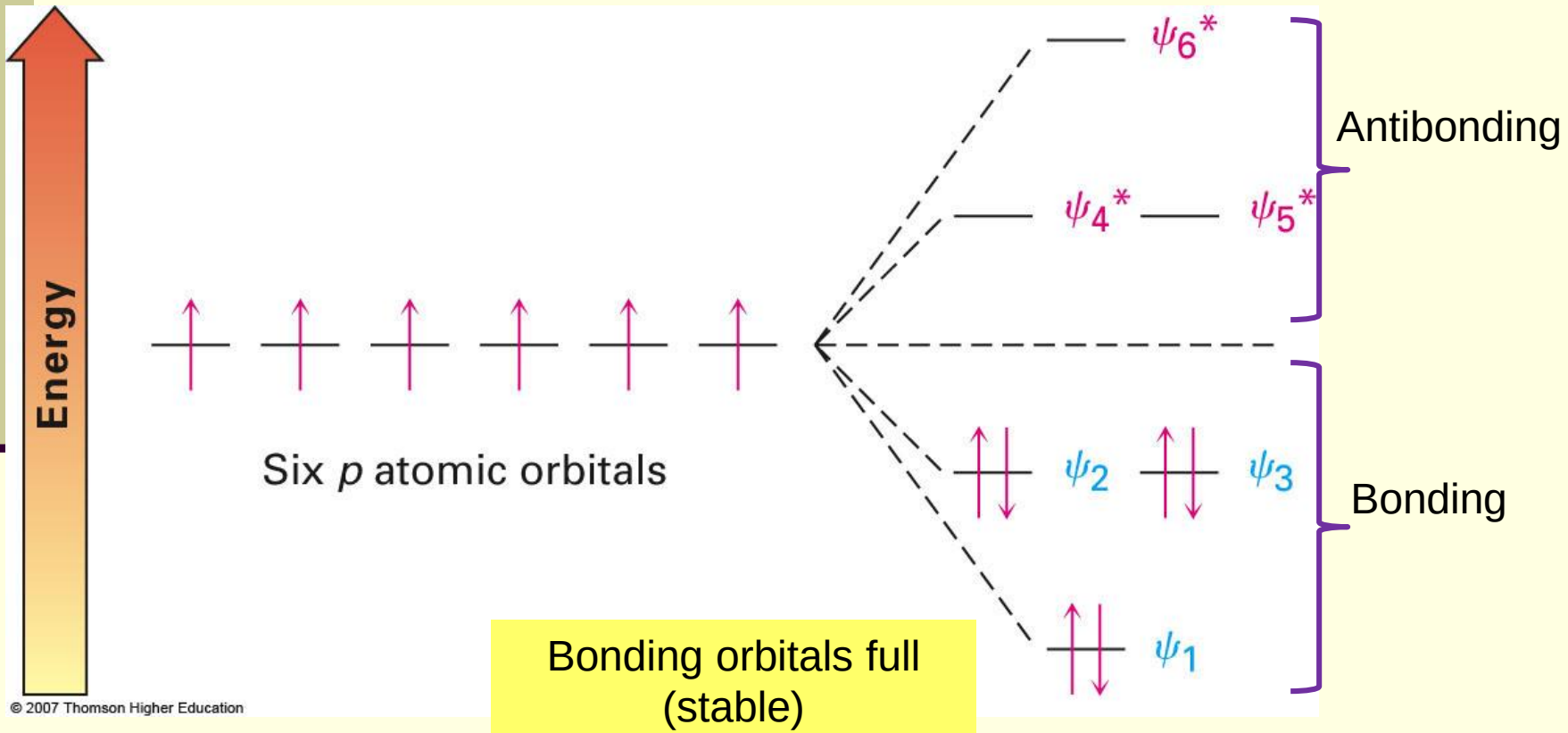
Why 4n +2?

- Template for molecular orbitals:



Why 4n +2?

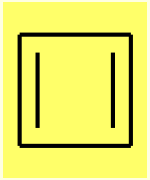


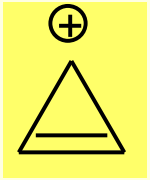


Bonding orbitals full (stable)

Learning Check:

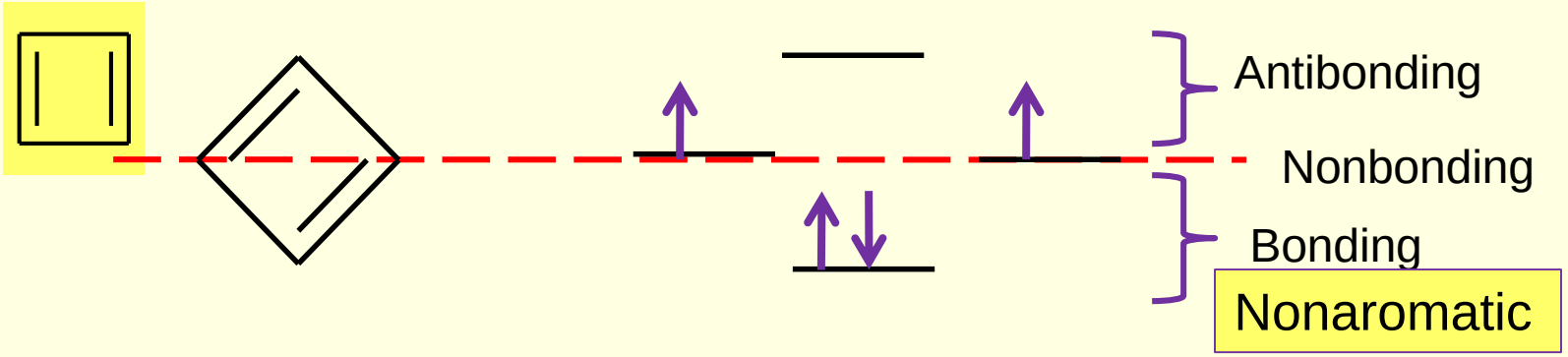
- Show using molecular orbitals whether the following are aromatic.

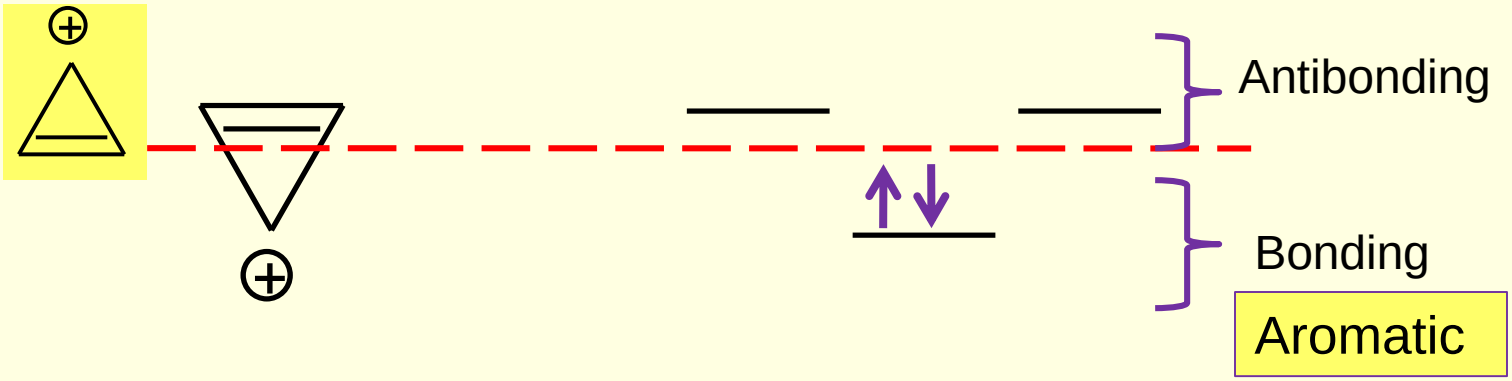




Solution:

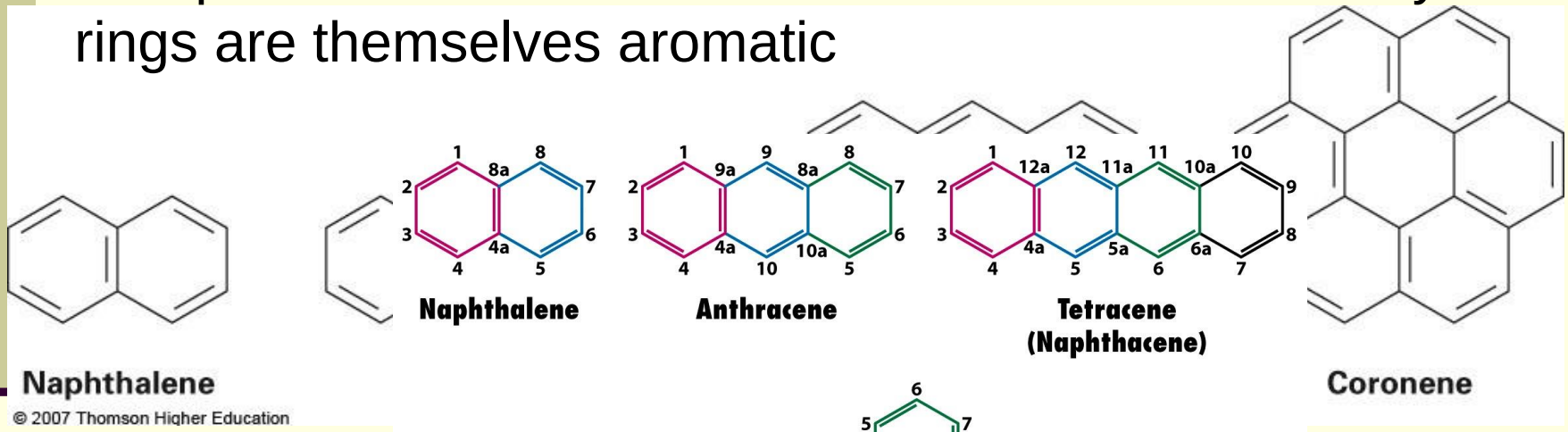
- Show using molecular orbitals whether the following are aromatic.

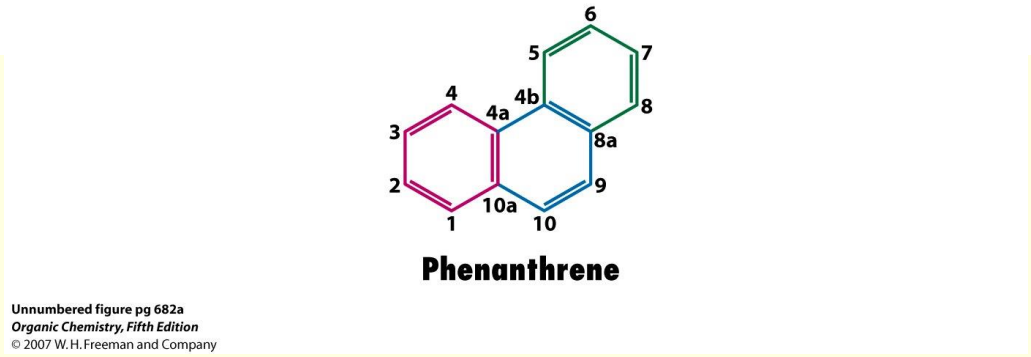




Polycyclic Aromatic Compounds

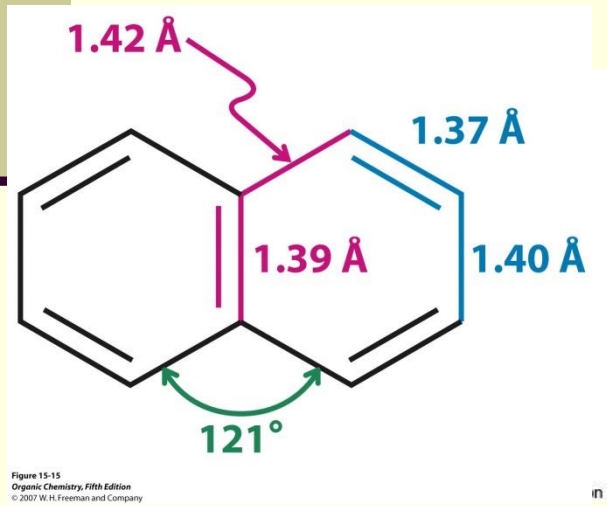
- Aromatic compounds can have rings that share a set of carbon atoms (fused rings)
- Compounds from fused benzene or aromatic heterocycle rings are themselves aromatic

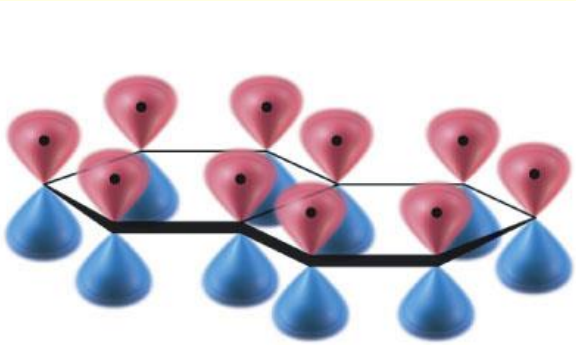


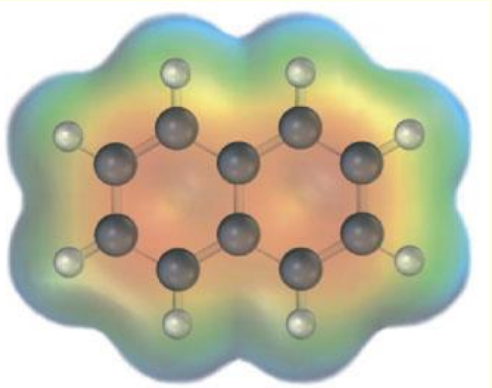


Naphthalene Orbitals

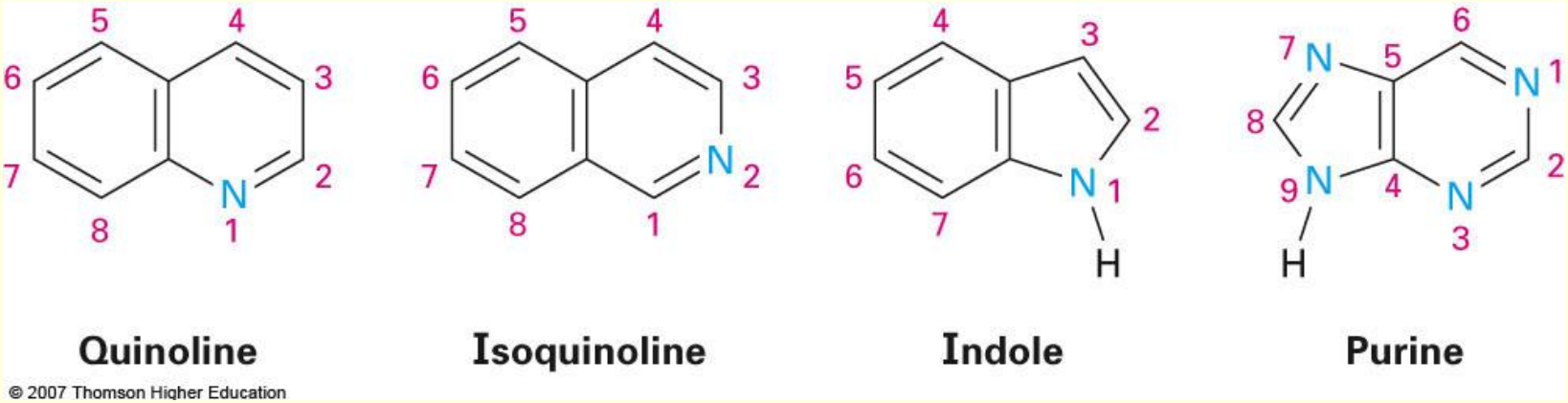
- Three resonance forms and delocalized electrons





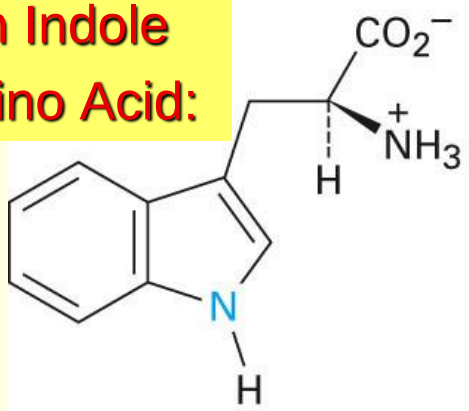


Polycyclic Hetero-aromatics



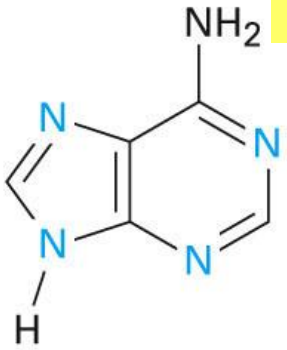
N Polycyclic-hetero-aromatics in Biochem

An Indole Amino Acid:



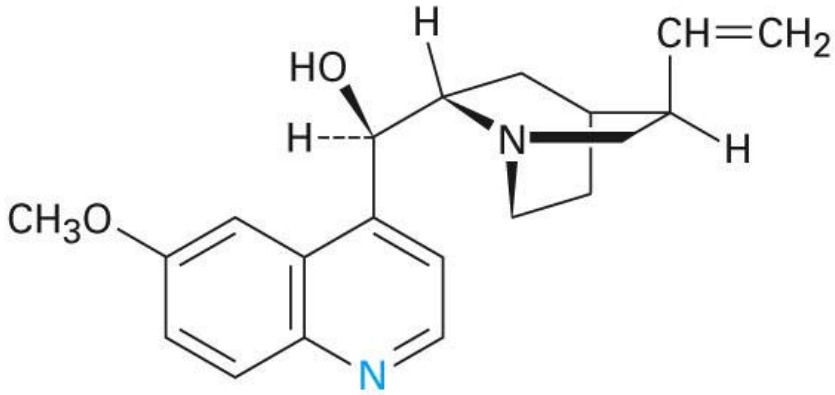
Tryptophan
(an amino acid)

Purines:



Adenine
(in DNA and RNA)

Guanine
(in DNA and RNA)

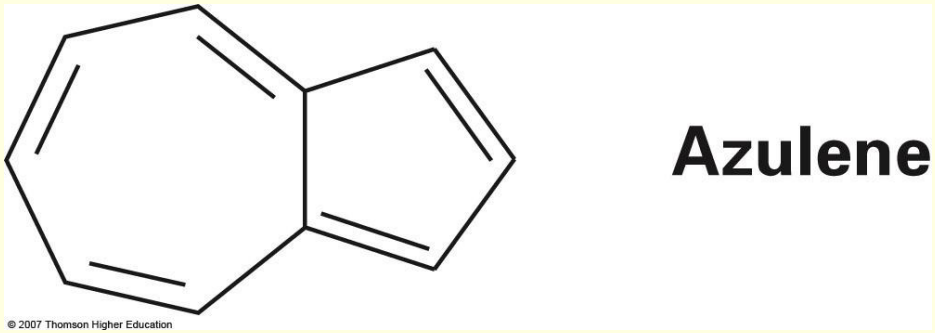


A Quinoline:

Quinine
(an antimalarial agent)

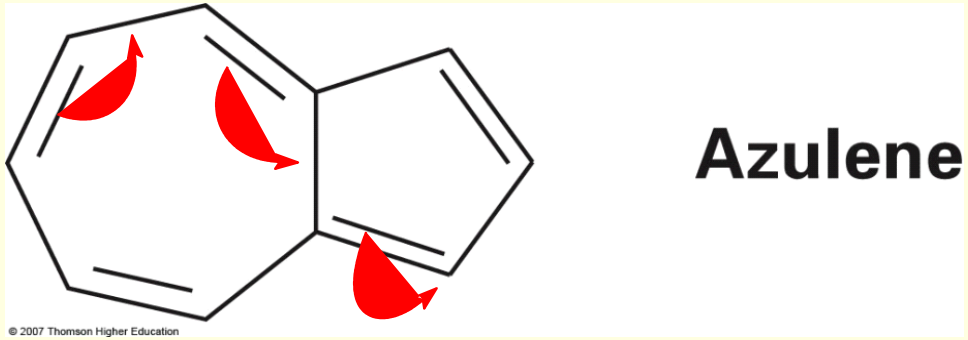
Learning Check:

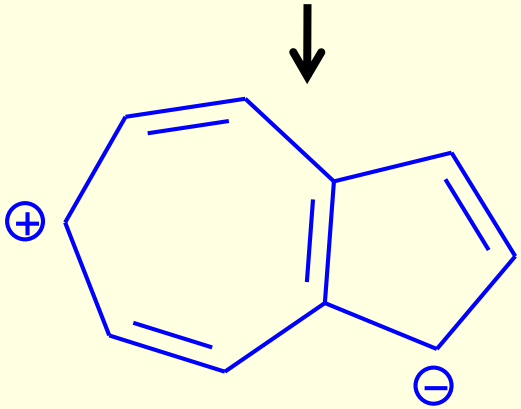
- **Azulene**, a beautiful blue hydrocarbon, is an isomer of naphthalene. Azulene is an aromatic compound with a large dipole. Draw a resonance form to show this.



Solution:

- **Azulene**, a beautiful blue hydrocarbon, is an isomer of naphthalene. Azulene is an aromatic compound with a large dipole. Draw a resonance form to show this.

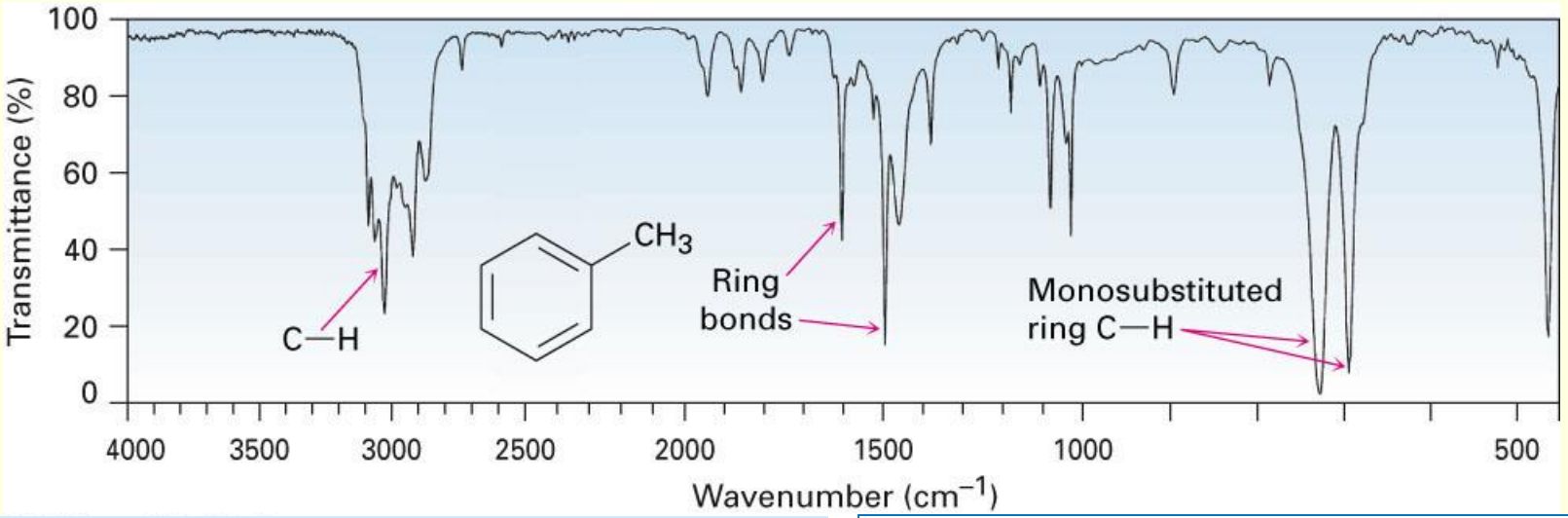




Forms 2 stable aromatic ions

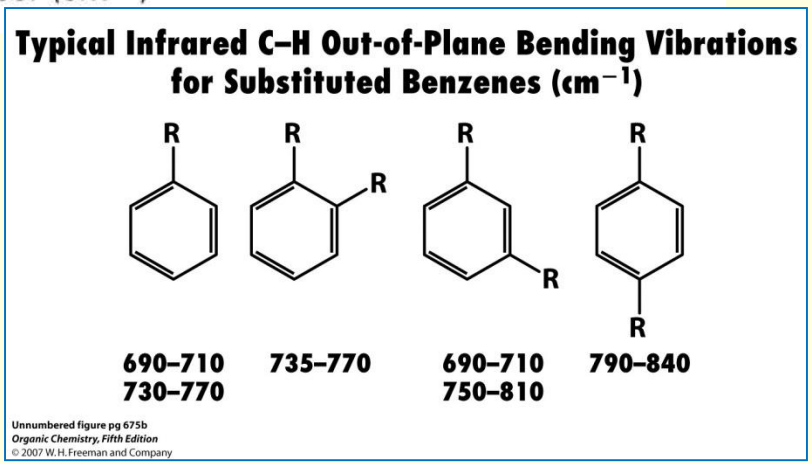
15.8 IR: Spectroscopy of Aromatic Compounds

- IR: Aromatic ring C–H stretching at 3030 cm^{-1} & peaks 1450 -1600 cm^{-}



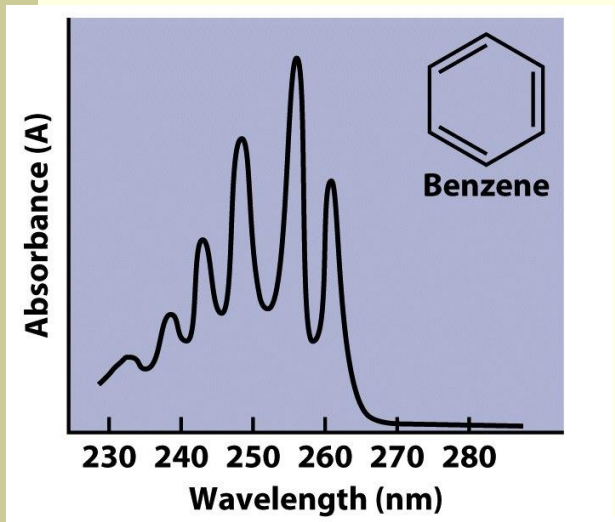
The IR spectra of benzene and its derivatives have characteristic bands at:

- •3030 cm^{-1} phenyl-H stretching
- •1500-2000 cm^{-1} aromatic C-C stretching
- •650-1000 cm^{-1} C-H out of plane bending

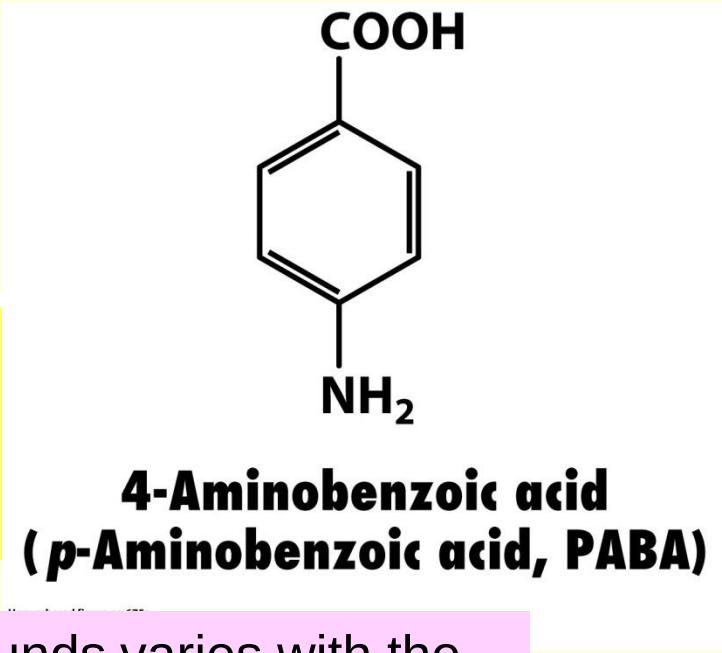


UV: Spectroscopy of Aromatic Compounds

- UV: Peak near 205 nm and a less intense peak in 255-275 nm range



Simple substituted benzenes absorb between 250 and 290 nm.

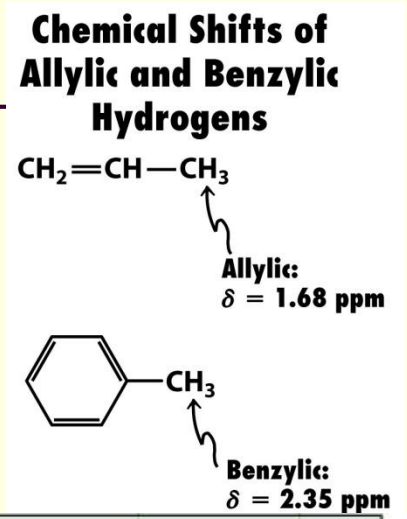


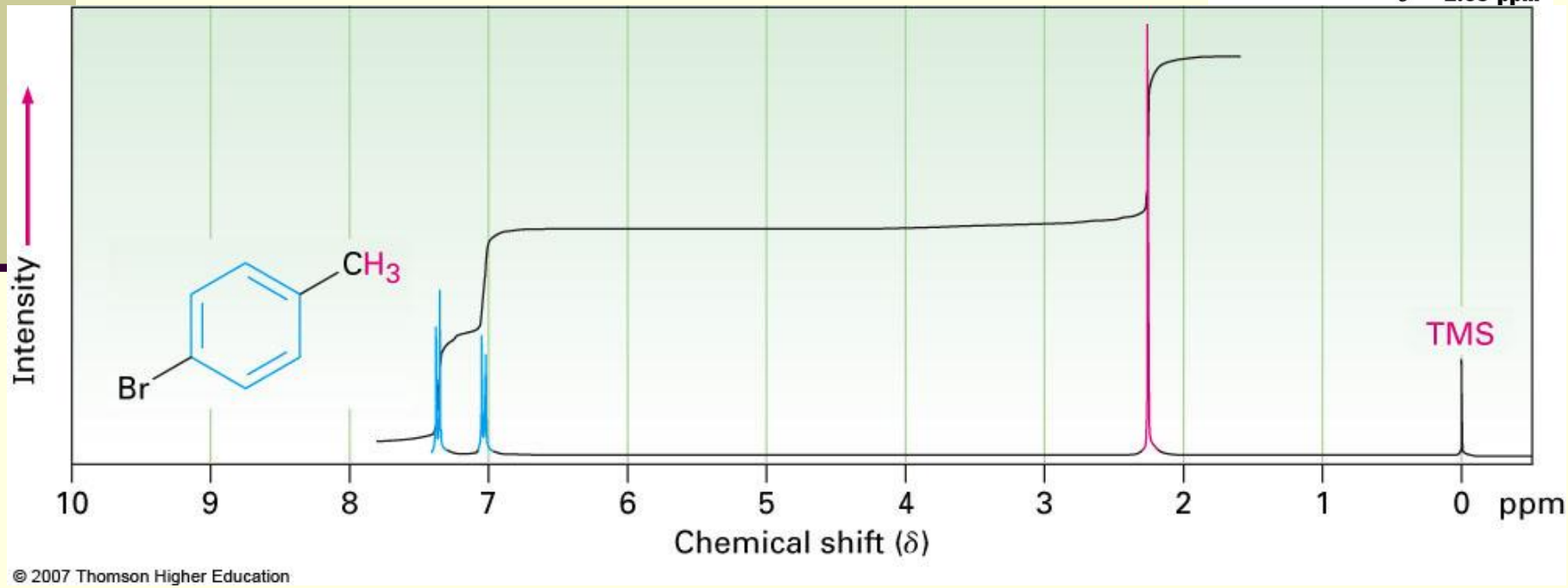
4-Aminobenzoic acid (PABA) has λ_{max} of 289 nm and a high extinction coefficient (18,600). It is used in sunscreen lotions to filter out harmful UV light in this wavelength region.

The electronic spectra of aromatic compounds varies with the introduction of substituents (useful in designing dye molecules).

^{1}H NMR Spectroscopy of Aromatics

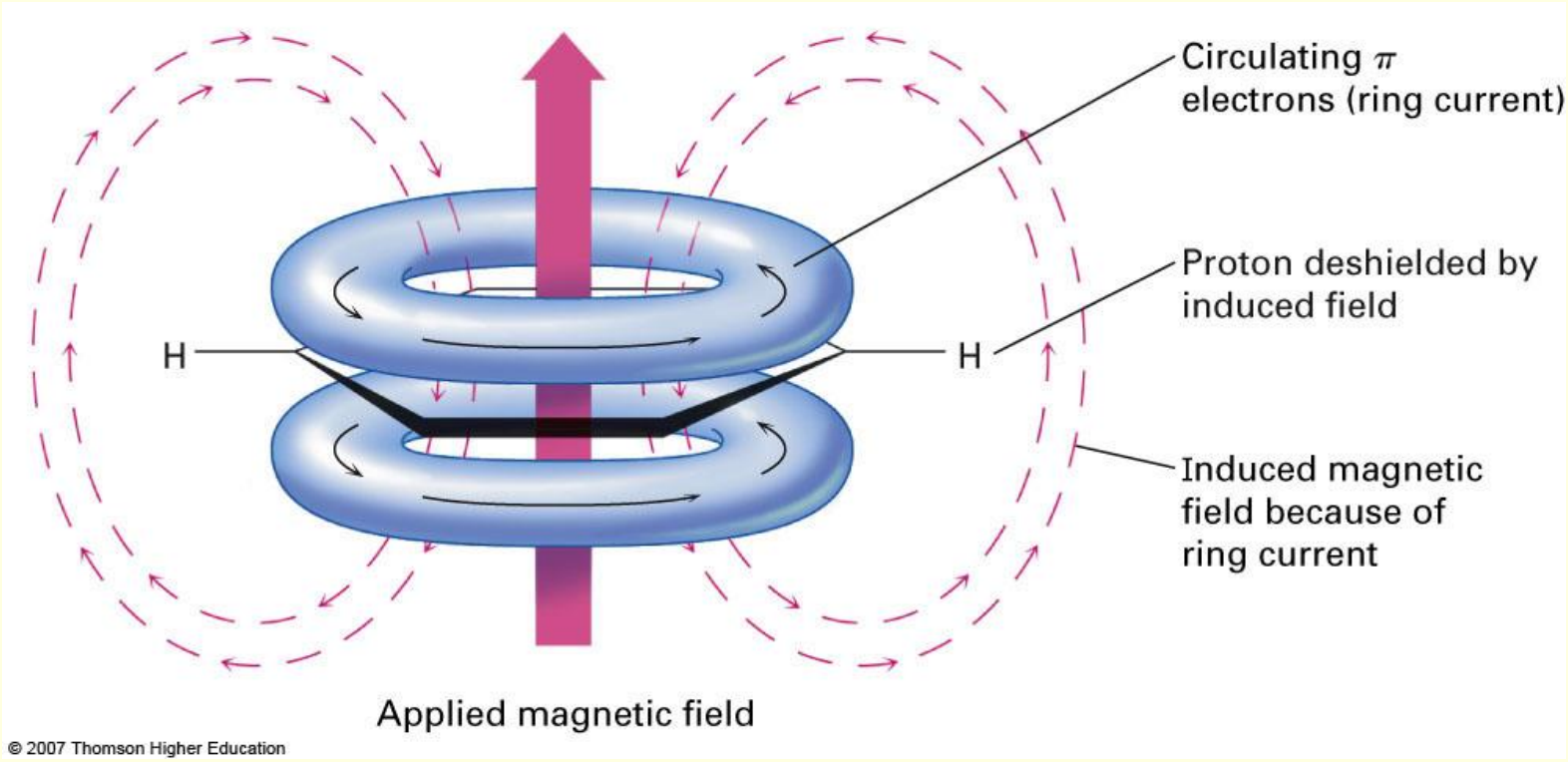
- ^{1}H NMR: Aromatic H's strongly deshielded by ring and absorb between δ 6.5 and δ 8.0



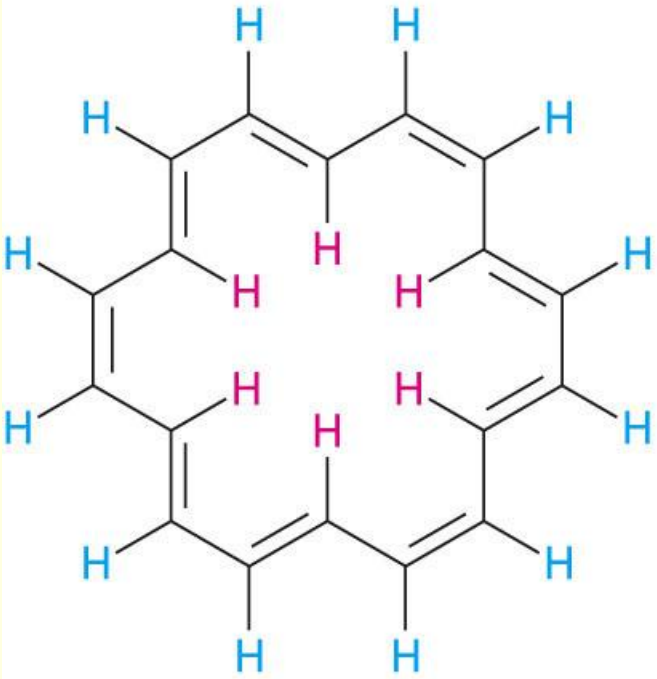


Ring Currents

- Aromatic ring oriented perpendicular to a strong magnetic field, delocalized π electrons producing a small local magnetic field
  - *Opposes* applied field in middle of ring but *reinforces* applied field outside of ring



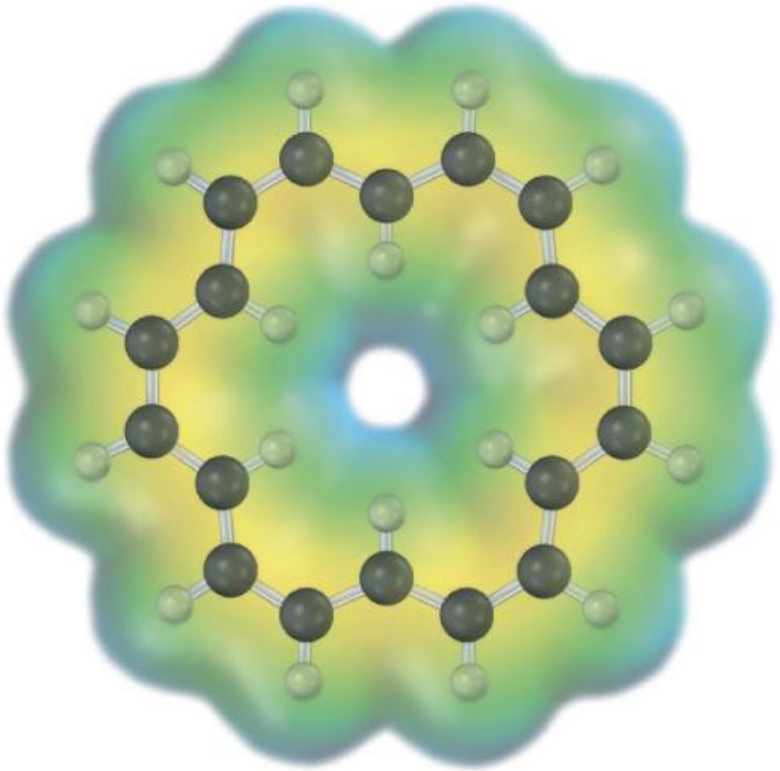
Ring Currents



[18]Annulene

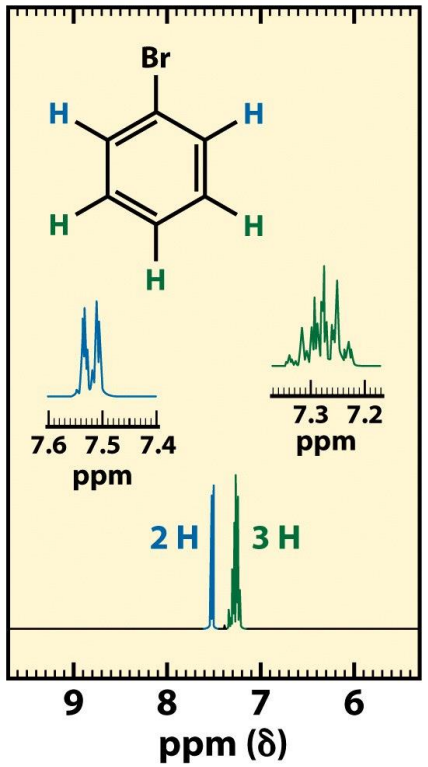
Inside H: −3.0 δ

Outside H: 9.3 δ

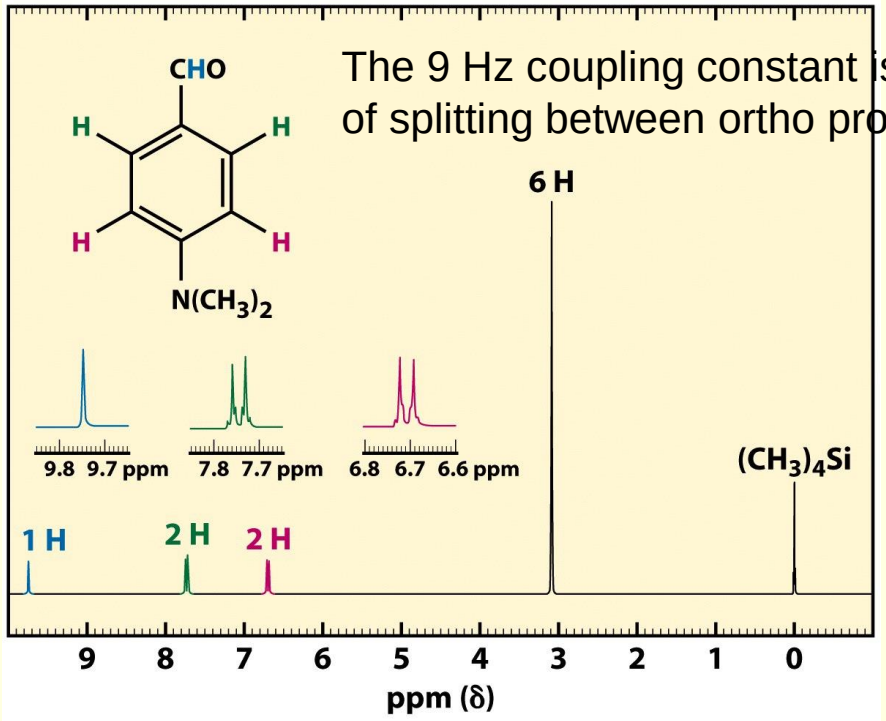


^{1}H NMR Spectroscopy of Aromatics

- H NMR Peak pattern is characteristic of positions of substituents



Monosubstituted



The 9 Hz coupling constant is typical of splitting between ortho protons.

Para – Disubstituted
dd (doublet of doublets)

^{1}H NMR Spectroscopy of Aromatics

Aromatic Coupling Constants

J_{ortho} = 6–9.5 Hz
J_{meta} = 1.2–3.1 Hz
J_{para} = 0.2–1.5 Hz

3 types of coupling can be seen in spectrum of 1-methoxy-2,4-dinitrobenzene (2,4-dinitroanisole).

- **Ortho hydrogen** (to methoxy)

  Doublet, δ=7.23 ppm, J = 9 Hz

- Hydrogen flanked by nitro groups

  Doublet, δ=8.76 ppm, J = 3 Hz

- **Remaining ring hydrogen**

  Doublet of doublets, δ=8.45 ppm,

Para coupling between C3 and C6 is too small to be resolved.

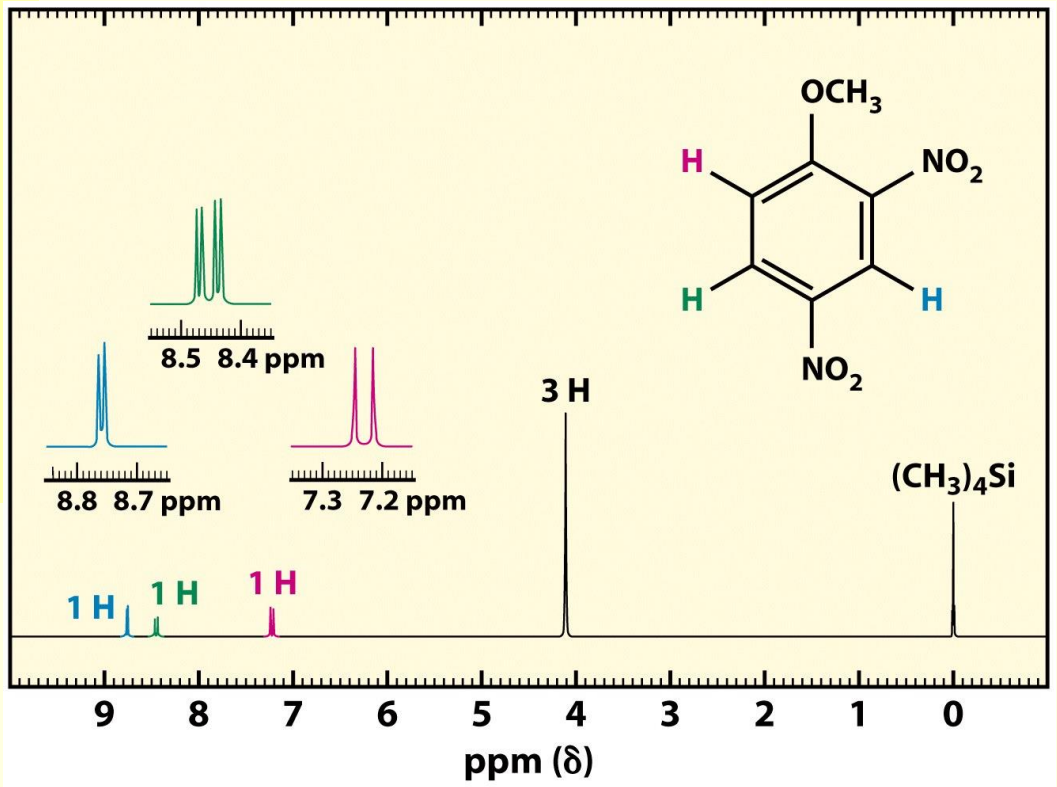
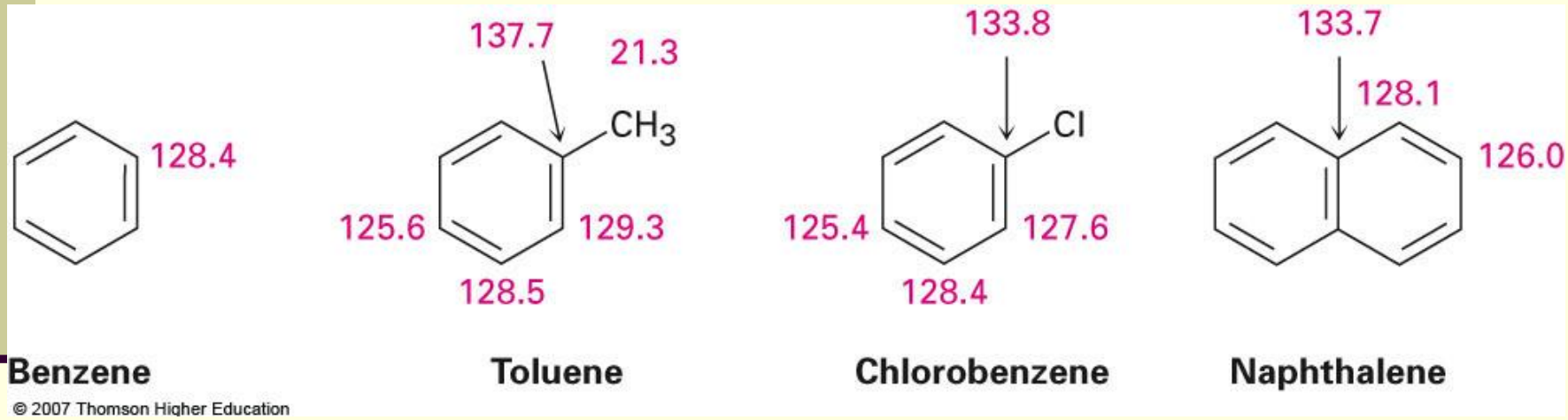


Figure 15-12
Organic Chemistry, Fifth Edition

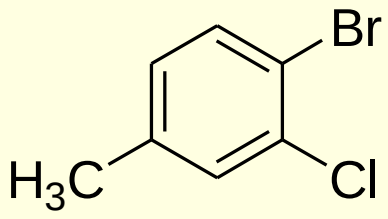
^{13}C NMR of Aromatic Compounds

- Carbons in aromatic ring absorb at δ 110 to 140
- Shift is distinct from alkane carbons but in same range as alkene carbons

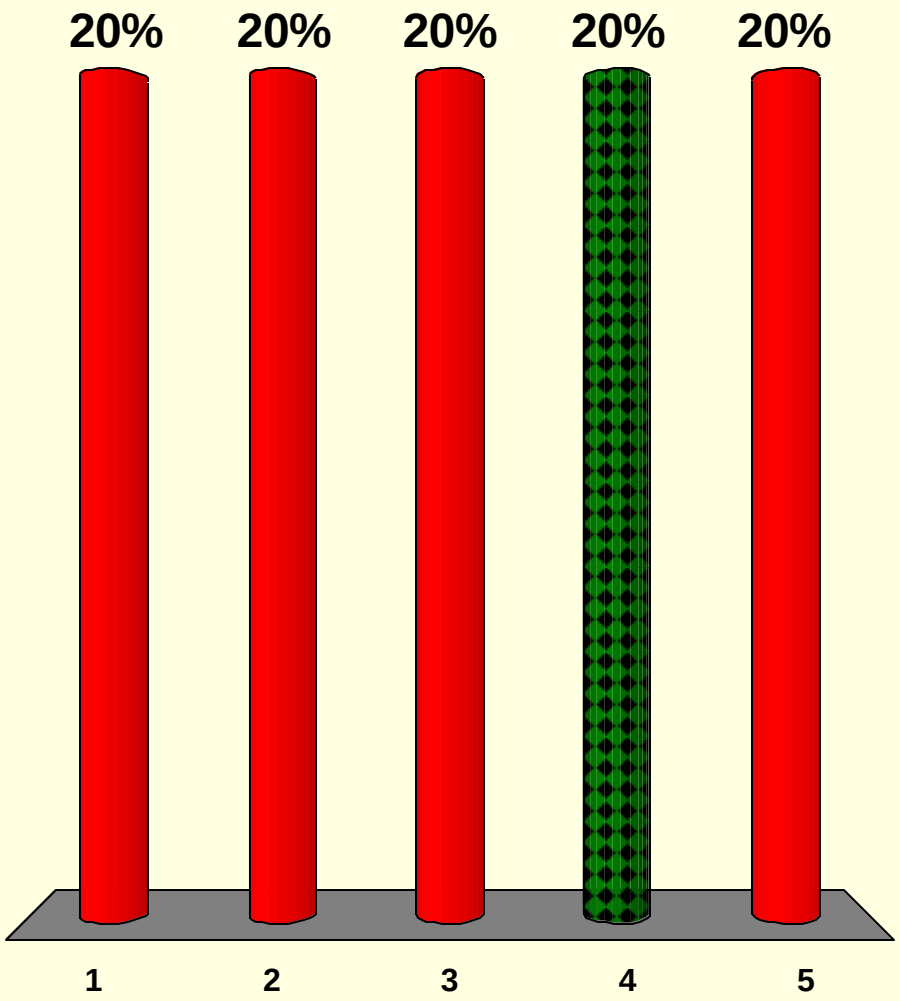


The ^{13}C NMR spectra of benzene derivatives not greatly affected by ring current shifts, since the induced ring current flows directly above and below the ring carbons.

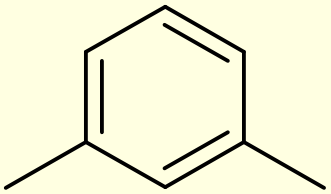
What is the IUPAC name of the following compound?



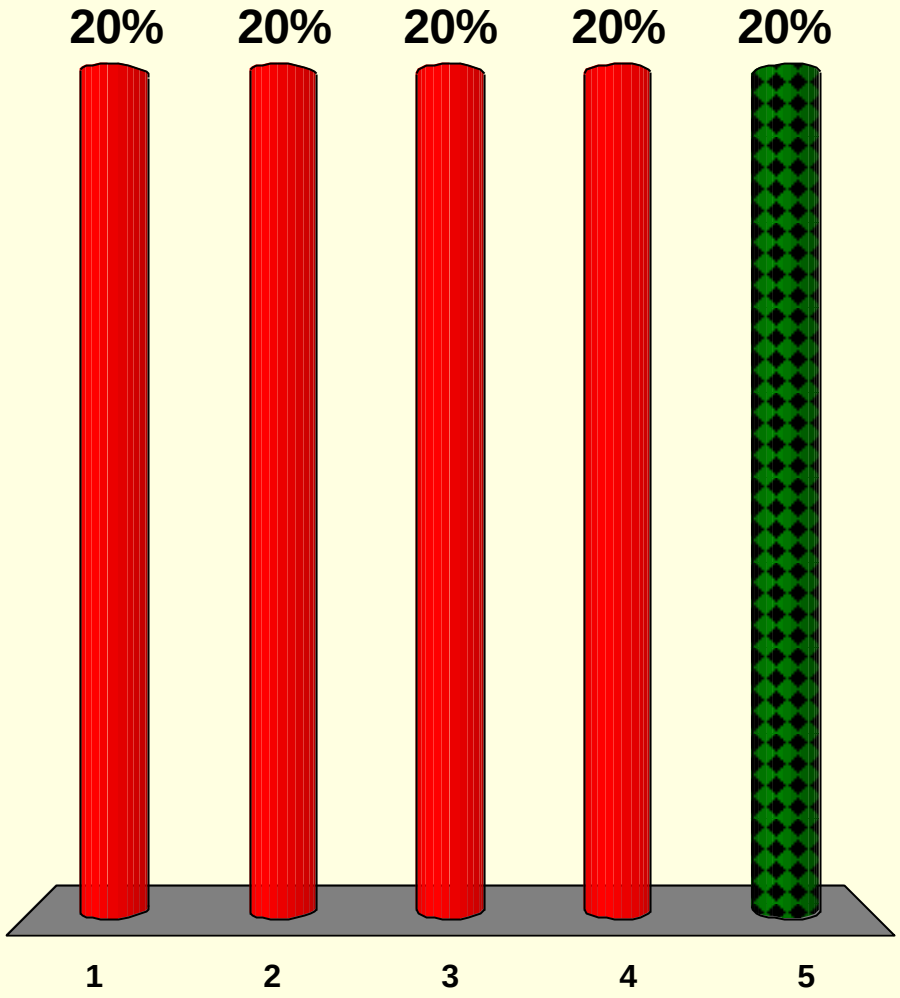
1. 4-bromo-3-chloro-1-methylbenzene
2. 1-chloro-2-bromo-5-methylbenzene
3. 1-bromo-2-chlorotoluene
4. 4-bromo-3-chlorotoluene
5. 2-bromo-1-chlorotoluene



Which of the following names incorrectly describes the relationship between the substituents for the derivative shown below?

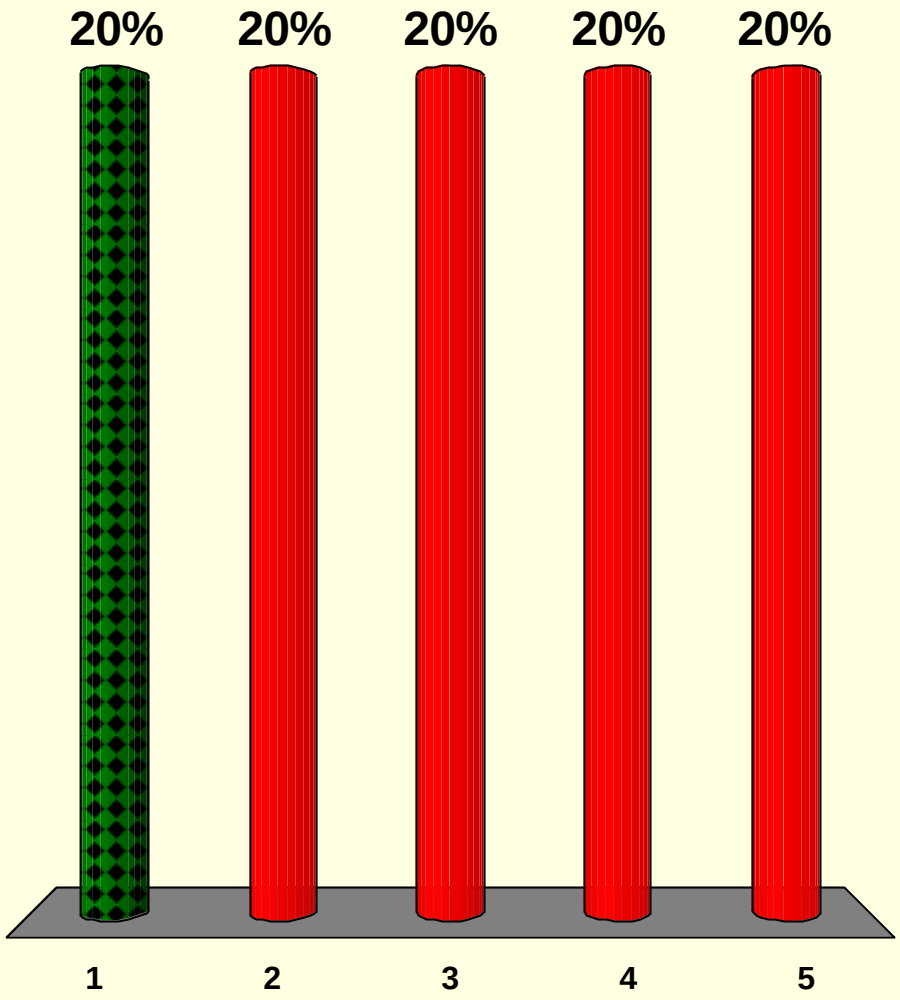


1. *m*-xylene
2. 1,3-dimethylbenzene
3. 3-methyltoluene
4. *m*-methyltoluene
5. *ortho*-xylene

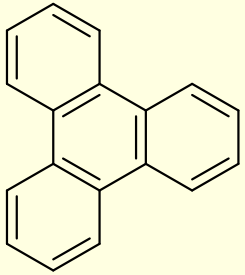


Which of the following **is not** a condition for aromaticity?

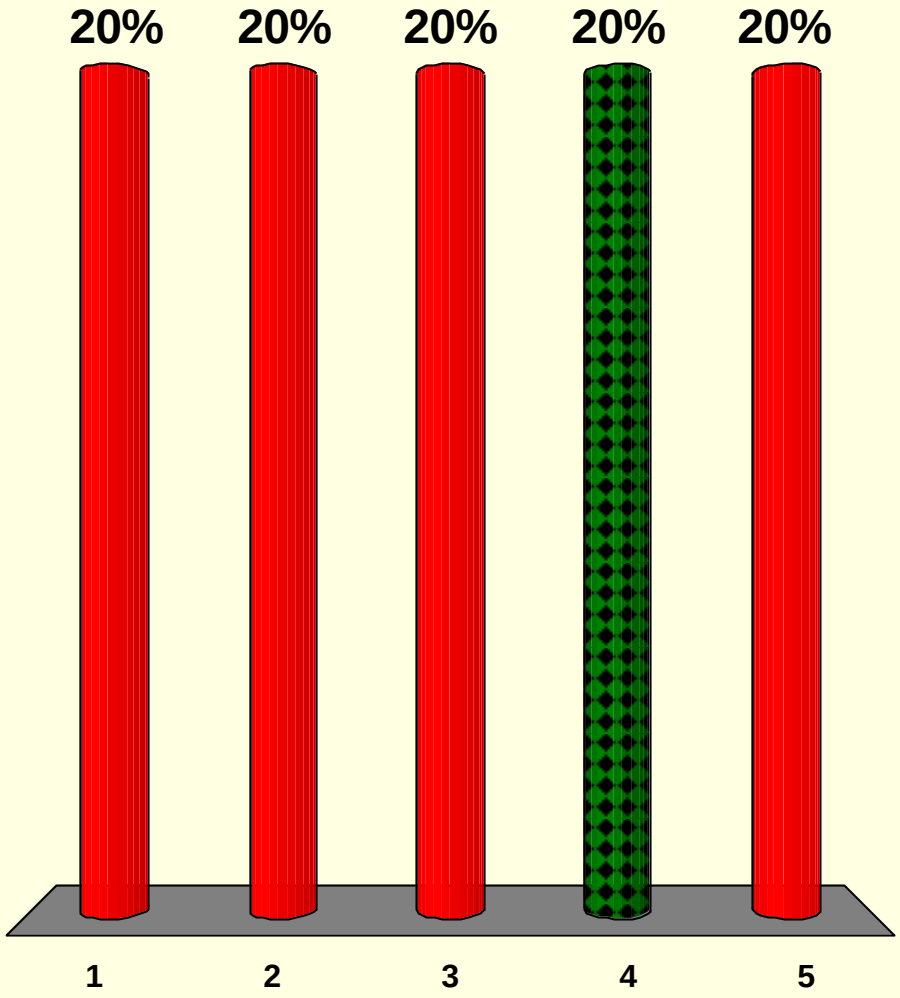
1. The molecule must be a 6-membered ring.
2. The molecule must have planar or nearly planar π system.
3. The molecule must have $(4n+2)$ π electrons in the ring.
4. The molecule must show ring currents effects in its NMR spectrum.
5. Each atom in the ring must contribute one *p* orbital to the system.



What is the name of the class of compounds to which the molecule shown belongs?

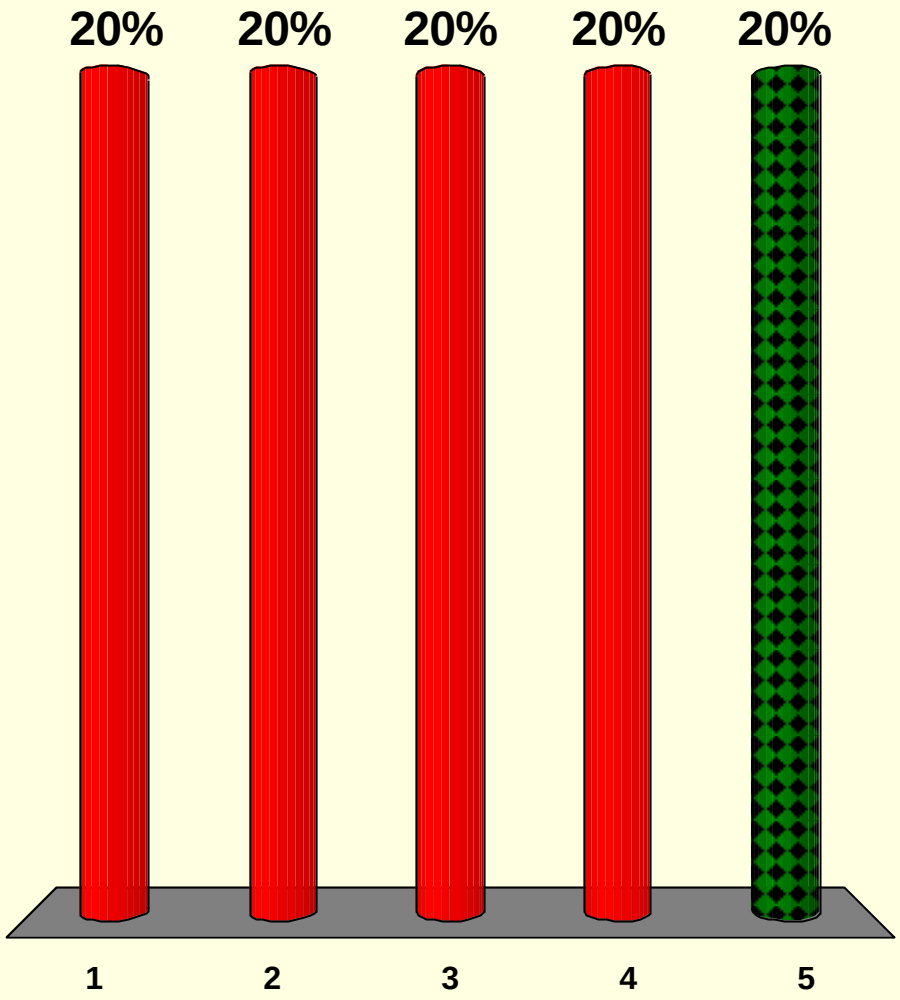


1. annulenes
2. heterocyclic aromatics
3. bicyclic compounds
4. polycyclic aromatic hydrocarbons
5. trisubstituted benzenes



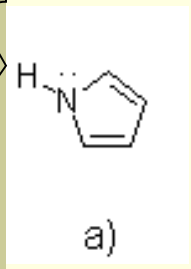
Which process would convert 1,3,5-cycloheptatriene into an aromatic substance?

1. an addition of one electron
2. a removal of one electron
3. an abstraction of a hydrogen atom
4. an abstraction of a proton
5. an abstraction of a hydride



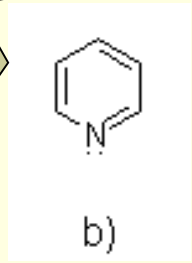
Which of the following compounds is not aromatic?

1.



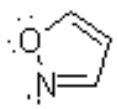
a)

2.



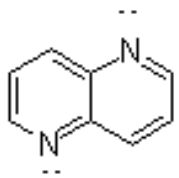
b)

3.



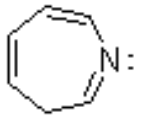
c)

4.

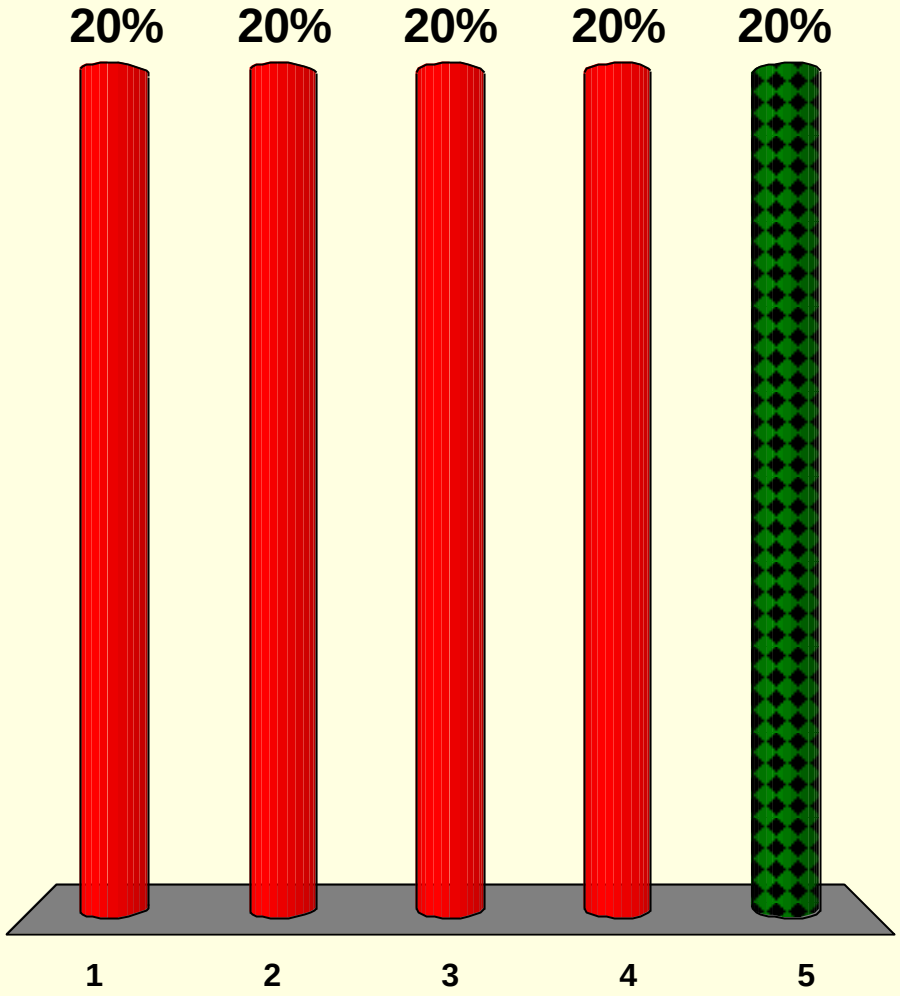


d)

5.

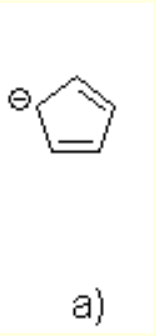


e)

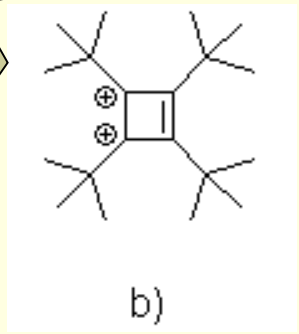


Which of the following compounds is antiaromatic?

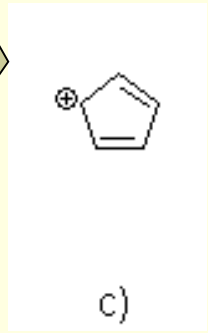
1.



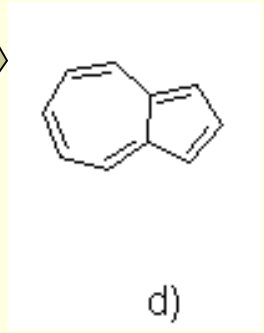
2.



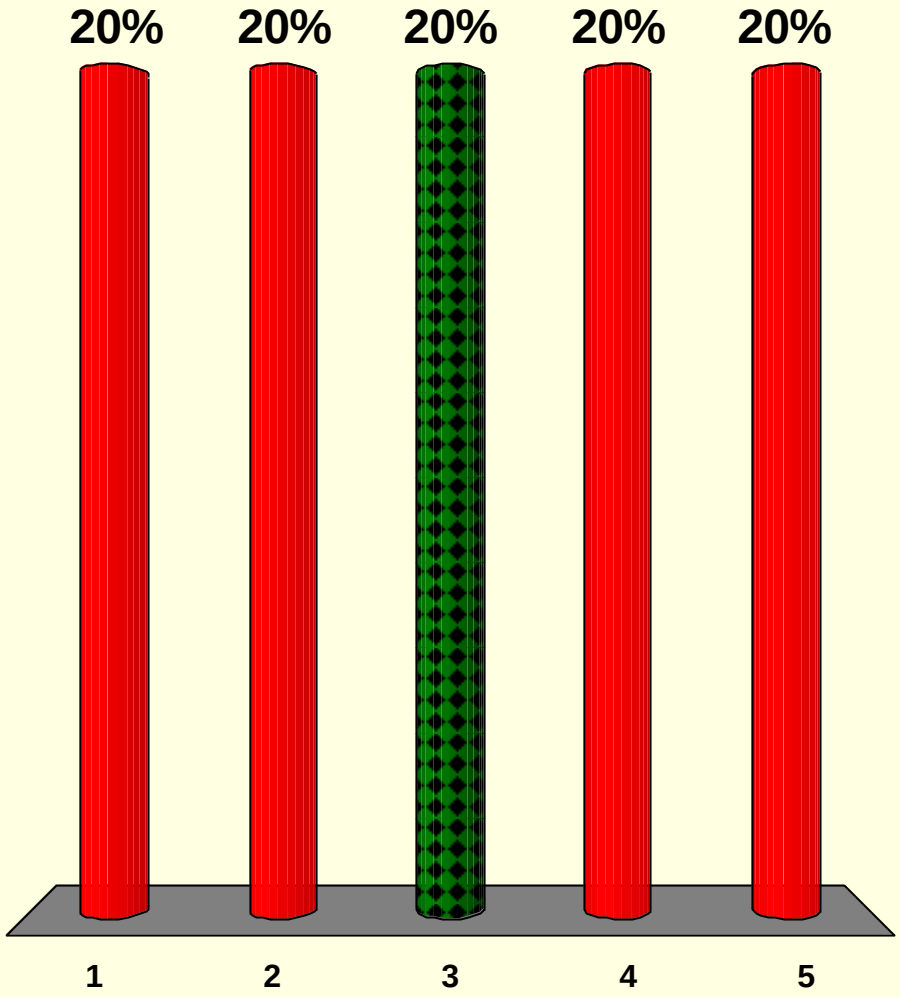
3.



4.



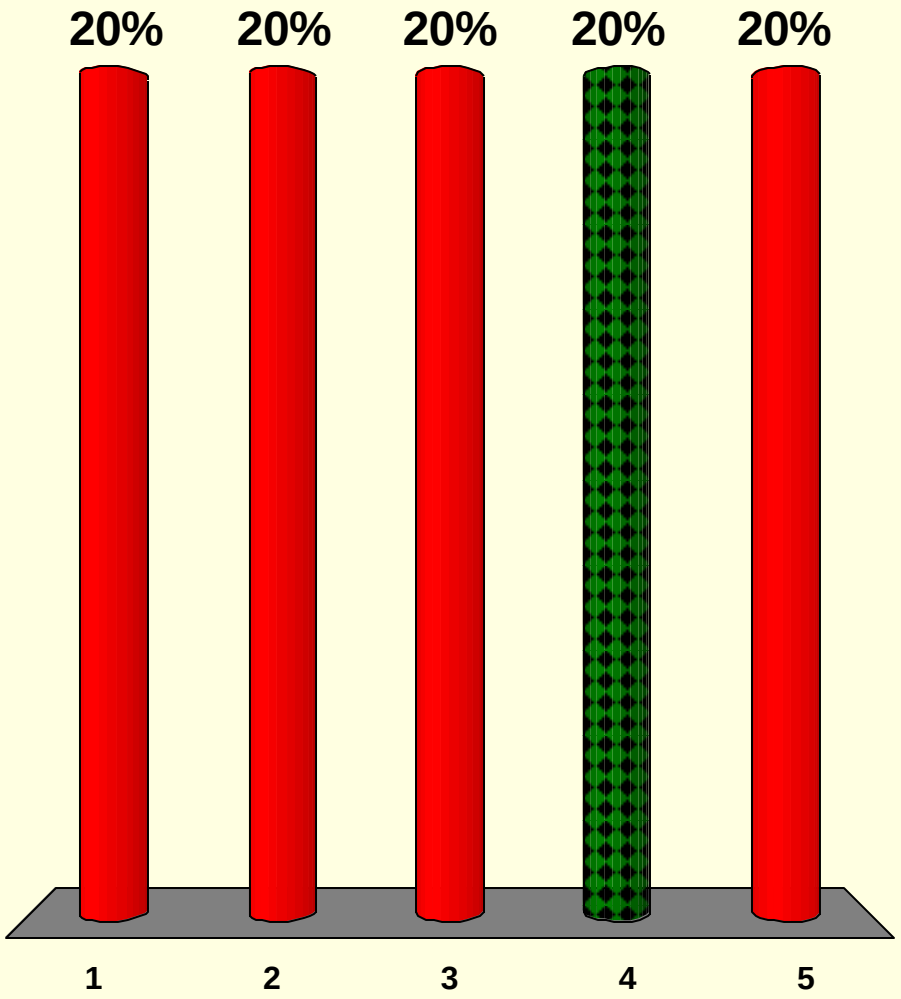
5.



The heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, and benzene are –28, -55, and –49 kcal/mol, respectively.

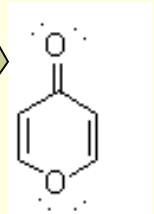
How much is benzene stabilized when compared to a hypothetical 1,3,5-cyclohexatriene?

1. 6 kcal/mol
2. 21 kcal/mol
3. 27 kcal/mol
4. 35 kcal/mol
5. 49 kcal/mol



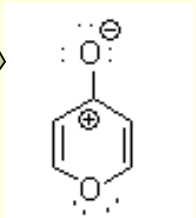
Which of the following resonance structures is not aromatic?

1.



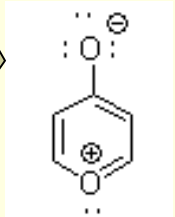
a)

2.



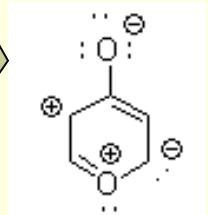
b)

3.



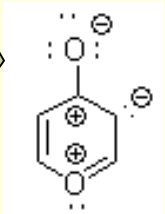
c)

4.

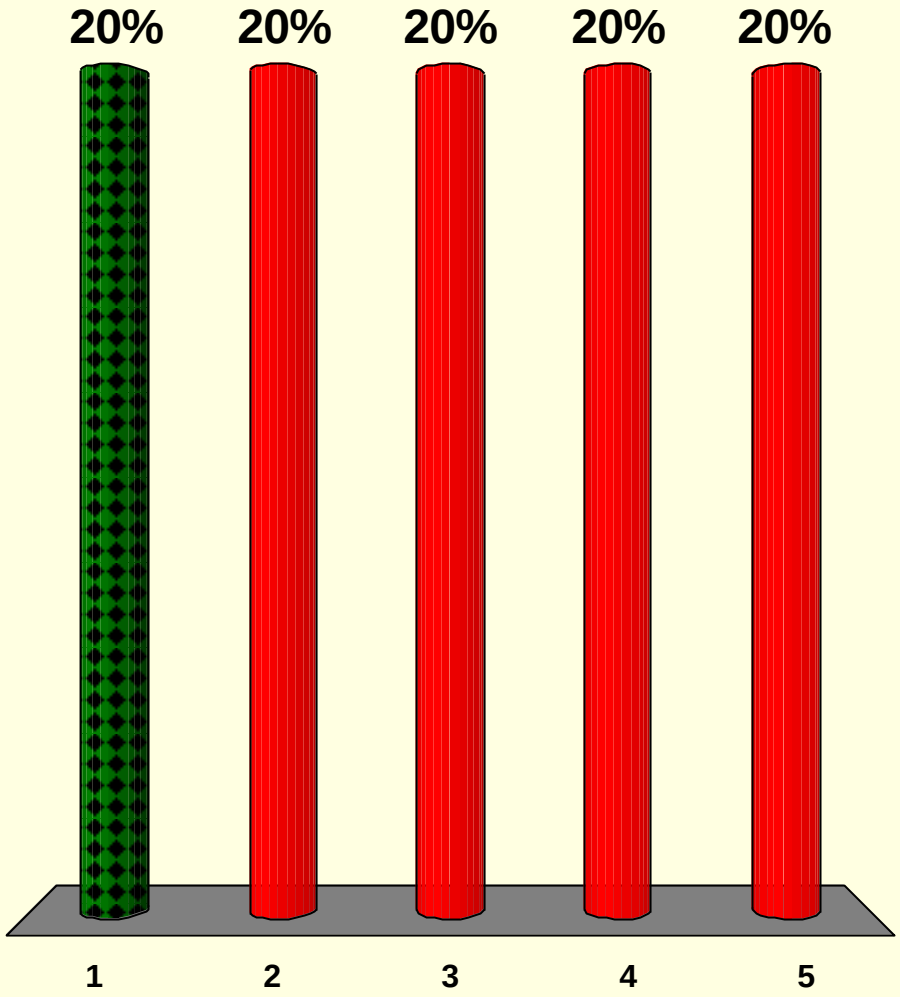


d)

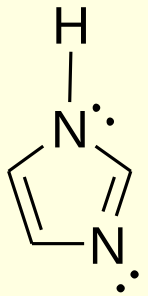
5.



e)

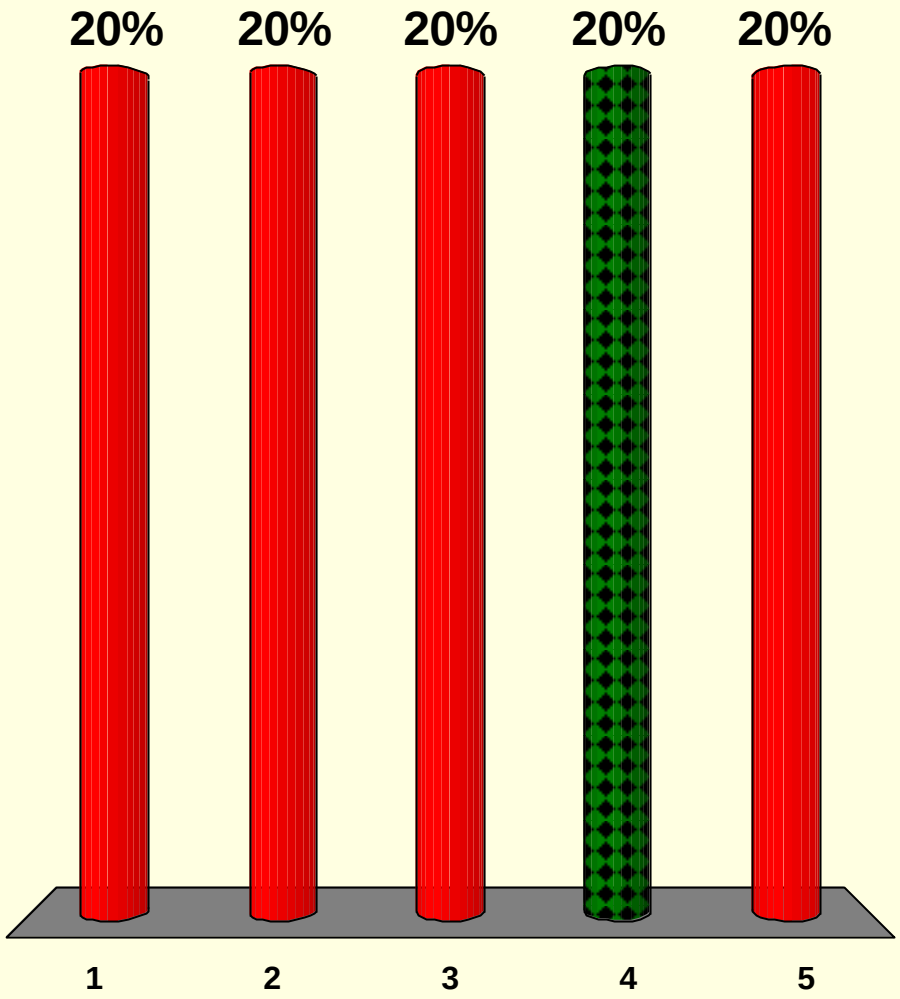


How many π electrons are in imidazole?

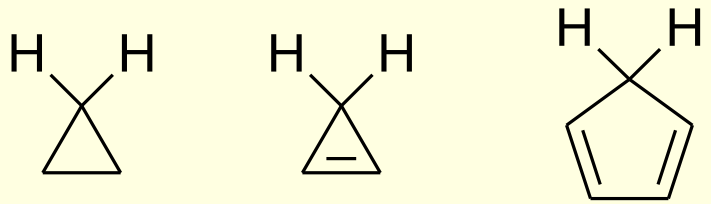


imidazole

1. 0
2. 2
3. 4
4. 6
5. 8

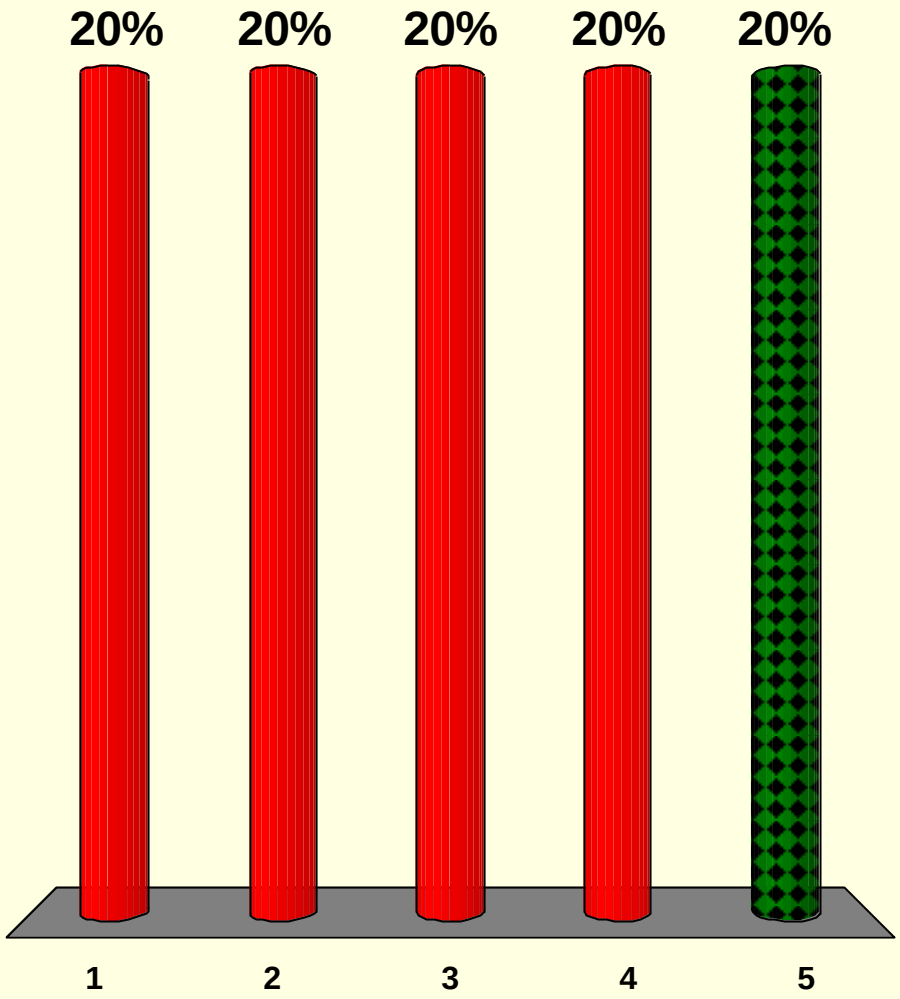


What is the correct ranking of the pK_a values for the following carbon acids?



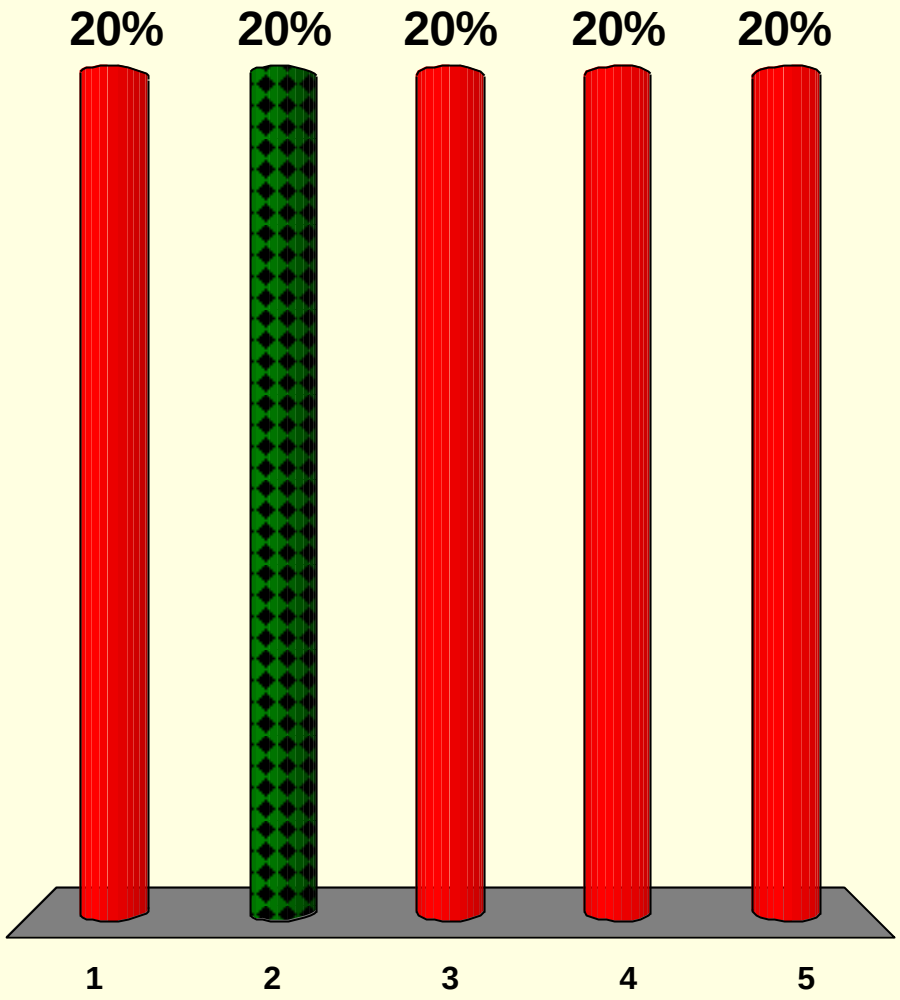
A B C

1. A < B < C
2. A < C < B
3. B < A < C
4. B < C < A
5. C < A < B

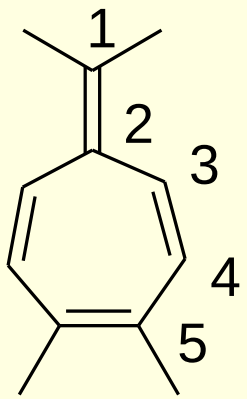


Which of the following is the best characterization of the cyclopentadienyl cation?

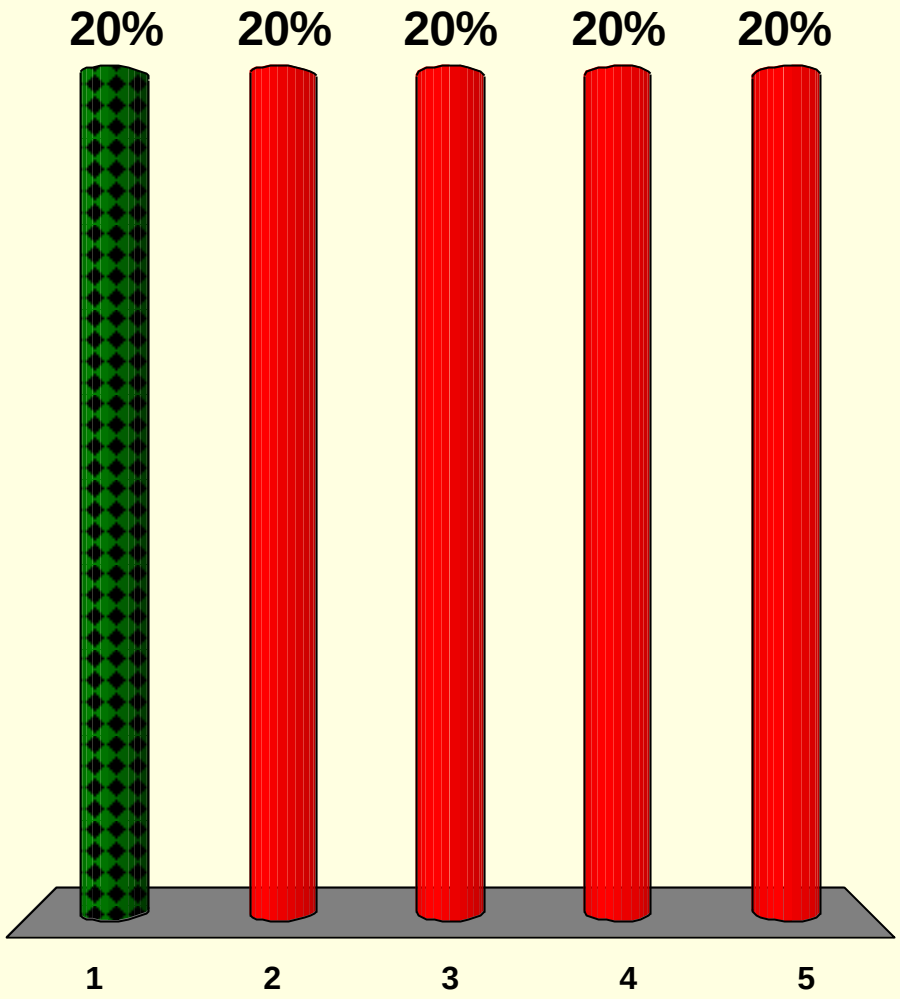
1. hyperconjugated
2. antiaromatic
3. vinylic
4. allylic
5. benzylic



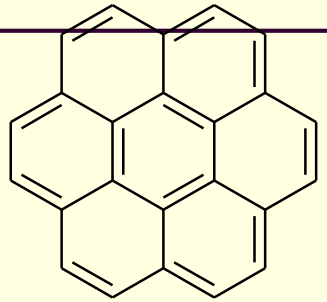
What is the most likely protonation site in the conjugated alkene shown below?



1. 1
2. 2
3. 3
4. 4
5. 5

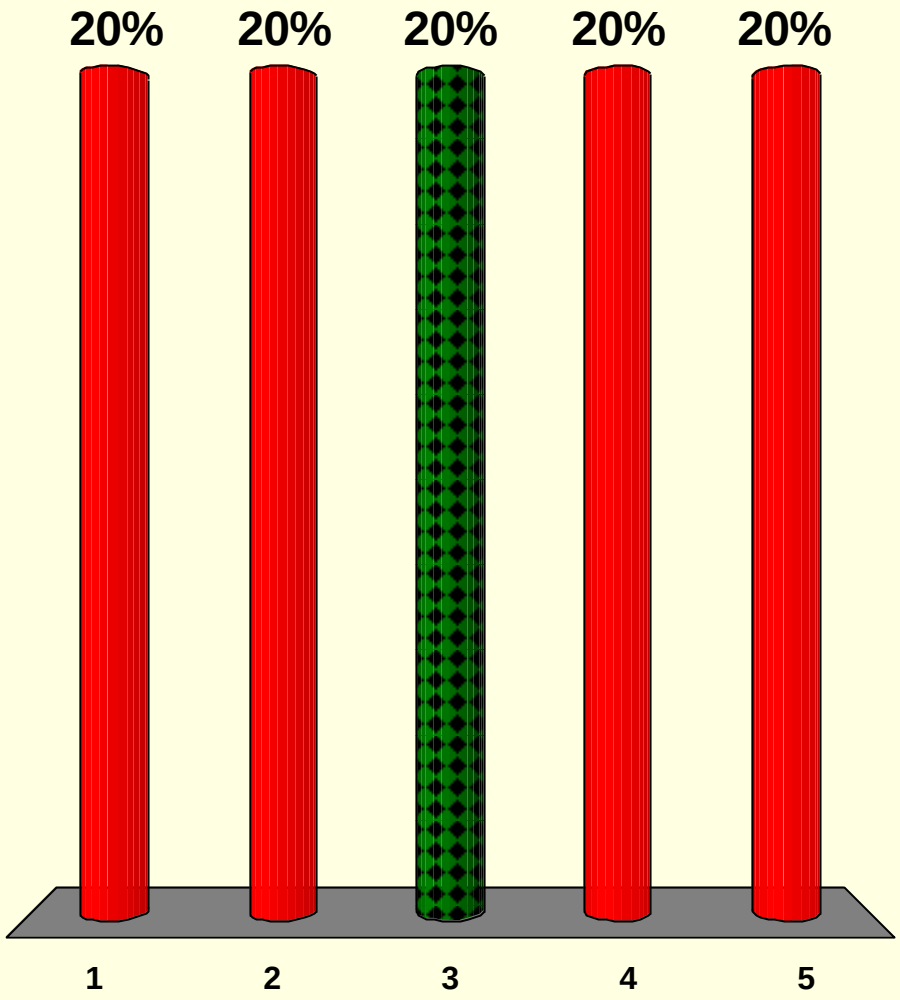


The coronene shown below is planar. What is true about it?

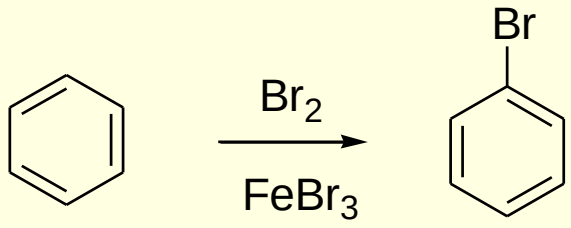


coronene

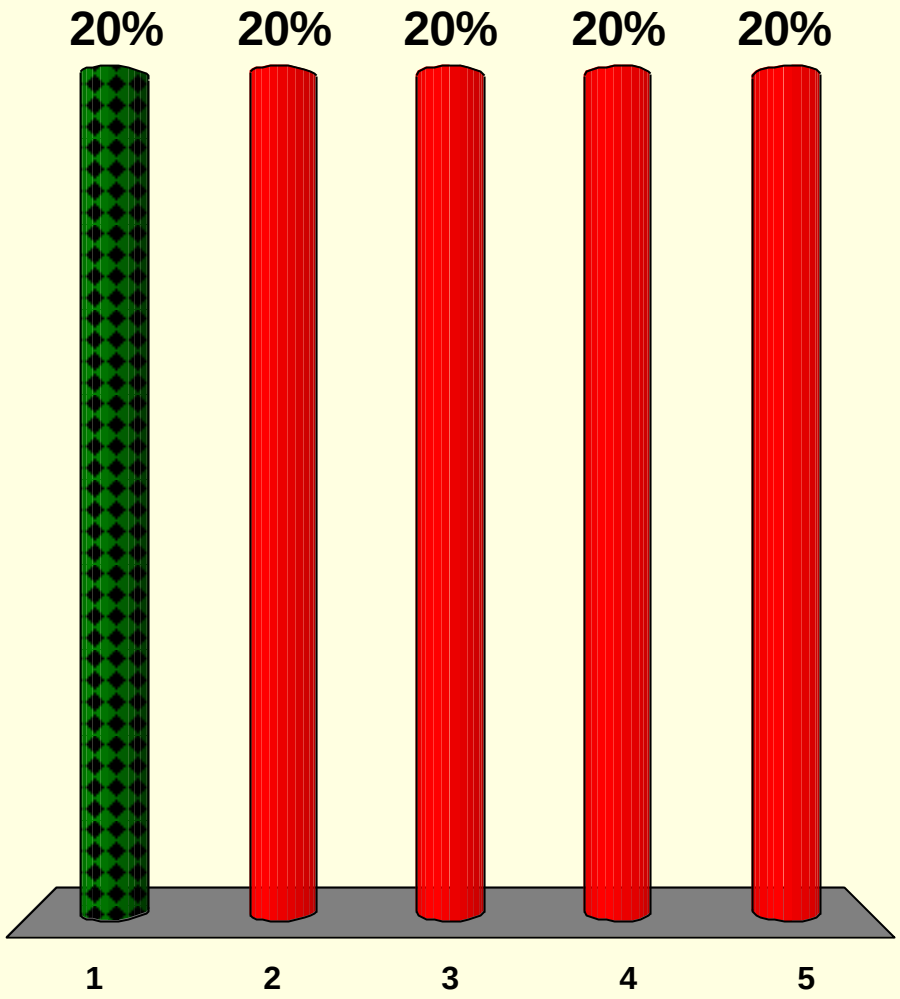
1. It is aromatic because it has (4n + 2) π electrons.
2. It is antiaromatic because it has (4n) π electrons.
3. It is aromatic because it has two π rings each with (4n + 2) π electrons.
4. It is antiaromatic because Hückel rule applies only to single rings.
5. It is non-aromatic.



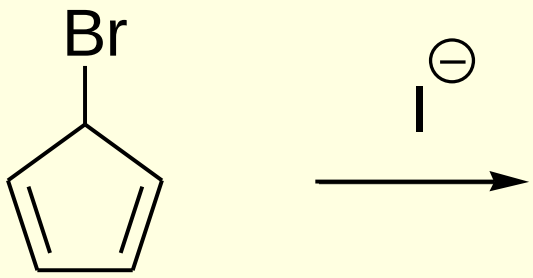
Benzene undergoes substitution when reacted with Br_2, as contrasted with other compounds containing π bonds where addition is the norm. What is the main reason for this behavior?



1. addition would lead to non aromatic system
2. substitution gives product of higher energy
3. production of HBr results in the very stable byproduct
4. aromatic systems react faster because the intermediate is stabilized by resonance
5. the transition state of the first step is aromatic



What is the most likely mechanism of the following reaction?



1. S_N1
2. S_N2
3. E1
4. E2
5. E1cB