Benzene and Aromaticity

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1st Semester

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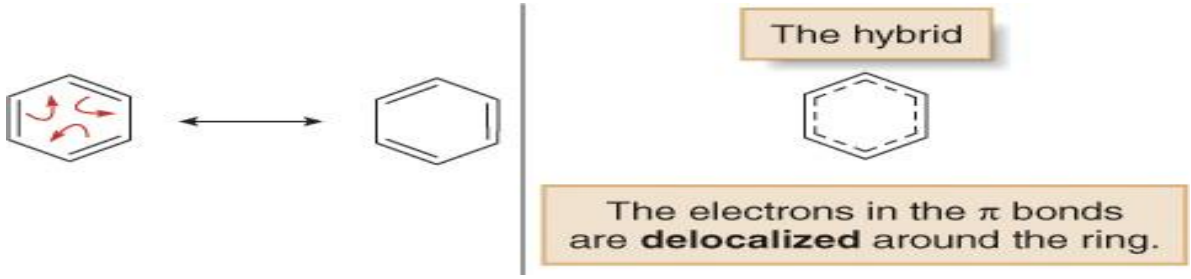
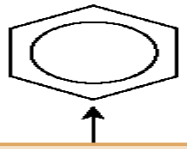
Benzene and Aromatic Compounds

- **Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).**
- **The resonance description of benzene consists of two equivalent Lewis structures, each with three double bonds that alternate with three single bonds.**
- **The true structure of benzene is a resonance hybrid of the two Lewis structures, with the dashed lines of the hybrid indicating the position of the π bonds.**



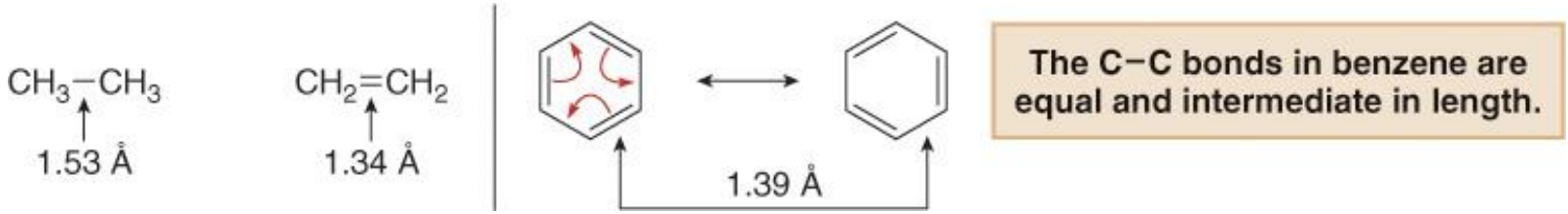
- **Because each π bond has two electrons, benzene has six π electrons.**

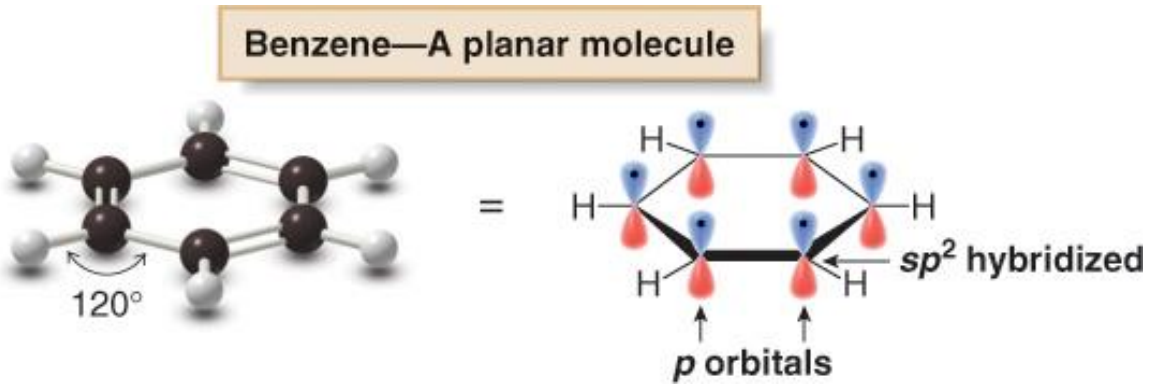
Some texts draw benzene as a hexagon with an inner circle:



The circle represents the **six π electrons,** distributed over the six atoms of the ring.

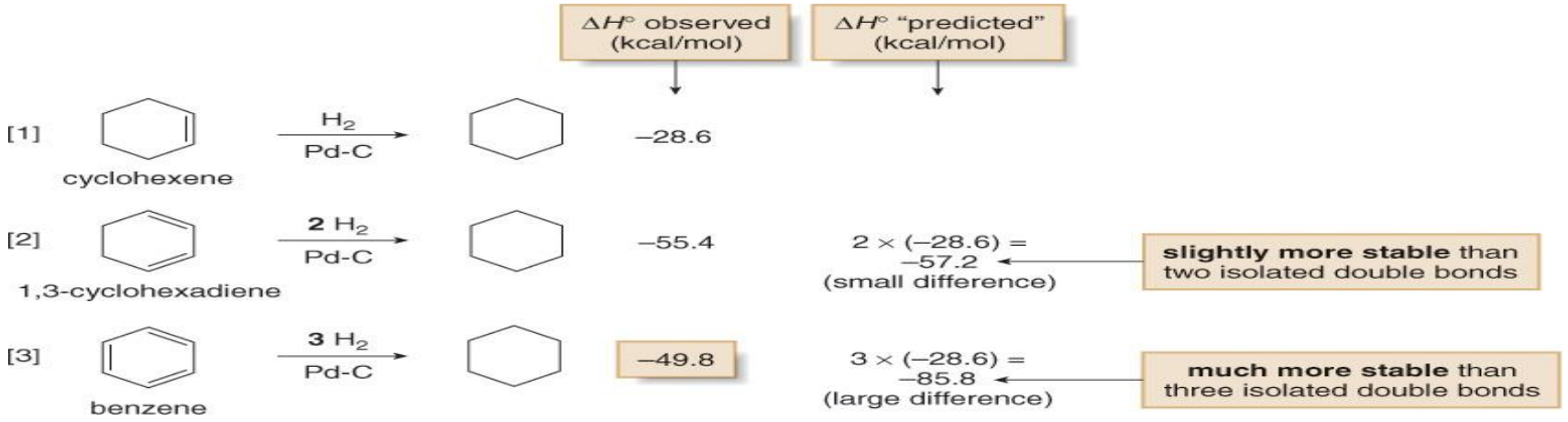
- **In benzene, the actual bond length (1.39 Å) is intermediate between the carbon—carbon single bond (1.53 Å) and the carbon—carbon double bond (1.34 Å).**



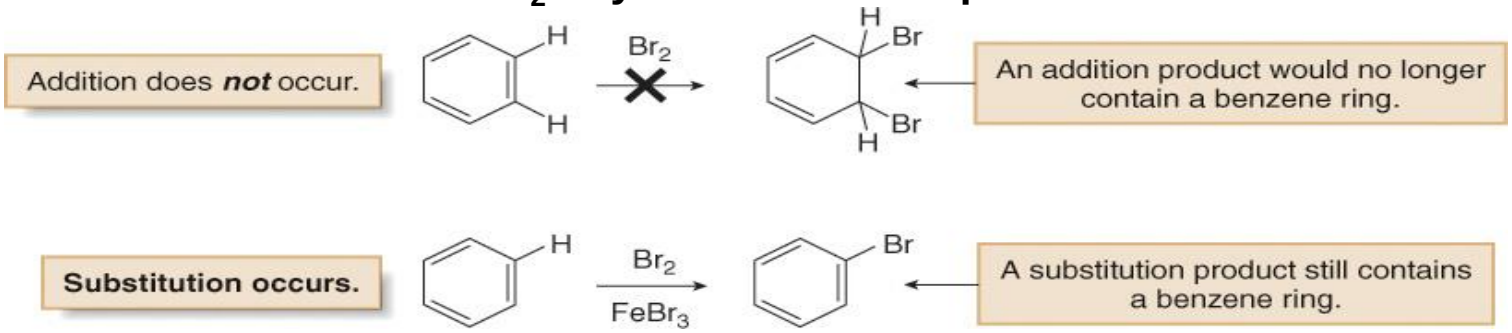


Stability of Benzene

- **Consider the heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene and benzene, all of which give cyclohexane when treated with excess hydrogen in the presence of a metal catalyst.**

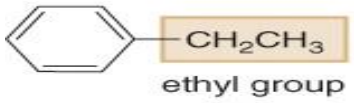


- **The low heat of hydrogenation of benzene means that benzene is especially stable. This unusual stability is characteristic of aromatic compounds.**
- **Benzene's unusual behavior is not limited to hydrogenation. Benzene does not undergo addition reactions.**
- **Benzene does not react with Br_2 to yield an addition product.**

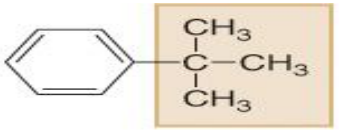


Nomenclature of Benzene Derivatives

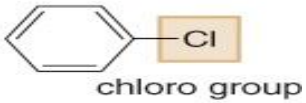
- **To name a benzene ring with one substituent, name the substituent and add the word benzene.**



ethylbenzene

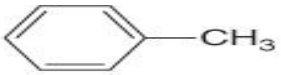


tert-butylbenzene

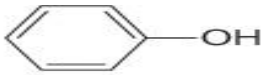


chlorobenzene

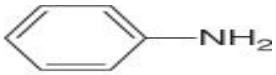
- **Many monosubstituted benzenes have common names which you must also learn.**



toluene (methylbenzene)

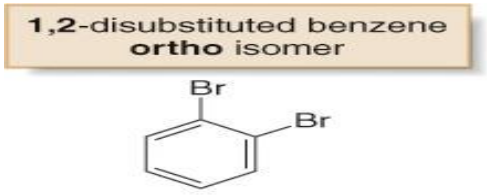


phenol (hydroxybenzene)

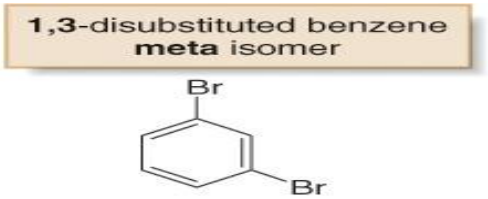


aniline (aminobenzene)

- **There are three different ways that two groups can be attached to a benzene ring, so a prefix—ortho, meta, or para—can be used to designate the relative position of the two substituents.**



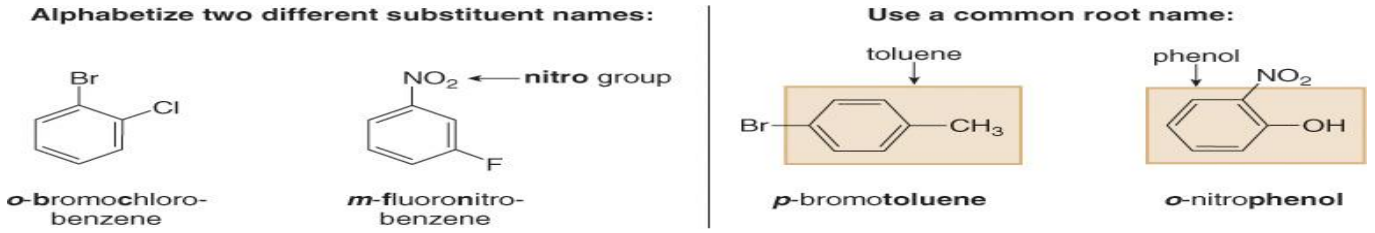
***ortho*-dibromobenzene**
or
***o*-dibromobenzene**
or 1,2-dibromobenzene



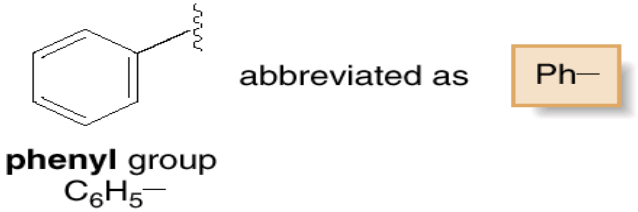
***meta*-dibromobenzene**
or
***m*-dibromobenzene**
or 1,3-dibromobenzene

***para*-dibromobenzene**
or
***p*-dibromobenzene**
or 1,4-dibromobenzene

- **If the two groups on the benzene ring are different, alphabetize the names of the substituent preceding the word benzene.**
- **If one substituent is part of a common root, name the molecule as a derivative of that monosubstituted benzene.**



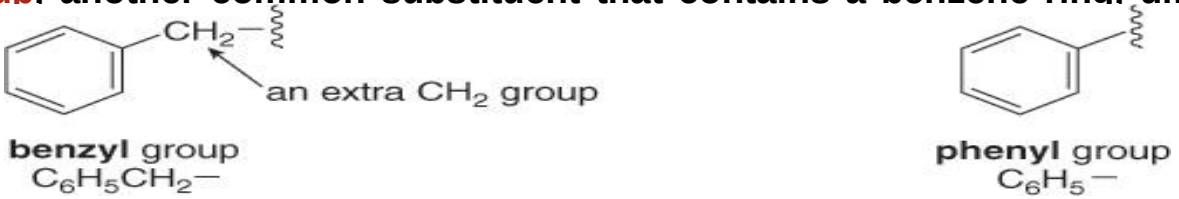
- **A benzene substituent is called a phenyl group, and it can be abbreviated in a structure as "Ph-".**



- A phenyl group (C_6H_5-) is formed by removing one hydrogen from benzene (C_6H_6).

- **Therefore, benzene can be represented as PhH, and phenol would be PhOH.**

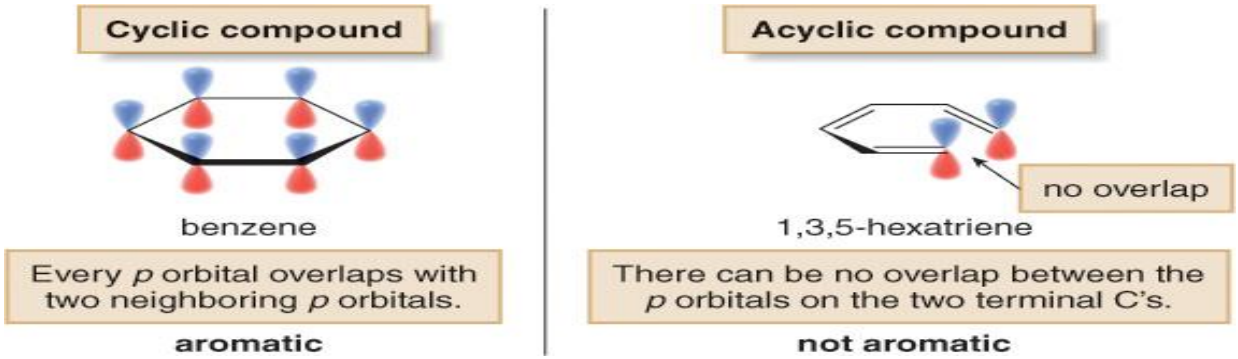
- **The benzyl group, another common substituent that contains a benzene ring, differs from a phenyl group.**



The Criteria for Aromaticity—Hückel's Rule

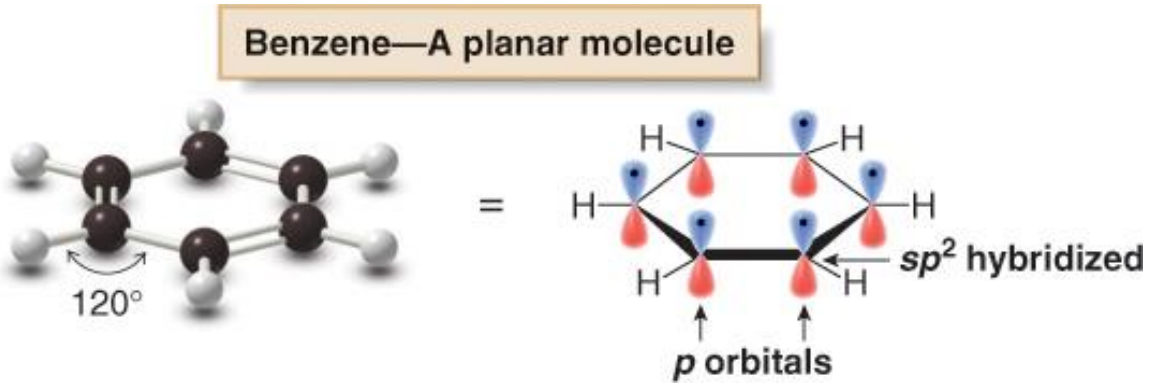
Four structural criteria must be satisfied for a compound to be aromatic.

[1] A molecule must be cyclic.



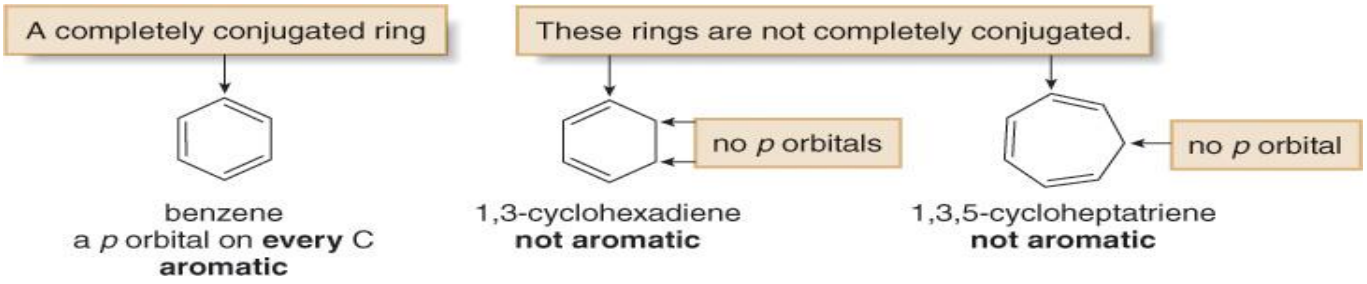
To be aromatic, each *p* orbital must overlap with *p* orbitals on adjacent atoms.

[2] A molecule must be planar.



[3] A molecule must be completely conjugated.

Aromatic compounds must have a *p* orbital on every atom.

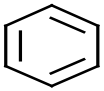


[4] A molecule must satisfy Hückel's rule, and contain a particular number of π electrons.

Hückel's rule:

An aromatic compound must contain 4n+2π electrons [n (integer no.) = 0, 1, 2, and so…]

Benzene is aromatic and especially stable because it contains 6 π electrons. Cyclobutadiene is nonaromatic and especially unstable because it contains 4 π electrons.

Benzene	Cyclobutadiene
An aromatic compound	non-aromatic compound
	
4n+2= 6 π e	4n+2=4 π e
4n=6 - 2=4	4n= 4 - 2 =2
n=4/4=1	n=2/4 = 1.5
aromatic	non-aromatic

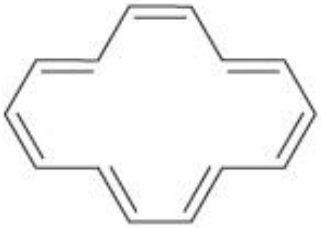
Note that Hückel's rule refers to the number of π electrons, not the number of atoms in a particular ring.

Table 17.2 The Number of π Electrons That Satisfy Hückel's Rule

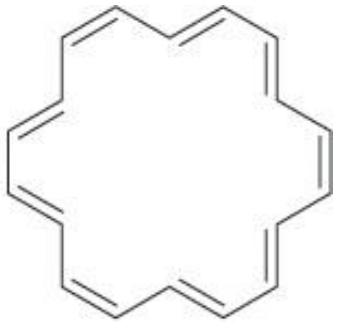
n	4*n* + 2
0	2
1	6
2	10
3	14
4, etc.	18

Examples of Aromatic Rings

- **Completely conjugated rings larger than benzene are also aromatic if they are planar and have $4n + 2$ π electrons.**
- **Hydrocarbons containing a single ring with alternating double and single bonds are called annulenes.**
- **To name an annulene, indicate the number of atoms in the ring in brackets and add the word annulene.**

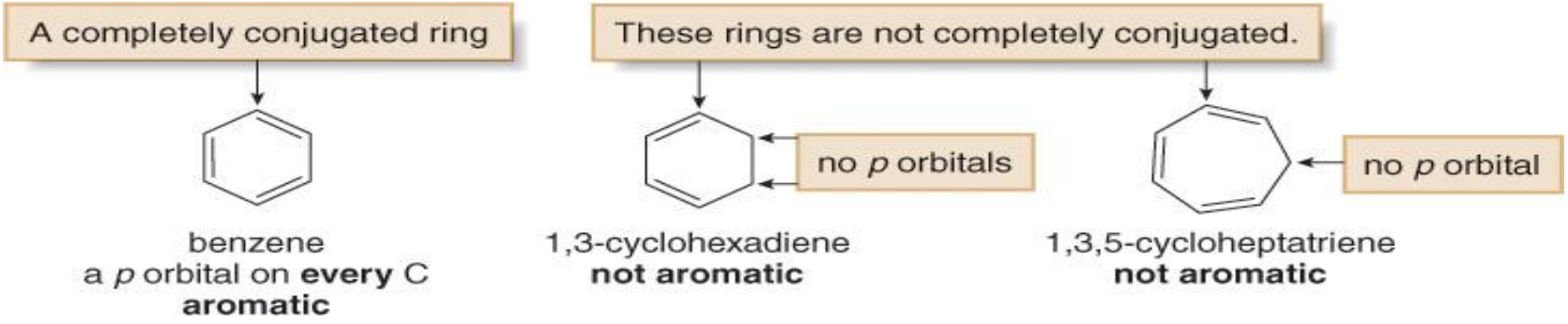


[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic

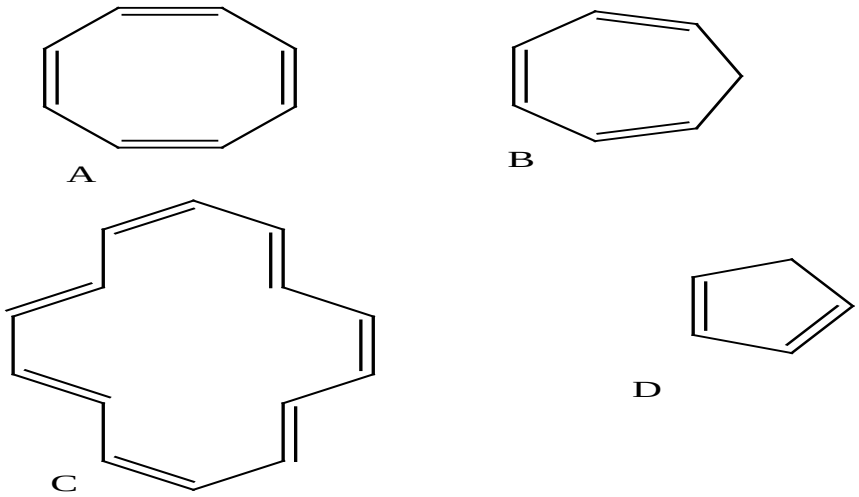


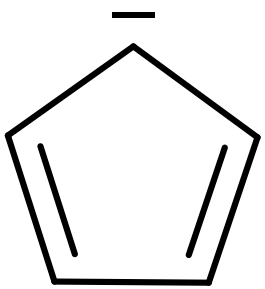
[18]-annulene
$4n + 2 = 4(4) + 2 =$
18 π electrons
aromatic

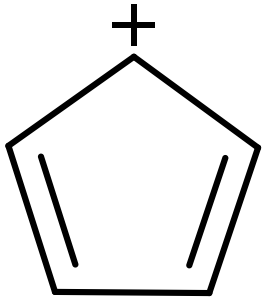
- **Thus, although five resonance structures can also be drawn for the cyclopentadienyl cation and radical, only the cyclopentadienyl anion has 6 π electrons, a number that satisfies Hückel's rule.**

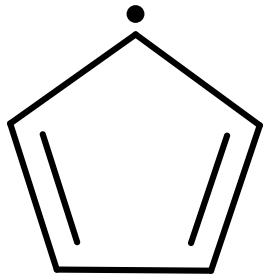


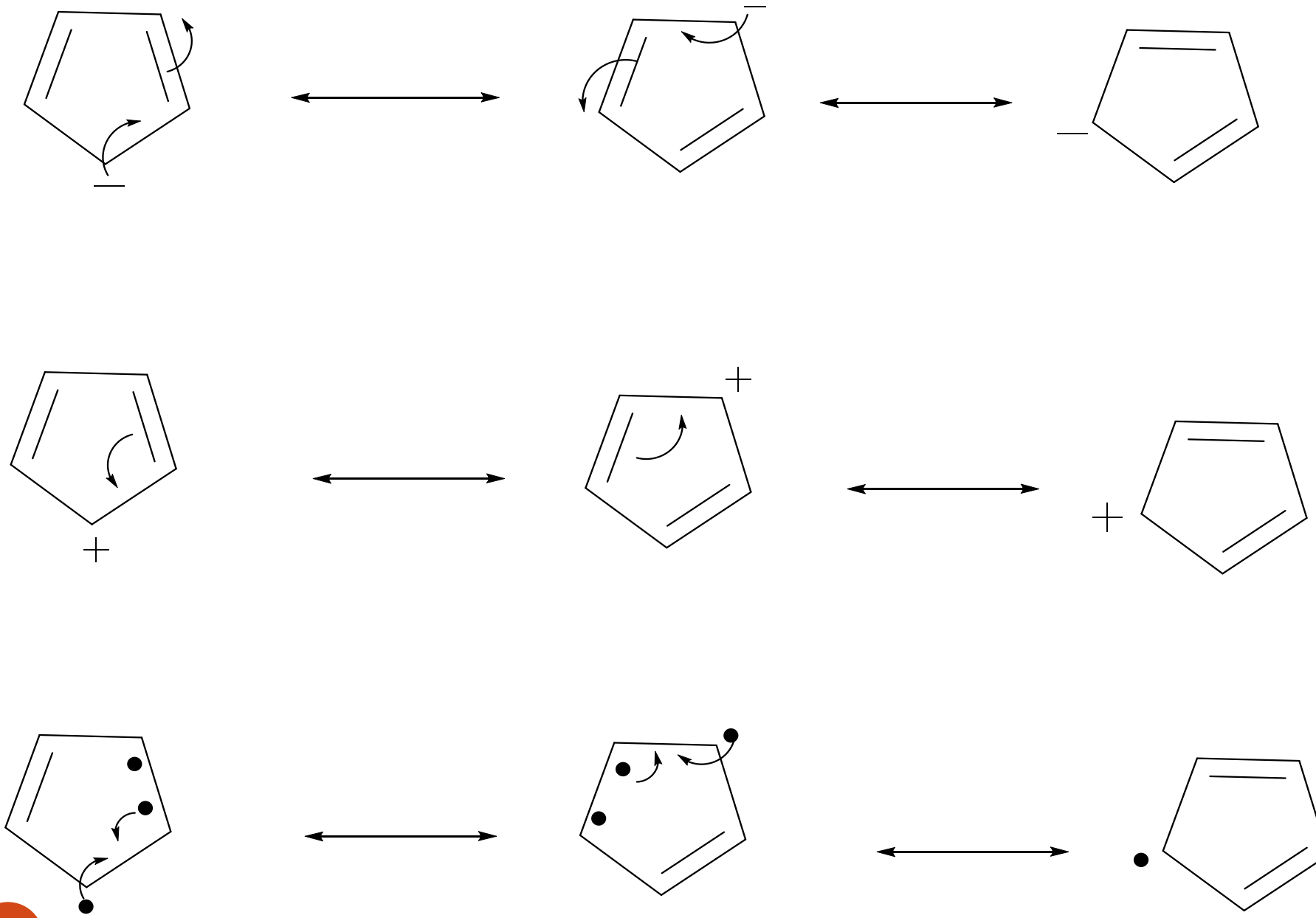
Indicate which of the following are aromatic and non-aromatic?



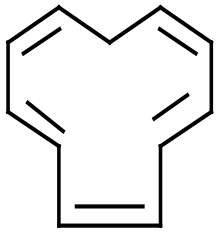




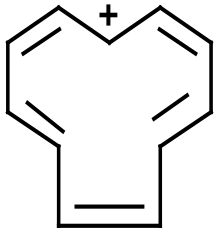




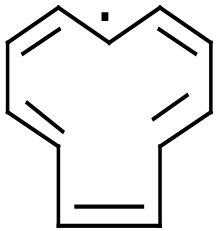
•From among the molecules and ions shown, all of which are based on cycloundecapentaene, identify those which satisfy the criteria for aromaticity.



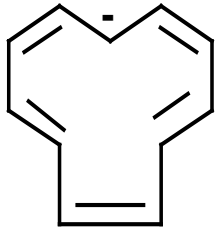
a) cycloundecapntaene



b) cycloundecapntaene cation



c) cycloundecapntaene radical



d) cycloundecapntaene anion

- **Select the best definition of an aromatic compound.**

A. A compound that contains 4n + 2 pi electrons.
B. A compound that has a filled valence shell.
C. A compound that displays unusual stability compared to an alkene.
D. A compound that undergoes electrophilic substitution