

Benzene and Aromatic Compounds

Reading: Wade chapter 16, sections 16-1- 16-15

Study Problems: 16-28, 16-32, 16-33, 16-38, 16-41

Key Concepts and Skills:

- Be able to construct the M.O.'s of a cyclic system of p-orbitals similar to benzene
- Use the polygon rule to draw the energy diagram of a cyclic system of p orbitals., and fill in the electrons to show whether a given compound or ion is aromatic or antiaromatic
- Use Huckel's rule to predict whether a given annulene, heterocycle or ion will be aromatic, antiaromatic, or non-aromatic.
- Use IR, NMR, and UV to determine the structure of aromatic compounds

Lecture Topics:

I. Benzene: Structure

Benzene was originally discovered as a hydrocarbon possessing a low C/H ratio:1:1.

C_6H_6 :

Benzene has unusual stability: Does not undergo addition reactions like isolated alkenes or conjugated dienes:

Benzene and its derivatives are referred to as "Aromatic compounds"

Structure: 6 sp^2 hybridized carbon atoms, all C-C bonds are the same length, all bond angles are 120° . 6 π electrons are delocalized over the entire molecule, forming a circle or circuit of electrons above and below the ring plane:

The stability of benzene is due to its resonance energy, which can be calculated from heats of hydrogenation:

Annulenes are cyclic hydrocarbons with alternating single and double bonds

Question: Do all annulenes have the special stability of benzene?

NO! Cyclobutadiene is so reactive it cannot be isolated, and cyclooctatetraene displays the usual reactivity (addition reactions) of isolated alkenes:

II. Molecular Orbital Picture of Benzene

The six overlapping p-orbitals of benzene combine to form six molecular orbitals, 3 bonding M.O.'s and 3 antibonding M.O.'s. The lowest energy bonding M.O. has no nodes and has six bonding interactions (π_1); The highest energy antibonding orbital has six antibonding interactions and 3 nodes (π_6). Two additional bonding M.O.'s (π_2 and π_3) have a single node and are therefore **degenerate** (of equal energy), while two additional antibonding M.O.'s (π_4 and π_5) have two nodes each and are also degenerate:

Note that π_1 , π_2 , and π_3 are all filled bonding orbitals in which each electron pair can delocalize over several nuclei. The special stability of benzene results from its closed bonding shell, which is energetically very favorable.

For **Cyclobutadiene**, the situation is different. There is one all bonding low-energy M.O., two non-bonding M.O.'s with one node (2 antibonding interactions - 2 bonding interactions = 0 bonding interaction = non-bonding orbital) which are degenerate, and one antibonding orbital with two nodes and four antibonding interactions:

Since there are four electrons coming from each p-orbital, two go into the bonding orbital and one each goes into the non-bonding orbitals spin-parallel (Hund's rule), giving

unpaired electrons in π_2 and π_3 . These electrons are thus highly reactive (behaving as a diradical) and can each either accept an electron to form a bond or donate an electron to form a bond. This explains the instability of cyclobutadiene, as a result of its “open-shell” configuration for its highest lying electrons.

III. Polygon rule

The molecular orbital diagram for any cyclic hydrocarbon with alternating double and single bonds in conjugation can be easily drawn by simply placing its polygon with one vertex at the bottom and building up degenerate bonding, non-bonding and antibonding orbitals at all subsequent vertices. The lowest energy all bonding orbital with no nodes is at the bottom vertex, the highest vertex (or vertices) represent the greatest possible number of antibonding interactions. There is usually a symmetrical division between bonding and antibonding orbitals in the center of the polygon.

IV. Aromatic vs. Antiaromatic Compounds

All aromatic and anti-aromatic compounds have the following characteristics:

- a cyclic system of conjugated π -bonds
- each atom in the ring must contain an unhybridized p-orbital
- the unhybridized p orbitals must overlap to form a continuous ring of parallel orbitals
but, for **Aromatic compounds**: delocalization of electrons over the ring **lowers** the electronic energy
for **Antiaromatic compounds**: delocalization over the ring **increases** the electronic energy

Non-Aromatic compounds: do not have a continuous overlapping ring of p-orbitals

V. Huckel's rule

If the number of π electrons in the cyclic system is $4N+2$, the system is aromatic

If the number of π electrons in the cyclic system is $4N$, the system is antiaromatic

Where N is an integer.

Common aromatic systems have : 2, 6, 10, 14, 18 π electrons

Antiaromatic systems have: 4, 8, 12, 16, 20 π electrons

Cyclooctatetraene is predicted to be antiaromatic, yet it is a stable compound. It violates one of the rules for antiaromaticity: it exists in a "tub" conformation and is not planar, therefore there is no continuous overlap of p-orbitals in a ring:

A prime criterion for aromaticity/antiaromaticity is a planar conformation. Consider the following [10] annulenes; only one is aromatic (naphthalene) even though all have $4N+2=10\pi$ electrons.

Explain why the following systems are stable aromatics, unstable antiaromatics, or non-aromatic:

MO basis of $4N+2$ rule: based on the polygon approach to building up molecular orbitals, we know that a single all bonding M.O. of lowest energy contains two electrons; all subsequent bonding M.O.'s and non-bonding M.O.'s occur in pairs, so stable systems with closed bonding shells will contain $4N$ electrons beyond the two in the lowest bonding orbital (leading to the $4N+2$ rule for aromatic systems). Unstable (antiaromatic) systems will have open shells with high-lying unpaired electrons in the two highest occupied degenerate orbitals; this means there will be only a total of $4N$ electrons for these systems. See the polygram diagrams below:

VI. Aromatic Ions

The cyclopentadienyl anion and cation each have delocalized resonance forms, but only the cyclopentadienyl anion is stable and aromatic (6π electrons); the cyclopentadienyl cation (4π electrons) is antiaromatic:

Cyclopentadiene is quite acidic ($pK_a=16$), which makes sense because its conjugate base is the aromatic anion. It can be quantitatively deprotonated by t-butoxide ion. The cyclopentadienyl anion still reacts with electrophiles, yet it is more stable than non-aromatic, conjugated anions:

In contrast, the cyclopentadienyl cation is much less stable than other secondary carbocations since it is antiaromatic; it cannot be formed by dehydration of the corresponding doubly allylic alcohol

Similarly, the cycloheptatrienyl cation is aromatic, whereas the cycloheptatrienyl anion is antiaromatic. This explains the easy ionization of cycloheptatrienyl alcohols and the low acidity ($pK_a=39$) of cycloheptatriene:

Cyclooctatetraene forms an aromatic dianion on treatment with potassium metal. The dianion contains 10 π electrons, with all C-C bond lengths of 1.4 Å.

Explain why the following molecules may be considered aromatic. Consider resonance forms and explain why the first molecule has such a large dipole moment:

VII. Heterocyclic Aromatic compounds

Pyridine is the nitrogen analog of benzene, where one C-H bond is replaced with a nitrogen atom. The nitrogen is sp^2 hybridized; it has a lone pair occupying an sp^2 -orbital, and an unhybridized p orbital orthogonal to the bonding plane containing an electron which is delocalized in the pi orbital system above and below the ring plane. The nitrogen lone pair is basic, ($pK_b=8.8$) and protonated pyridine is also aromatic since the pi-orbital sextet is undisturbed by atom exchanged in the sp^2 bonding plane.

Pyrrole, a five-membered ring nitrogen analog of cyclopentadienyl anion, differs from pyridine in that its nitrogen lone pair is in a p-orbital and participates in the delocalized aromatic sextet.; thus, the nitrogen of pyrrole is non-basic, and protonation of this lone pair leads to an extremely acidic non-aromatic cation. The oxygen and sulfur analogs of pyrrole are furan and thiophene, both of which have a lone pair in a p-orbital participating in the aromatic sextet:

Imidazole is a five-membered ring heterocycle containing two nitrogen atoms, one of which is basic and one is non-basic. One of the ring nitrogens has a basic lone pair in an sp^2 orbital in the sigma bonding plane of the molecule; the other nitrogen has its lone pair in a p-orbital participating as part of the aromatic sextet. Protonation of imidazole gives a symmetrical cation in which the nitrogens become equivalent.

VIII. Polycyclic Aromatic Hydrocarbons (PAH's)

Naphthalene consists of two fused benzene rings, but contains 10 pi electrons (not $6+6=12$). The resonance energy of naphthalene is 60 kcal/mol, 12 kcal/mol less than twice benzene's resonance stabilization (36 kcal/mol), making the resonance energy per ring in naphthalene only 30 kcal/mol.

Anthracene and phenanthrene each have 14 π electrons. Anthracene has a resonance energy of 84 kcal/mol, or only 28 kcal/mol per ring. Both anthracene and phenanthrene are considerably less stable than benzene and therefore are more reactive. They undergo addition reactions and Diels Alder reactions in such a way that the aromaticity of two full benzene rings is preserved, which is energetically favorable:

IX. Nomenclature

Review the section on nomenclature in the text. Know structures for the common names: phenol, toluene, anisole, styrene, acetophenone, benzaldehyde, benzoic acid.

Positions on an aromatic ring: for two substituents in a **1,2-relationship** on the ring, the ring is **ortho** substituted; for two substituents on a ring in a **1,3-relationship**, the ring is **meta** substituted; for two substituents in a **1,4 relationship** on the ring, the ring is **para** substituted. Tri, tetra substituted benzene rings are named by using a numbering system from the highest priority substituent.

Abbreviations: a benzene ring as a substituent is termed a phenyl (Ph) group (C_6H_5); substituted benzene rings as substituents are termed aryl groups; and phenyl ring with a methylene group (C_7H_7) is termed a benzyl group:

X. Spectroscopy of Aromatics

NMR: Aromatic ring proton resonances are found in the 7-8 ppm region of 1H NMR spectra. Aromatic carbons resonate between 120-150 ppm in ^{13}C NMR spectra.

IR: the C=C stretch of aromatics is at 1600cm^{-1} and the aromatic C-H stretch is visible around 3030cm^{-1} .

UV: There are three main absorptions for benzene, at $\lambda_{\text{max}}=184\text{ nm}$, 204 nm, and 254 nm.

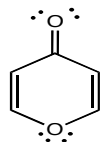
The band at 204 nm is termed the “moderate band” and most aromatics show the moderate absorption somewhere between 204-214 nm.

The band at 254 nm is termed the benzenoid band and consists of multiple peaks often referred to as “fine structure”. The benzenoid band of most aromatic falls between 254-264 nm.

An additional conjugated double bond increases λ_{max} by about 30 nm. Consider styrene (vinyl benzene): moderate band at 248 nm, benzenoid band at 282 nm.

Additional Problems for practice:

1. Which would you expect to be the most stable: the cyclononatetraenyl cation or anion? Why?
2. Upon reaction with acid, 4-pyrone is protonated on one of the oxygens to give a stable cationic product. Which oxygen is protonated and what is the structure of the protonated product? Explain the stability of the protonated product.



4-pyrone

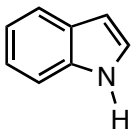
3. Pentalene, shown below, has never been isolated; however, the pentalene dianion is well known and quite stable. Explain



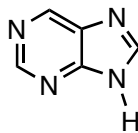
Pentalene

Pentalene dianion

4. Draw an energy diagram for the three molecular orbitals of the cyclopropenyl system. How are these three molecular orbitals occupied in the cyclopropenyl anion and cation? Which of these species is predicted to be the most stable and aromatic?
5. Draw the overlapping p-orbitals that make up the aromatic system of the following molecules. Indicate the location of the nitrogen lone pairs, and indicate whether each nitrogen in basic or non-basic. How many p electrons does each nitrogen donate to the aromatic pi system?



indole



purine