Bonding and Physical Properties

The Molecular Orbital Theory

MO Diagram of cyclic p-orbital system

Hexa-1,3,5-triene

Benzene

Conjugated Alkene  Cyclic Conjugated Alkene

Prepared by H.G
If delocalization was not possible, benzene should behave as a cyclohexatriene. Let us see how much more benzene is stable compared to this hypothetical localized structure. The heat of hydrogenation of cyclohexene has been experimentally determined to be 28.6 kcal/mol (Figure 3, A). If we consider $\text{C}_6\text{H}_6$ as just a cyclohexatriene, the heat of hydrogenation should be $3 \times 28.6 \text{ kcal/mol} = 85.8 \text{ kcal/mol}$ (Figure 3, C). However, when the heat of hydrogenation was experimentally determined for benzene, it was found to be 49.8 kcal/mol (Figure 3, B). Since hydrogenation of cyclohexatriene and benzene both lead to cyclohexane, the reason for the difference in their heat of hydrogenation should be due to the difference in their stabilities. From this, it is clear that benzene is 36 kcal/mol (i.e., $85.8 - 49.8 \text{ kcal/mol}$) more stable than ‘cyclohexatriene’. i.e. benzene with six delocalized π electrons is 36 kcal/mol more stable than ‘cyclohexatriene’ with six localized π electrons. Here, 36 kcal/mol is the resonance energy of benzene.

**Figure 3.** Aromaticity and Annulenes

- **Stability of an Alkene ??**
- **Heats of Hydrogenation ($\Delta H^\circ$) ??**
- **Resonance Energy**
Huckel Rule of Aromaticity:

1. The molecule must be cyclic, planar with uninterrupted cloud of $\pi$ electrons above and below the plane of the ring.

2. It should have $4n+2$ $\pi$ electrons.

**Cyclopropene**

2 electrons ($n = 0$); the delocalization is interrupted due to sp3 methylene; 
*Nonaromatic*

**Cyclopropenyl cation**

2 electrons ($4n+2$; $n = 0$); the delocalization of 2 electrons is possible through the empty p orbital; 
*Aromatic*

Resonance contributors in cyclopropenyl cation

Resonance Hybrid

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Antiaromatic:-

Cyclic, planar and completely conjugated compounds that contain 4n $\pi$ electrons are especially unstable and are said to be Antiaromatic

Cyclopropenyl anion
4 electron (even number of pairs; 4n, n = 1);
*Theoretically antiaromatic; not stable*

4 electrons (even number of pairs; 4n, n = 1)
Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation)
**Antiaromatic**
1) **Cyclobutadiene**

- 4 electrons (even number of pairs; 4n, n = 1)
- Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation)
- Antiaromatic

   Being antiaromatic, cyclobutadiene is unstable. It can be isolated only under controlled conditions such as in Argon matrix or using trapping agents such as dienes. Studies show that it has a rectangular structure rather than a square, with C-C bond length of 1.567 Å and C=C bond length of 1.346 Å.

   ![Triphenylborane](image)

2) **Cyclobutadienyl dication**

   - 2 electrons (4n+2; n = 0); the delocalization of 2 electrons is possible through the empty p orbitals
   - Aromatic

   e.g. Ionization of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene in SbF$_5$/SO$_2$ at -75°C leads to a dication whose formation and special stability is attributable to aromaticity.

   ![Cyclobutadienyl dication](image)
1) 

Cyclopentadiene

4 electron system (even number of pairs);
Does not have an uninterrupted ring of p orbital bearing atoms (conjugation);
Nonaromatic.

2) 

Cyclopentadienyl cation

4 electron (even number of pairs; 4n, n = 1;
Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation);
antiaromatic

3) 

Cyclopentadienyl anion

6 electron system (4n+2, n = 1), cyclic, planar with conjugation;
Aromatic.
8 π electron system;
If completely planar, this molecule will become antiaromatic
(bond angle for planar structure = 135° which can give considerable
angle strain in a cyclic structure involving sp² carbon atoms);
The molecule is actually boat shaped and nonaromatic.
(Nonaromatic form is more stable than an antiaromatic form)

All adjacent $p$ orbitals must be aligned so that the $\pi$ electron density can be
delocalized.

- cyclooctatetraene
  - not aromatic
- a tub-shaped, eight-membered ring

Adjacent $p$ orbitals cannot overlap. Electrons cannot delocalize.
Although a 6π electron system, one of the atoms in the cyclic structure can not contribute a p orbital for conjugation.

*Nonaromatic*

6π electron system, Cyclic, conjugated, planar with 4n+2 p electrons

*Aromatic*
Points to be Remembered

1. Aromatic—A cyclic, planar, completely conjugated compound with $4n + 2\pi$ electrons.

2. Antiaromatic—A cyclic, planar, completely conjugated compound with $4n\pi$ electrons.

3. Not aromatic (nonaromatic)—A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.

Note the relationship between each compound type and a similar open-chained molecule having the same number of $\pi$ electrons.
Annulenes are the family of completely conjugated, monocyclic hydrocarbons.

The annulenes are named as [n]-annulene where “n” is an even number that represents the number of C atoms in the ring.

Benzene
Each molecular orbital has its own energy as-

\[ E = \alpha + m_j \beta \]

\( E \) = Energy of the orbital

\( \alpha \) = Columb inetgral

   It is the energy of an Electron in a 2Pz orbital when the orbital does not overlap with any other orbital

\( \beta \) = Resonance integral

   It is the energy of an electron distributed over two or more overlapping 2Pz orbitals

\( m_j \) = Quantifier of \( \beta \)
How to Draw a Frost Diagram

\[ (\alpha - 2\beta) \]

\[ (\alpha + 2\beta) \]

Energy

Antibonding

\[ 2\beta \]

Bonding

\[ \alpha \]
Energy

\[ \alpha (\alpha + 2\beta) \]

\[ (\alpha - \beta) \]

Antibonding

Bonding

Frost Molecular Diagram For Three Membered System

\[ \Psi_1 \]

\[ \Psi_2 \]

\[ \Psi_3 \]
Frost Molecular Diagram For Four, Five, Six and Seven Membered System

4-membered

5-membered

6-membered

7-membered

Prepared by H.G.
If the polygon touches the circle at a horizontal diameter, that point would represent a nonbonding orbital (see illustrations below, Figure 7). Energy levels below this line indicate bonding MOs and those above are antibonding.

Frost diagrams - Illustrative examples

Figure 7.

Prepared by H.G
If the polygon touches the circle at a horizontal diameter, that point would represent a nonbonding orbital (see illustrations below, Figure 7). Energy levels below this line indicate bonding MOs and those above are anti-bonding.

Frost diagrams - Illustrative examples

Antibonding

Nonbonding

Bonding

Antibonding

Bonding

Antibonding

Bonding

Antibonding

Bonding

Antiaromatic

Aromatic

(chooses to be nonaromatic by adopting tub-shaped conformation)

Prepared by H.G
NEXT Class

More about Aromaticity

cyclopropenone (aromatic)
cycloheptatrienone (aromatic)
Cyclopentadienone (antiaromatic)