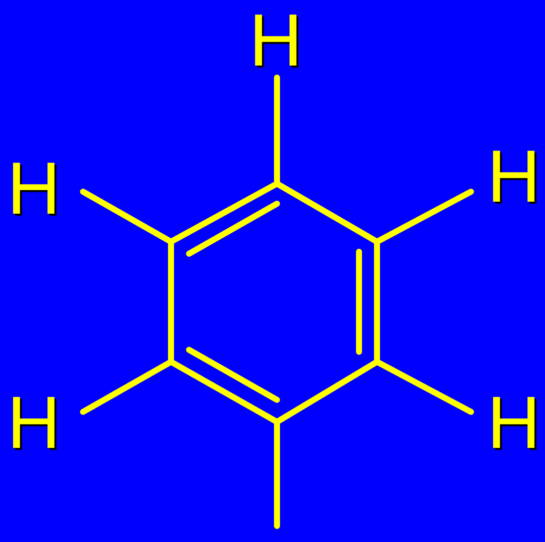
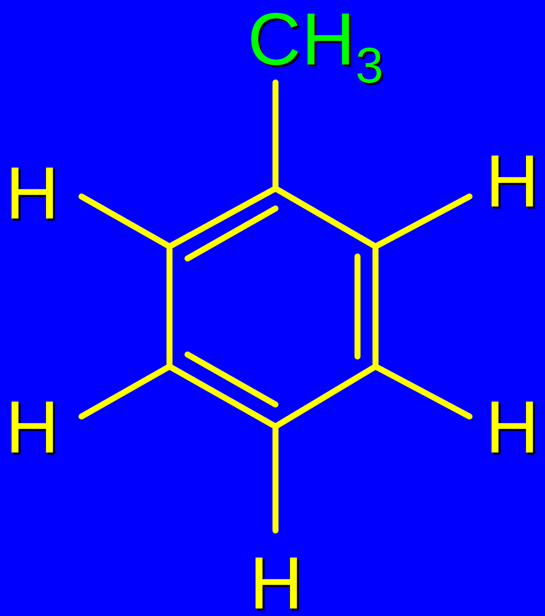
Chapter 11
Arenes and Aromaticity

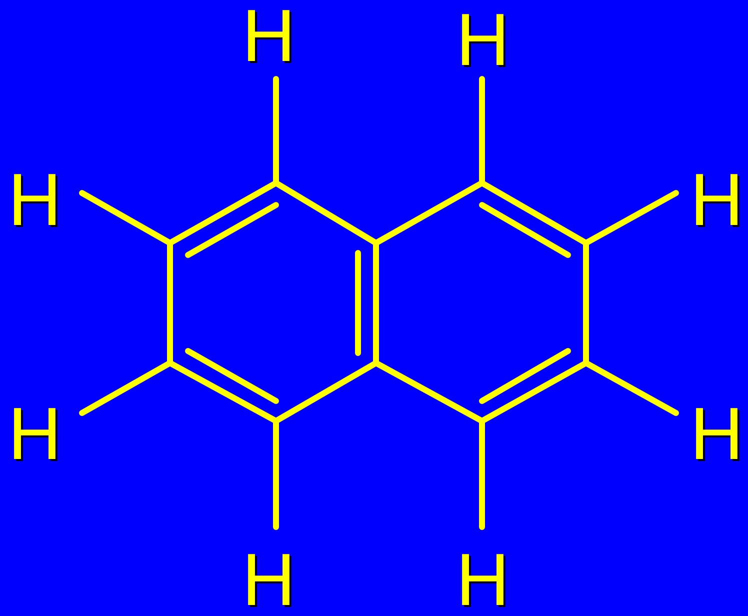
Examples of Aromatic Hydrocarbons



Benzene



Toluene



Naphthalene

11.1
Benzene

Some history

1825 Michael Faraday isolates a new hydrocarbon from illuminating gas.

1834 Eilhardt Mitscherlich isolates same substance and determines its empirical formula to be C_nH_n. Compound comes to be called *benzene*.

1845 August W. von Hofmann isolates benzene from coal tar.

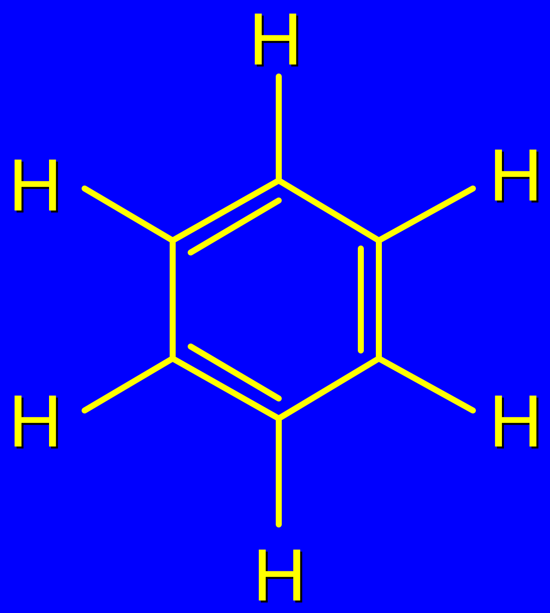
1866 August Kekulé proposes structure of benzene.

11.2

Kekulé and the Structure of Benzene

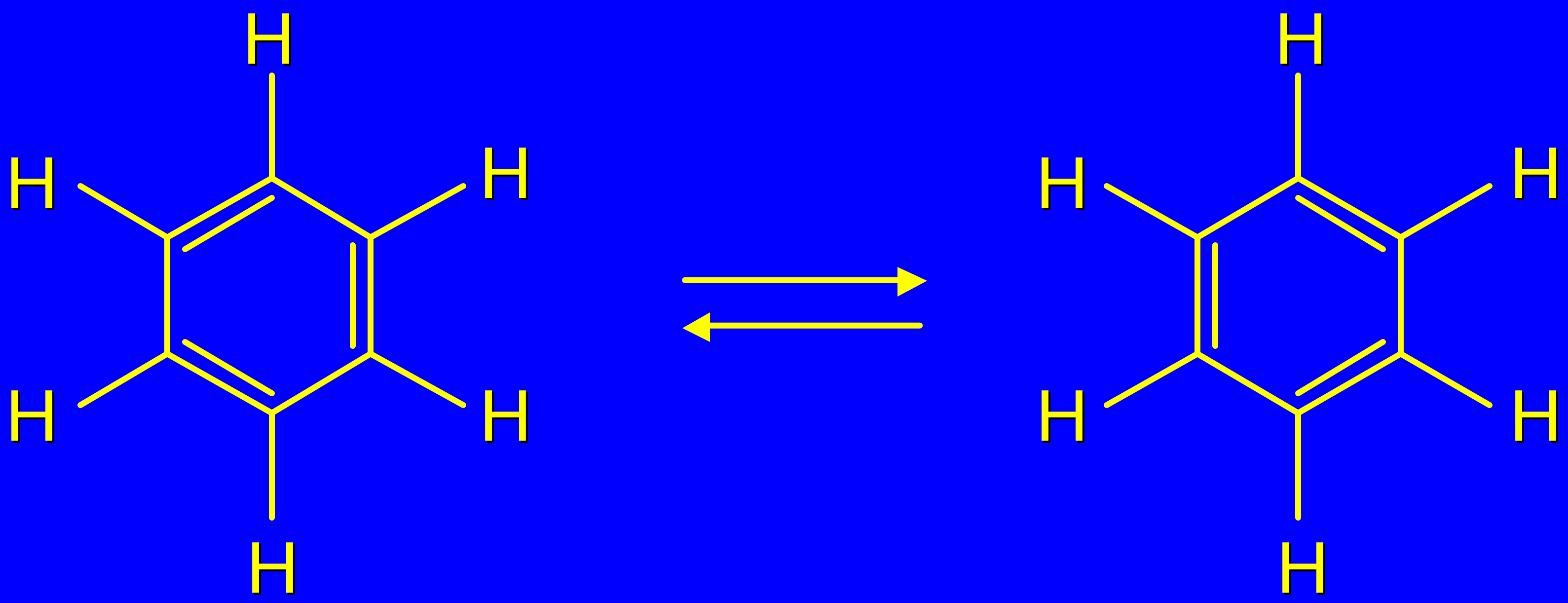
Kekulé Formulation of Benzene

Kekulé proposed a cyclic structure for C_6H_6 with alternating single and double bonds.



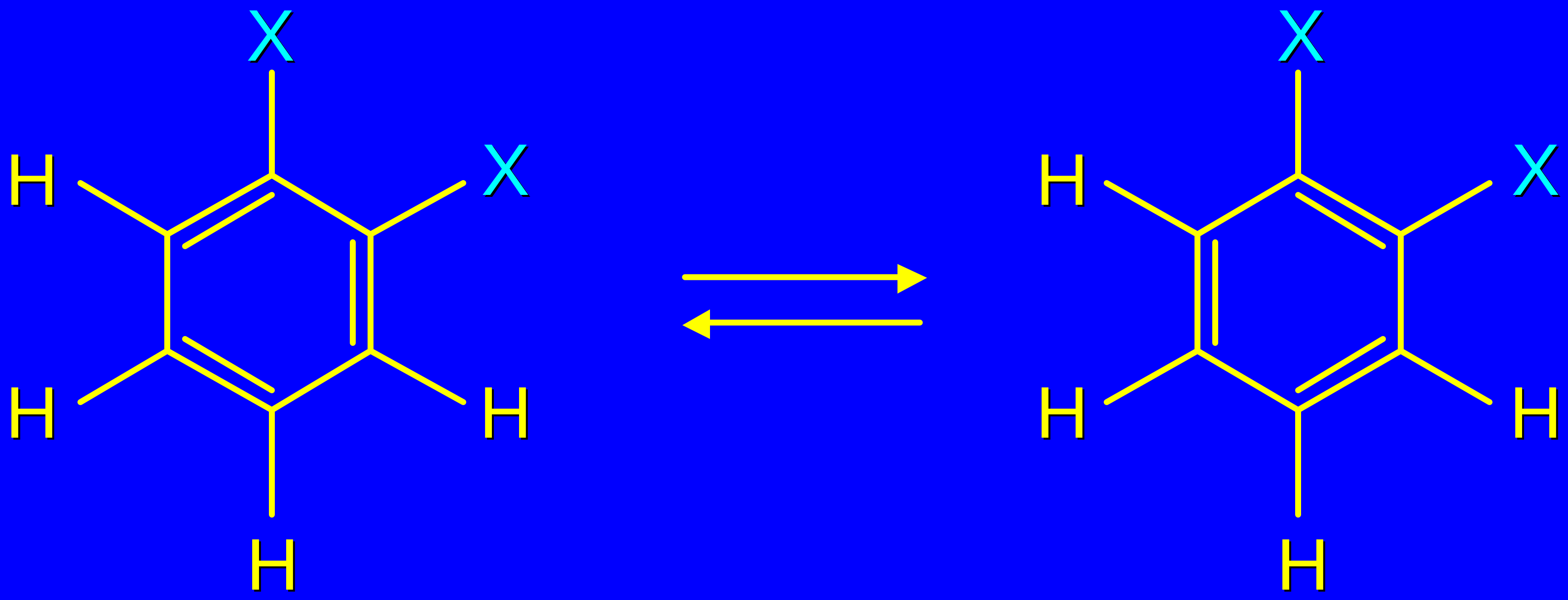
Kekulé Formulation of Benzene

Later, Kekulé revised his proposal by suggesting a rapid equilibrium between two equivalent structures.



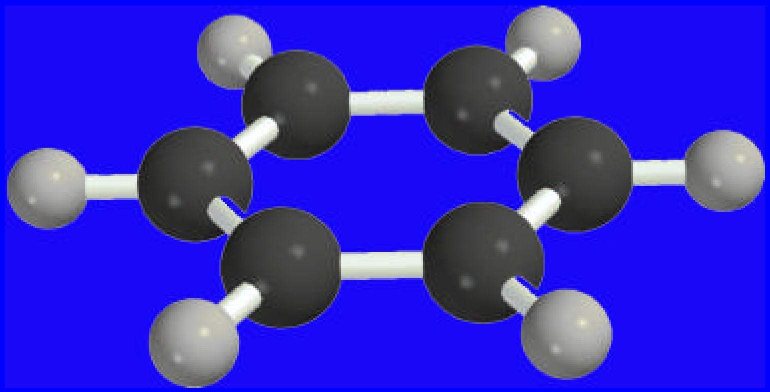
Kekulé Formulation of Benzene

However, this proposal suggested isomers of the kind shown were possible. Yet, none were ever found.



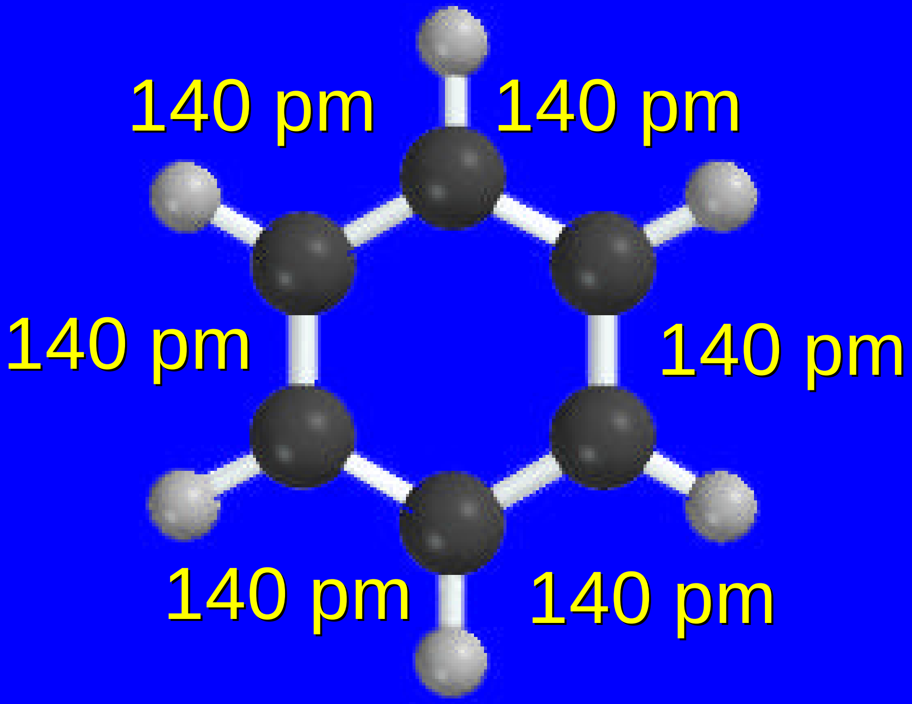
Structure of Benzene

Structural studies of benzene do not support the Kekulé formulation. Instead of alternating single and double bonds, all of the C—C bonds are the same length.

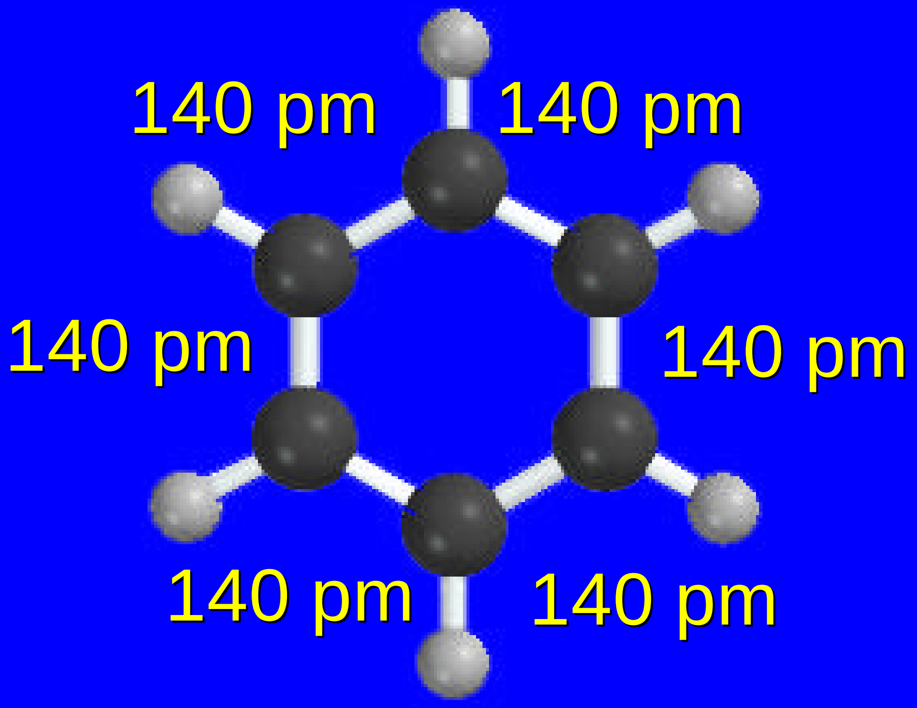


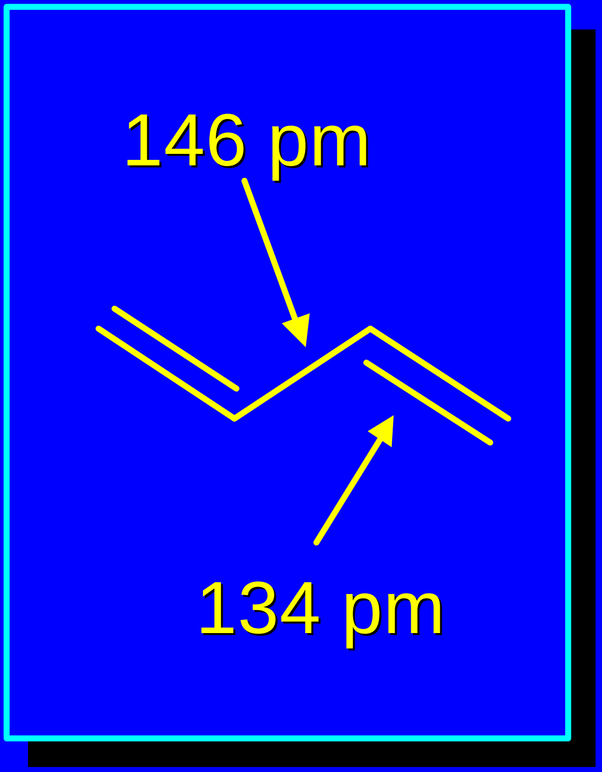
Benzene has the shape of a regular hexagon.

All C—C bond distances = 140 pm



All C—C bond distances = 140 pm





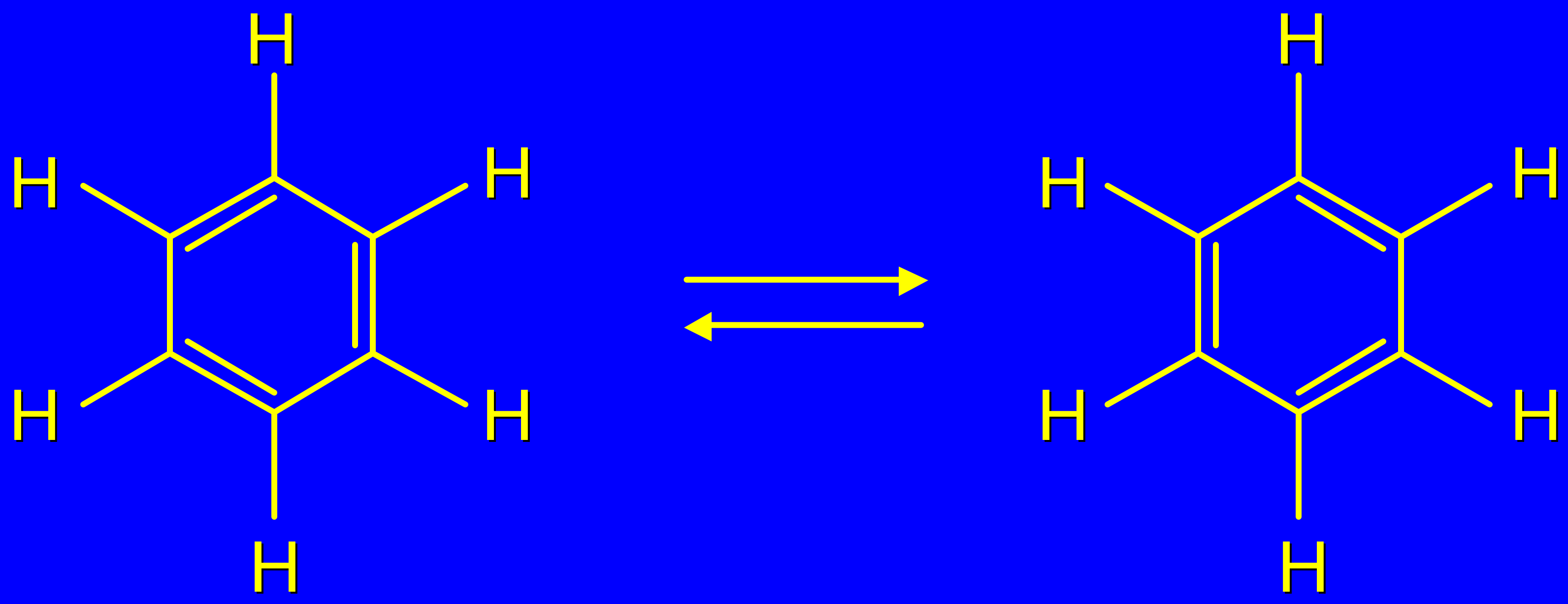
140 pm is the average between the C—C single bond distance and the double bond distance in 1,3-butadiene.

11.3

A Resonance Picture of Bonding in Benzene

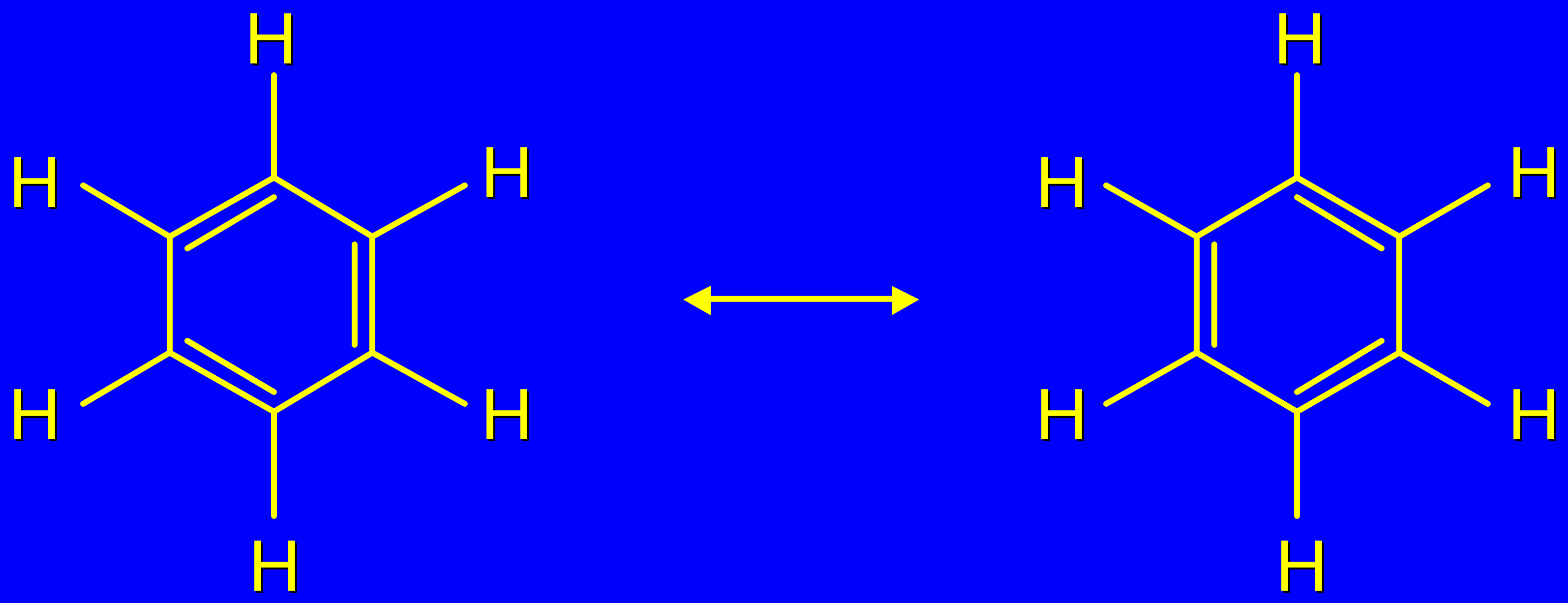
Kekulé Formulation of Benzene

Instead of Kekulé's suggestion of a rapid equilibrium between two structures:

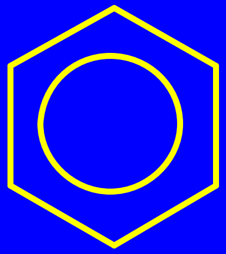


Resonance Formulation of Benzene

express the structure of benzene as a *resonance hybrid* of the two Lewis structures. Electrons are not localized in alternating single and double bonds, but are delocalized over all six ring carbons.



Resonance Formulation of Benzene



Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two Kekulé structures)

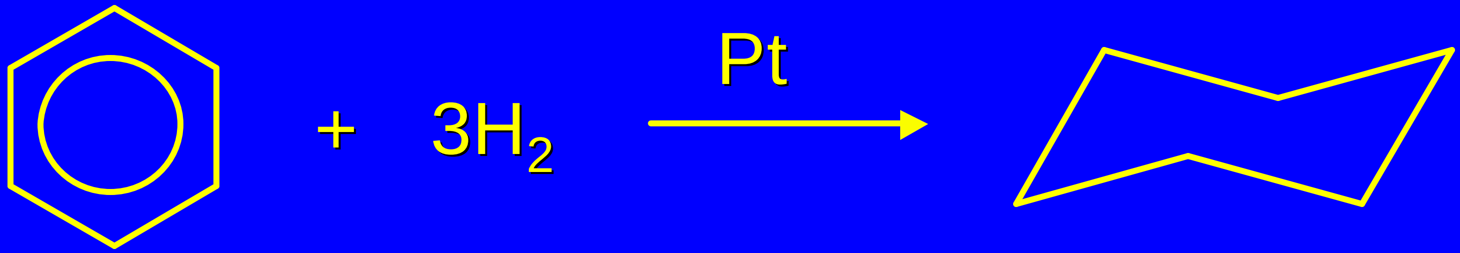
11.4
The Stability of Benzene

benzene is the best and most familiar example of a substance that possesses "special stability" or "aromaticity"

aromaticity is a level of stability that is substantially greater for a molecule than would be expected on the basis of any of the Lewis structures written for it

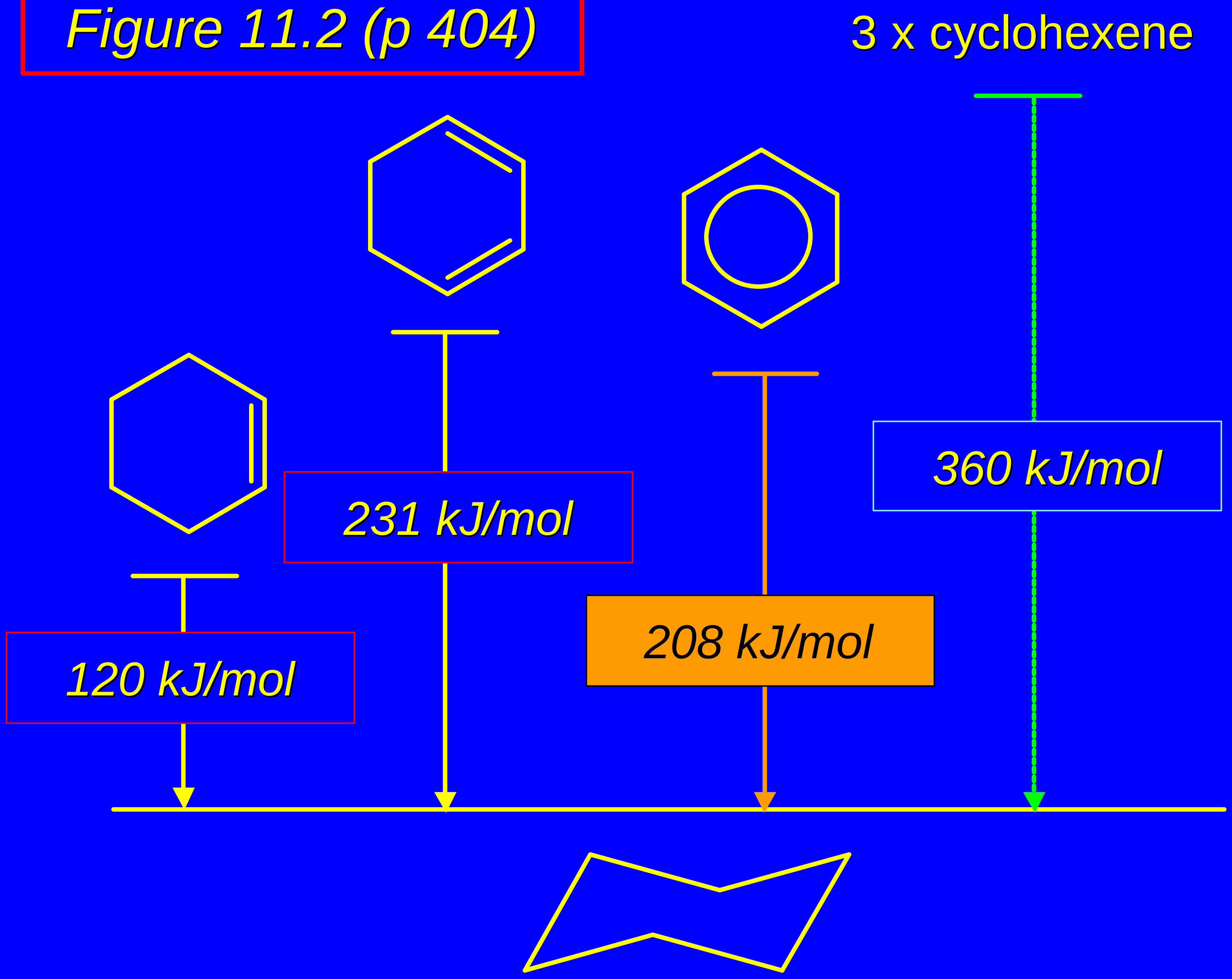
Thermochemical Measures of Stability

heat of hydrogenation: compare experimental value with "expected" value for hypothetical "cyclohexatriene"



$\Delta H° = -208$ kJ

Figure 11.2 (p 404)



3 x cyclohexene

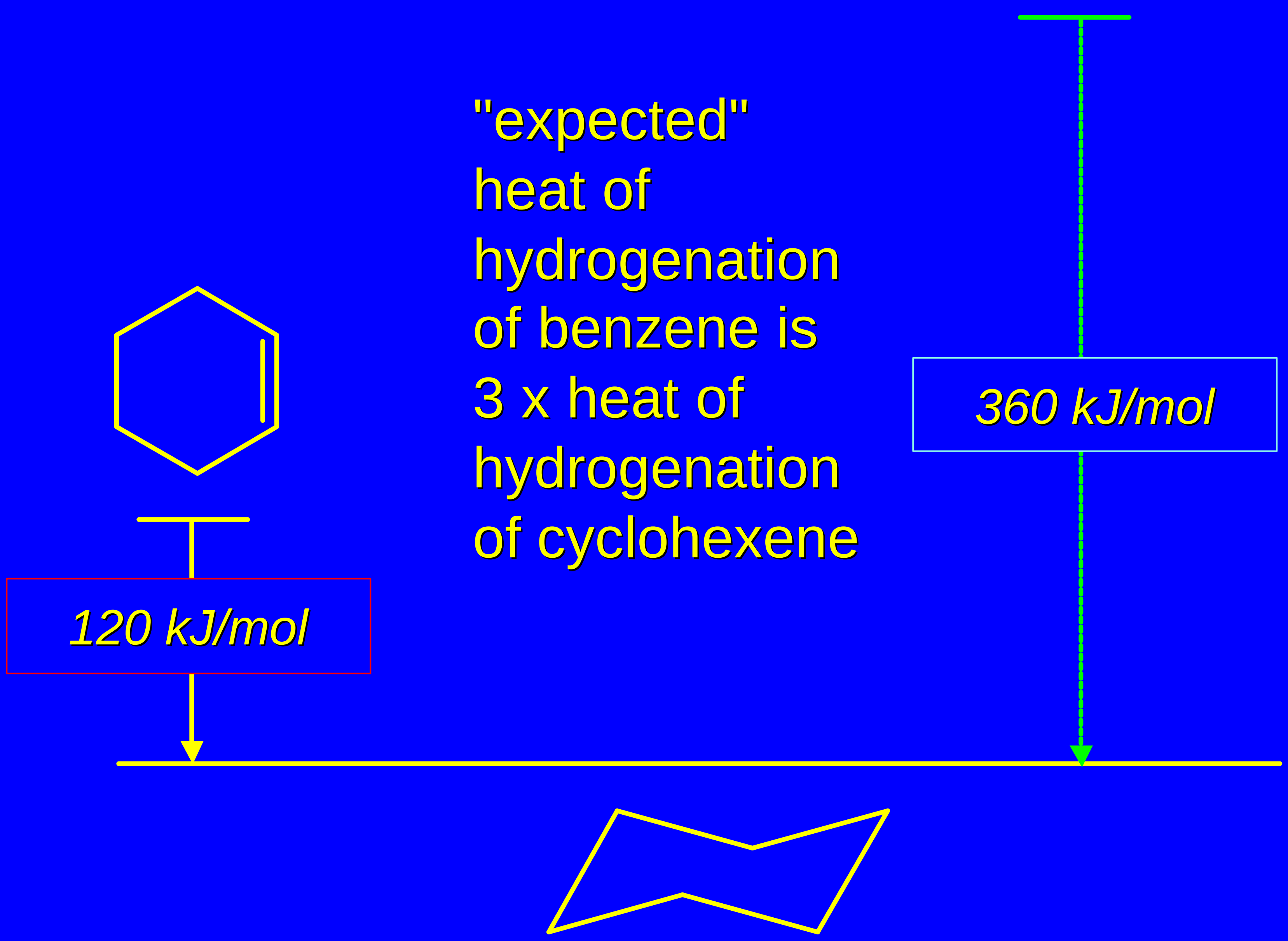
360 kJ/mol

231 kJ/mol

208 kJ/mol

120 kJ/mol

Figure 11.2 (p 404)



3 x cyclohexene

"expected" heat of hydrogenation of benzene is 3 x heat of hydrogenation of cyclohexene

120 kJ/mol

360 kJ/mol

Figure 11.2 (p 404)

observed heat of hydrogenation is 152 kJ/mol less than "expected"

benzene is 152 kJ/mol more stable than expected

152 kJ/mol is the resonance energy of benzene

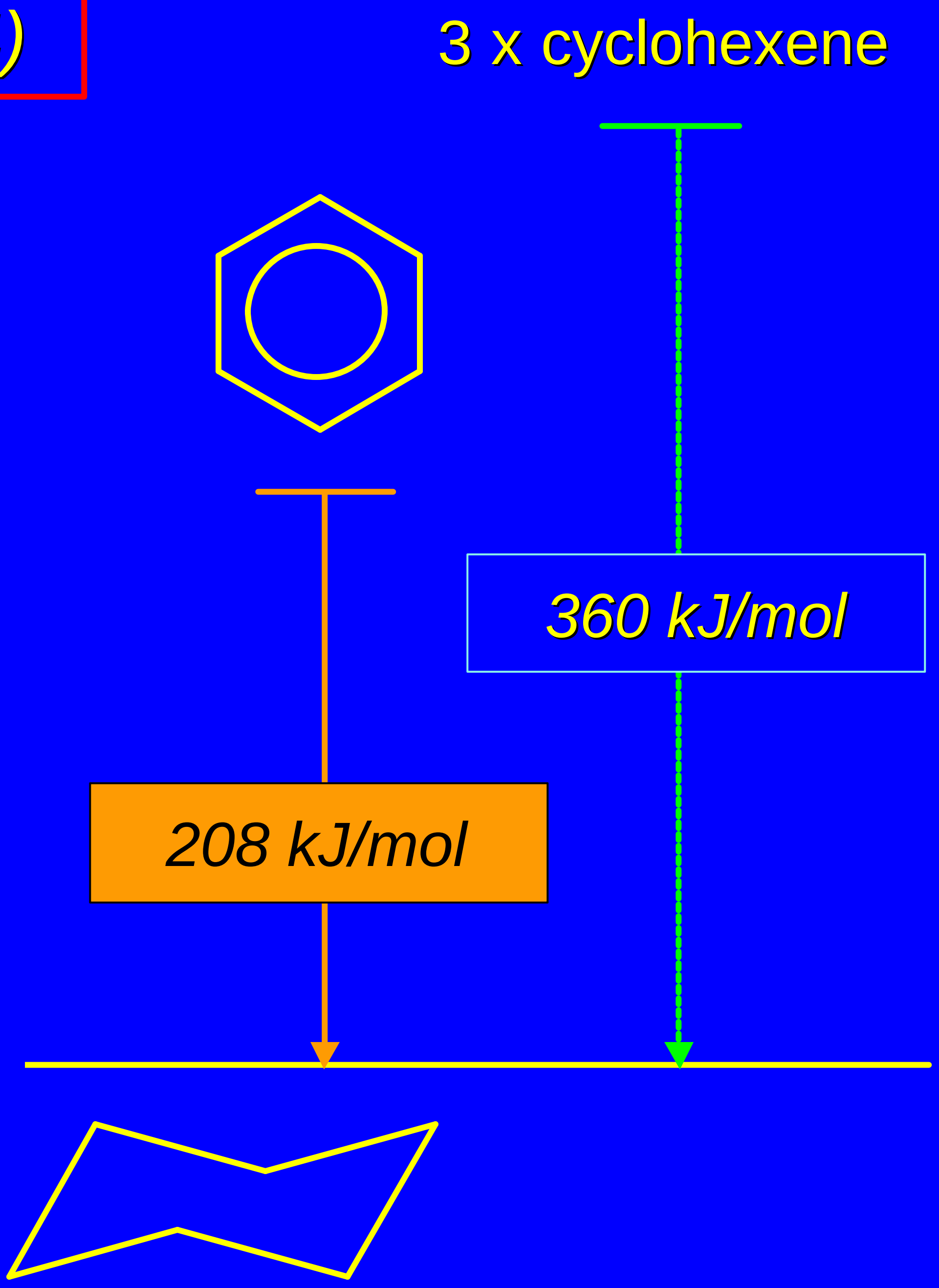


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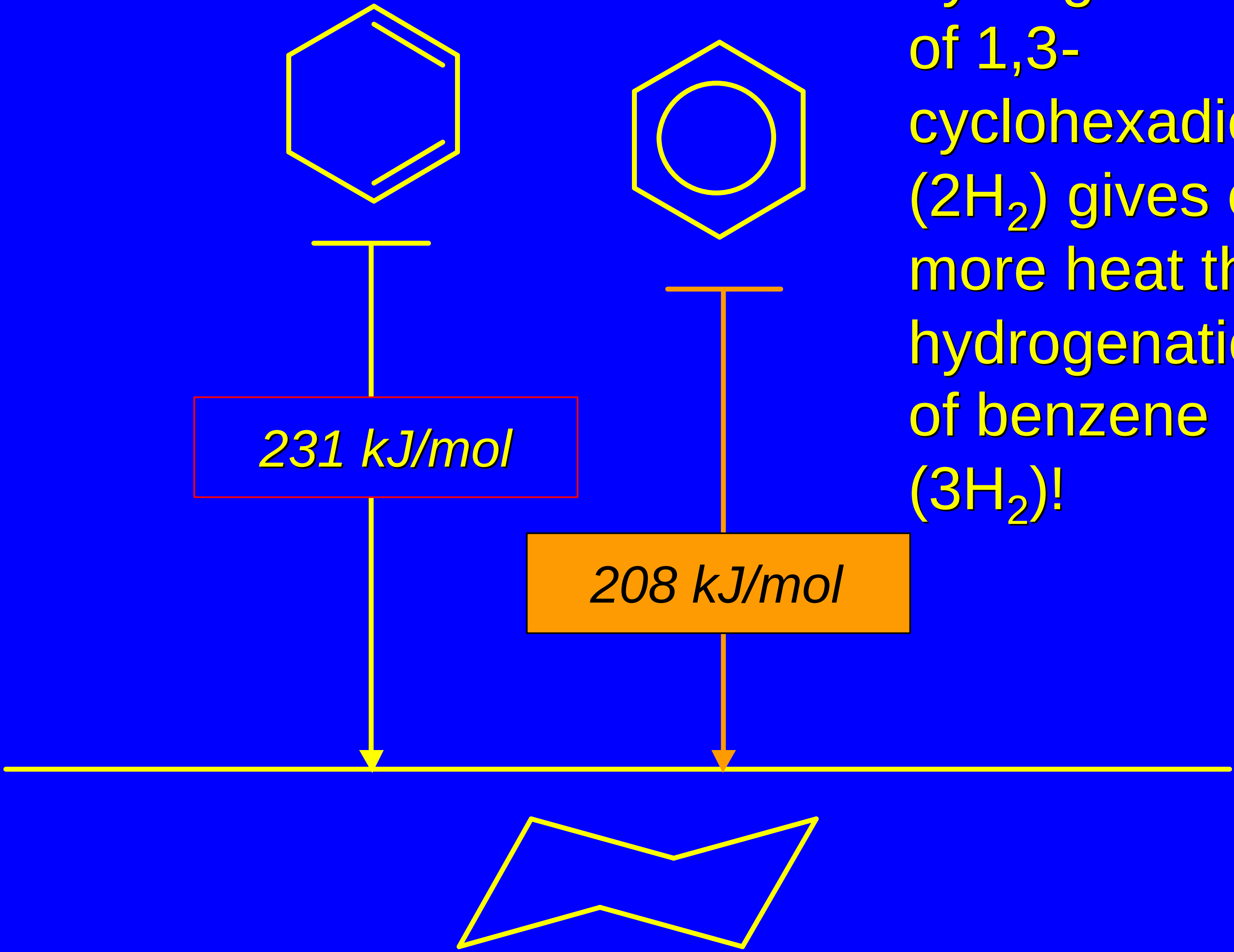
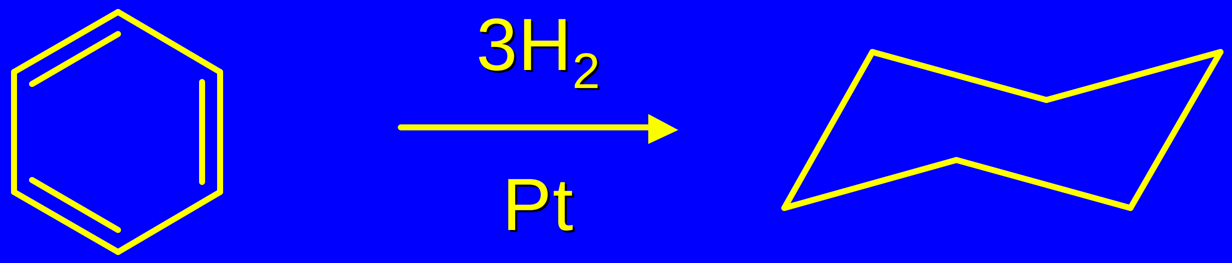
Figure 11.2 (p 404)

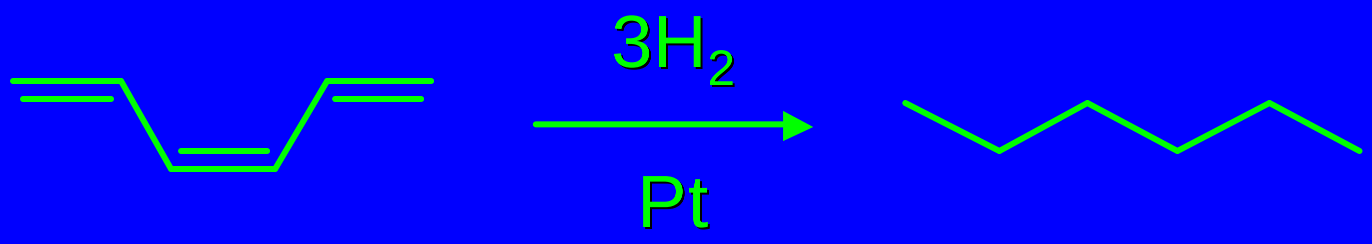


hydrogenation of 1,3-cyclohexadiene ($2H_2$) gives off more heat than hydrogenation of benzene ($3H_2$)!

Cyclic conjugation versus noncyclic conjugation



heat of hydrogenation = 208 kJ/mol



heat of hydrogenation = 337 kJ/mol

Resonance Energy of Benzene

compared to localized 1,3,5-cyclohexatriene

152 kJ/mol

compared to 1,3,5-hexatriene

129 kJ/mol

exact value of resonance energy of benzene depends on what it is compared to, but regardless of model, benzene is more stable than expected by a substantial amount

11.5

An Orbital Hybridization View of Bonding in Benzene

Orbital Hybridization Model of Bonding in Benzene

Planar ring of 6 *sp*^{2} hybridized carbons

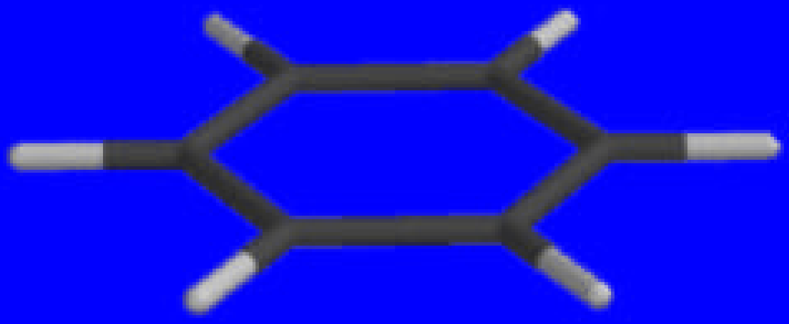


Figure 11.3

Orbital Hybridization Model of Bonding in Benzene

Each carbon contributes a *p* orbital

Six *p* orbitals overlap to give cyclic *p* system; six *p* electrons delocalized throughout *p* system

Figure 11.3

Orbital Hybridization Model of Bonding in Benzene

High electron density above and below plane of ring

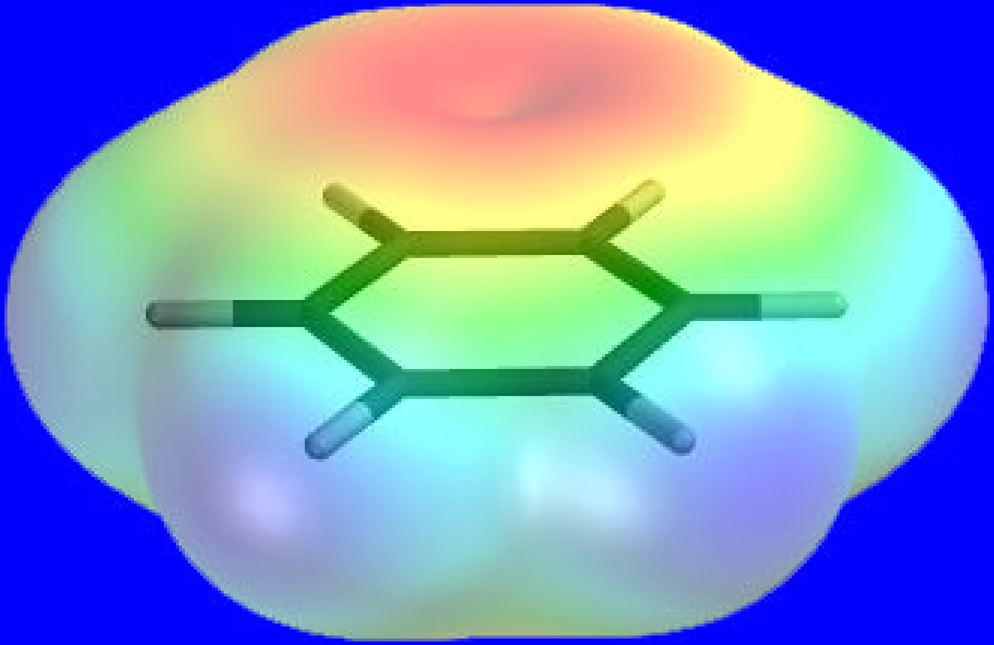
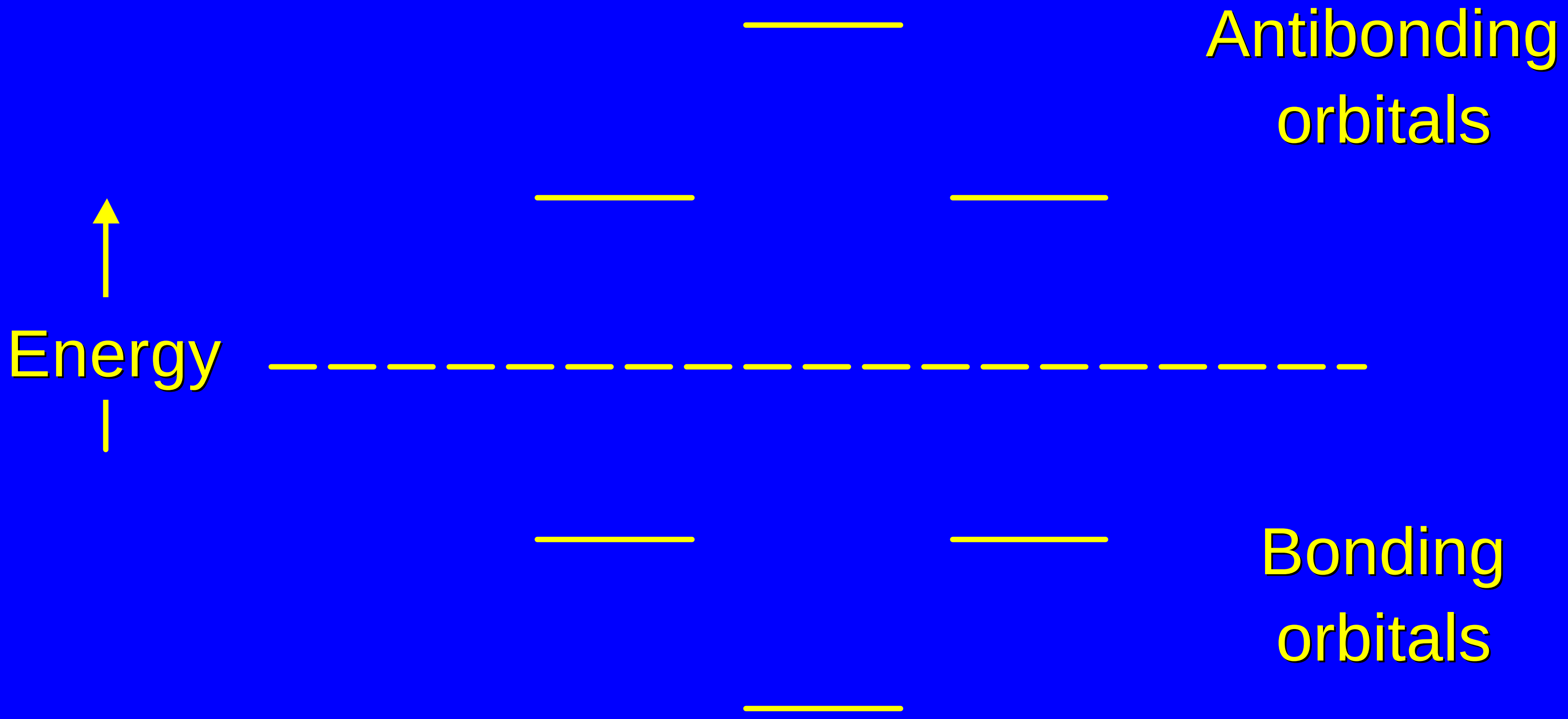


Figure 11.3

11.6

The *p* Molecular Orbitals of Benzene

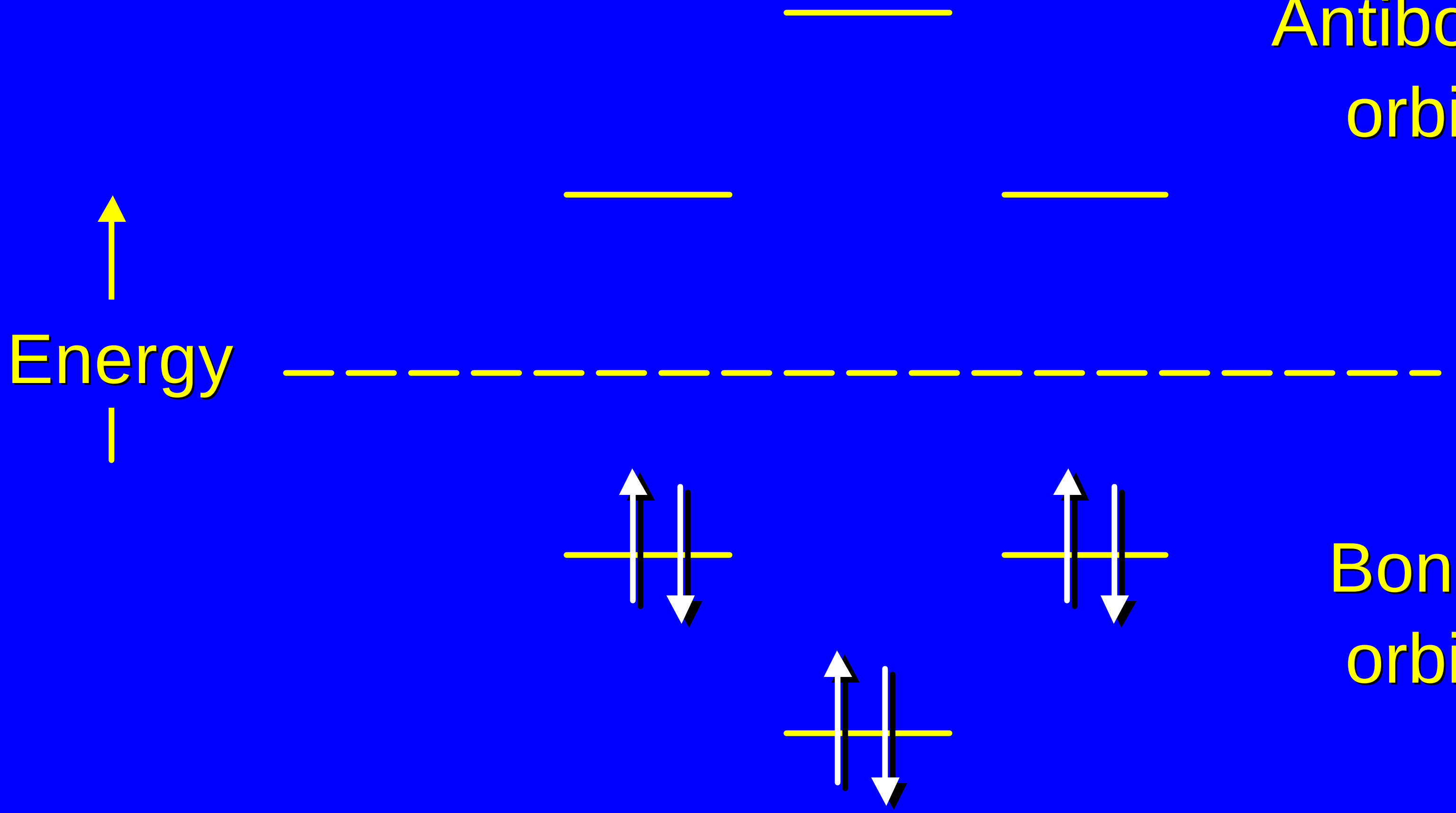
Benzene MOs



6 *p* AOs combine to give 6 *p* MOs

3 MOs are bonding; 3 are antibonding

Benzene MOs



Energy

Antibonding orbitals

Bonding orbitals

All bonding MOs are filled

No electrons in antibonding orbitals

The Three Bonding p MOs of Benzene