

1.4.8: Benzene and Aromaticity

Learning Objectives

- Apply Hückel theory to describing the pi bonding in cyclical conjugated system
- Identify the origin of aromaticity within Hückel theory to describe extra stabilization in certain cyclical conjugated systems

The previous sections addressed the π orbitals of linear conjugated system. Here we address conjugated systems of **cyclic conjugated hydrocarbons** with the general formula of C_nH_n where n is the number of carbon atoms in the ring. The molecule from this important class of organic molecule that you are most familiar with is benzene (C_6H_6) with $n = 6$, although many other molecules exist like cyclobutadiene (C_4H_4) with $n = 4$ (Figure 10.7.1).

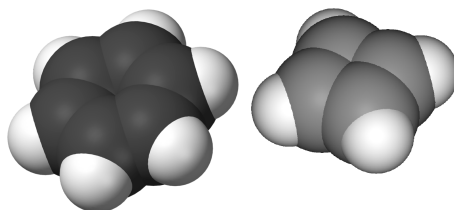


Figure 10.7.1 : Space-filling model of benzene (left) and cyclobutadiene (right). Carbon atoms are indicated in black, while hydrogen atoms are indicated in white. (Public domain; Benjah-bmm27 and Edgar181, respectively).

Structure of Benzene

The structure of benzene is an interesting historical topic. In 1865, the German chemist Friedrich August Kekulé published a paper suggesting that the structure of benzene contained a ring of six carbon atoms with alternating single and double bonds. Within this argument, two resonance structures can be formulated.

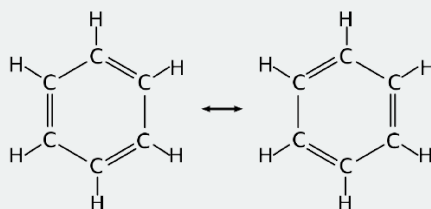


Figure 10.7.2 : Resonance structures of benzene.

However, X-ray diffraction shows that all six carbon-carbon bonds in benzene are of the same length, at 140 pm. The C–C bond lengths are greater than a double bond (135 pm), but shorter than a typical single bond (147 pm). This means that neither of the structures in Figure 10.7.2 are correct and the true 'structure' of benzene is a mixture of the two. As discussed previously, that such a valence bond perspective results in a **delocalization energy** within a molecular orbital approach.

Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular determinant

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \quad (1.4.8.1)$$

with the six roots $x = \pm 2, \pm 1, \pm 1$. This corresponds to the following energies (ordered from most stable to least since $\beta < 0$):

- $E_1 = \alpha + 2\beta$
- $E_2 = \alpha + \beta$
- $E_3 = \alpha + \beta$

- $E_4 = \alpha - \beta$
- $E_5 = \alpha - \beta$
- $E_6 = \alpha - 2\beta$

The two pairs of $E = \alpha \pm \beta$ energy levels are two-fold degenerate (Figure 10.7.3).

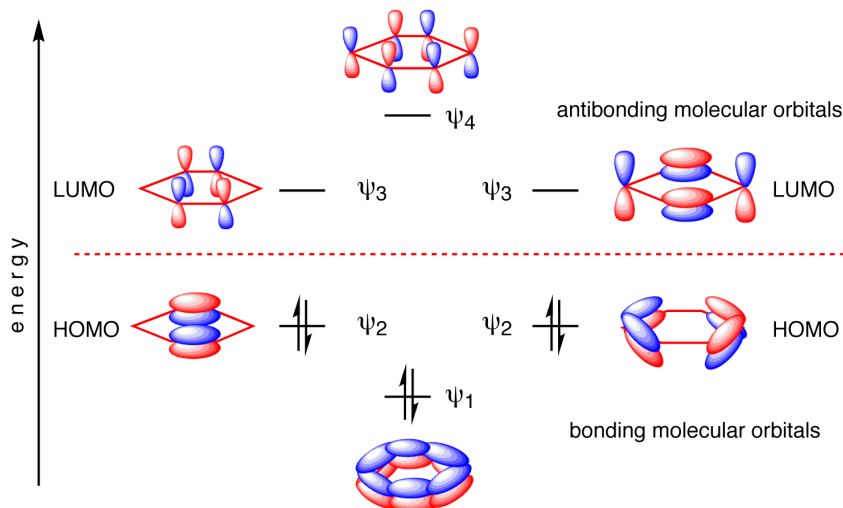


Figure 10.7.3 : The π molecular orbitals for benzene. The dashed lines represent the energy of an isolated p orbitals and all orbitals below this line are bonding. All orbitals above it are antibonding. (CC BY-NC-SA 4.0; Nick Greeves via ChemTube3D)

The resulting wavefunctions are below (expanded in terms of carbon $|2p\rangle$ atomic orbitals).

$$\begin{aligned}
 |\psi_1\rangle &= \frac{1}{\sqrt{6}} [|2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle] \\
 |\psi_2\rangle &= \frac{1}{\sqrt{4}} [|2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle] \\
 |\psi_3\rangle &= \frac{1}{\sqrt{3}} \left[|2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle \right] \\
 |\psi_4\rangle &= \frac{1}{\sqrt{4}} [|2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle] \\
 |\psi_5\rangle &= \frac{1}{\sqrt{3}} \left[|2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle \right] \\
 |\psi_6\rangle &= \frac{1}{\sqrt{6}} [|2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle]
 \end{aligned}$$

Each of the carbons in benzene contributes one electron to the π -bonding framework (Figure 10.7.3). This means that all bonding molecular orbitals are fully occupied and benzene then has an electron configuration of $\pi_1^2\pi_2^2\pi_3^2$. With the three lowest molecular orbitals occupied, the total π -bonding energy is

$$\begin{aligned}
 E_{tot}(\text{benzene}) &= 2(\alpha + 2\beta) + 4(\alpha + \beta) \\
 &= 6\alpha + 8\beta
 \end{aligned} \tag{1.4.8.2}$$

Since the energy of a localized double bond is $2(\alpha + \beta)$, as determined from the analysis of ethylene, the delocalization energy of benzene is

$$\begin{aligned}
 \Delta E &= E_{tot}(\text{benzene}) - 3E_{tot}(\text{ethylene}) \\
 &= (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) \\
 &= 2\beta
 \end{aligned}$$

The experimental thermochemical value is -152 kJ mol^{-1} .

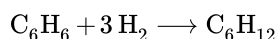
1.4.8.1: Aromaticity

In general, cyclic polyenes are only closed shell (i.e., each electron paired up) and extra stable for with $(4n + 2)\pi$ electrons ($n=0,1,2,\dots$). These special molecules have the highest delocalization energies and are said to be “aromatic”. For benzene this is 2β (Equation 1.4.8.2), which is the energy by which the delocalized π electrons in benzene are more stable than those in three isolated double bonds.

Hückel's Rule

A stable, closed-shell conjugated cyclic structure is obtained for molecules with $(4n + 2)\pi$ electrons with $n=2, 6, 10, \dots$ electrons.

Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product.



In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 11.9 kJ mol^{-1} . If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 23.9 kJ mol^{-1} on complete hydrogenation, and 1,3,5-cyclohexatriene to release 35.9 kJ mol^{-1} . These heats of hydrogenation ΔH_{hyd} reflect the relative thermodynamic stability of the compounds (Figure 10.7.4).

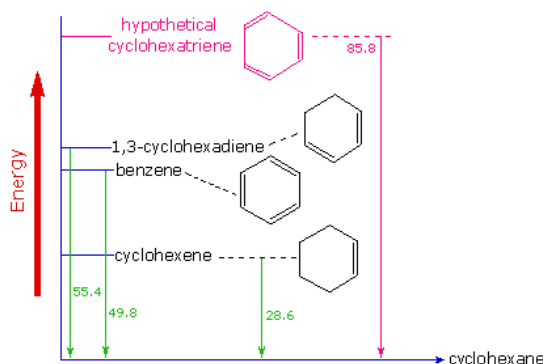


Figure 10.7.4 : Experimental evidence for aromatic stabilization energy in benzene from the heat of hydrogenation. Energies are in kcal/mol. (CC BY-NC-SA 4.0; William Resusch);

In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 8.1 kJ mol^{-1} , presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary 15 kJ mol^{-1} more stable than expected. This additional stability is a characteristic of all aromatic compounds.

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