The previous sections addressed the $\pi$ orbitals of linear conjugated system. Here we address conjugated systems of **cyclic conjugated hydrocarbons** with the general formula of $\text{(C}_n\text{H}_n\text{)}$ 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 ($\text{(C}_6\text{H}_6\text{)}$) with $n=6$), although many other molecules exist like cyclobutadiene ($\text{(C}_4\text{H}_4\text{)}$) with $n=4$) (Figure \(\PageIndex{1}\)).

Figure \(\PageIndex{1}\): 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.

![Resonance structures of benzene](image)

Figure \(\PageIndex{2}\): 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 structures Figure \(\PageIndex{2}\) 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.
Aromatic systems provide the most significant applications of Hückel theory. For benzene, we find the secular determinant

\[
\begin{vmatrix}
 x & 1 & 0 & 0 & 0 & 1 \\
 1 & x & 1 & 0 & 0 & 0 \\
 0 & 1 & x & 1 & 0 & 0 \\
 0 & 0 & 1 & x & 1 & 0 \\
 0 & 0 & 0 & 1 & x & 1 \\
 1 & 0 & 0 & 0 & 1 & x
\end{vmatrix} = 0
\]

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 \(\PageIndex{3}\)).

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

\[
\begin{align*}
|\psi_1\rangle &= \frac{1}{\sqrt{6}} \left[ |2p_{z1}\rangle + |2p_{z2}\rangle + |2p_{z3}\rangle + |2p_{z4}\rangle + |2p_{z5}\rangle + |2p_{z6}\rangle \right] \\
|\psi_2\rangle &= \frac{1}{\sqrt{4}} \left[ |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle - |2p_{z5}\rangle \right] \\
|\psi_3\rangle &= \frac{1}{\sqrt{3}} \left[ |2p_{z1}\rangle + \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle - |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle + \frac{1}{2}|2p_{z6}\rangle \right] \\
|\psi_4\rangle &= \frac{1}{\sqrt{4}} \left[ |2p_{z2}\rangle - |2p_{z3}\rangle + |2p_{z4}\rangle - |2p_{z5}\rangle \right] \\
|\psi_5\rangle &= \frac{1}{\sqrt{3}} \left[ |2p_{z1}\rangle - \frac{1}{2}|2p_{z2}\rangle - \frac{1}{2}|2p_{z3}\rangle + |2p_{z4}\rangle - \frac{1}{2}|2p_{z5}\rangle - \frac{1}{2}|2p_{z6}\rangle \right] \\
|\psi_6\rangle &= \frac{1}{\sqrt{6}} \left[ |2p_{z1}\rangle - |2p_{z2}\rangle + |2p_{z3}\rangle - |2p_{z4}\rangle + |2p_{z5}\rangle - |2p_{z6}\rangle \right]
\end{align*}
\]
Each of the carbons in benzene contributes one electron to the π-bonding framework (Figure \(\PageIndex{3}\)). 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

\[
E_{\text{tot}} (\text{benzene}) = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta \quad \text{(Equation 32)}
\]

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

\[
\Delta E = E_{\text{tot}} (\text{benzene}) - 3E_{\text{tot}} (\text{ethylene}) = (6\alpha + 8\beta) - 3 \times 2(\alpha + \beta) = 2\beta
\]

The experimental thermochemical value is \(-152 \text{ kJ mol}^{-1}\).

**Aromaticity**

In general, cyclic polyenes are only closed shell (i.e., each electron paired up) and extra stable for with \((4n+2)\) π electrons \((n=0,1,2\ldots)\). These special molecules have the highest delocalization energies and are said to be “aromatic”. For benzene this is \((2\beta)\) (Equation \(\ref{32}\)), 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 \((4n+2)\) electrons with \(n=2, 6, 10, \ldots\) 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 \(11.9 \text{ kJ mol}^{-1}\). 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 \(23.9 \text{ kJ mol}^{-1}\) on complete hydrogenation, and 1,3,5-cyclohexatriene to release \(35.9 \text{ kJ mol}^{-1}\). These heats of hydrogenation \(\Delta H_{\text{hyd}}\) reflect the relative thermodynamic stability of the compounds (Figure \(\PageIndex{4}\)). In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about \(8.1 \text{ kJ mol}^{-1}\), presumably due to conjugation of the double bonds. Benzene, however, is an extraordinary \(15 \text{ kJ mol}^{-1}\) more stable than expected. This additional stability is a characteristic of all aromatic compounds.
Figure \(\PageIndex{4}\): Experimental evidence for aromatic stabilization energy in benzeno from the heat of hydrogenation. Energies are in kcal/mol. (CC-SA-BY-NC; William Resuch);

**Contributors**

- Wikipedia