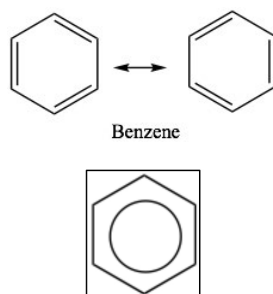
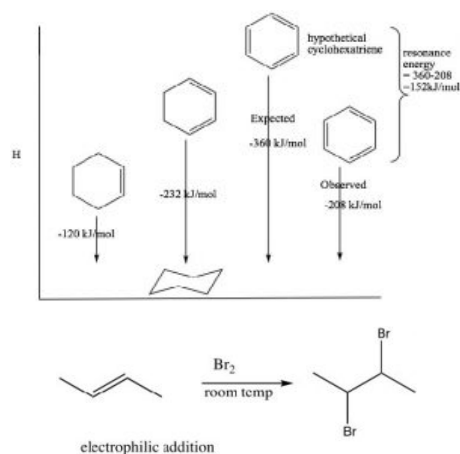


8.5: Aromaticity

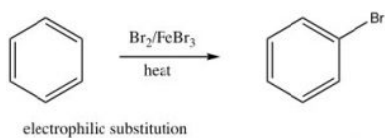
After considering some of the properties of conjugated systems, we now move on to what might be the ultimate in conjugated systems, as exemplified by benzene C_6H_6 . While many of the properties of benzene and its derivatives are similar in some ways to those of open-chained conjugated systems, there are important differences. Benzene has the property known as aromaticity and we say that benzene is aromatic. In everyday language, the term aromatic implies that something smells; usually in a good way. While benzene does have a fairly strong smell^[7], in chemistry, aromatic has come to mean a particular set of properties that emerge from the molecular structure of some molecules. Benzene is the simplest and most common example of an aromatic compound. The structure of benzene was something of a puzzle for quite a long time; it eventually came to be written in the form of what are now called Kekulé structures in which double and single bonds appear to alternate around the ring. We can write two equivalent resonance structures which contribute equally to the overall structure of the molecule. While these models can serve us well when trying to figure out what the electrons are doing during reactions, neither is not adequate to represent the actual structure of benzene. Sometimes, you will see benzene written with a circle in the middle (β) to indicate that, in reality, there are no single or double bonds present; rather, there is the same electron density (1.5 bonds) between all the carbons.



Benzene has some rather remarkable properties which led chemists to classify it as a member of a completely different type of functionality. For example, benzene is much more stable than one might imagine—even for a conjugated system. The heat of hydrogenation of benzene is -208 kJ/mol , while the ΔH of hydrogenation of the isolated double bond in cyclohexene is 130 kJ/mol . We can see the effects of conjugation in 1,3-cyclohexadiene, which is $\sim 232 \text{ kJ/mol}$ (not 260 as might be expected if it were conjugated). Similarly, if benzene were not conjugated, we would expect a heat of hydrogenation to be $3 \times 130 = 390 \text{ kJ/mol}$. Therefore, the difference between the expected and the actual hydrogenation energy must be due to the stabilization conferred by resonance.



This stability is called the resonance energy and, in aromatic compounds like benzene, it has a significant effect on the properties of the substance and types of reactions that a molecule participates in. For example, benzene does not react with electrophiles in the same way as isolated alkenes or even open-chained conjugated alkenes. Recall that the most common reactivity of simple alkenes is the **electrophilic addition** of $E-Nu$, where E is an electrophile and Nu is the nucleophile, across the double bond. In contrast, benzene undergoes **electrophilic substitution**; typically the reaction conditions require a catalyst and extensive heating. We will discuss the mechanism of this reaction shortly, but for now the important thing to note is that it is difficult to disrupt the aromatic ring of electrons and, when that does happen, the aromatic ring regenerates.



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