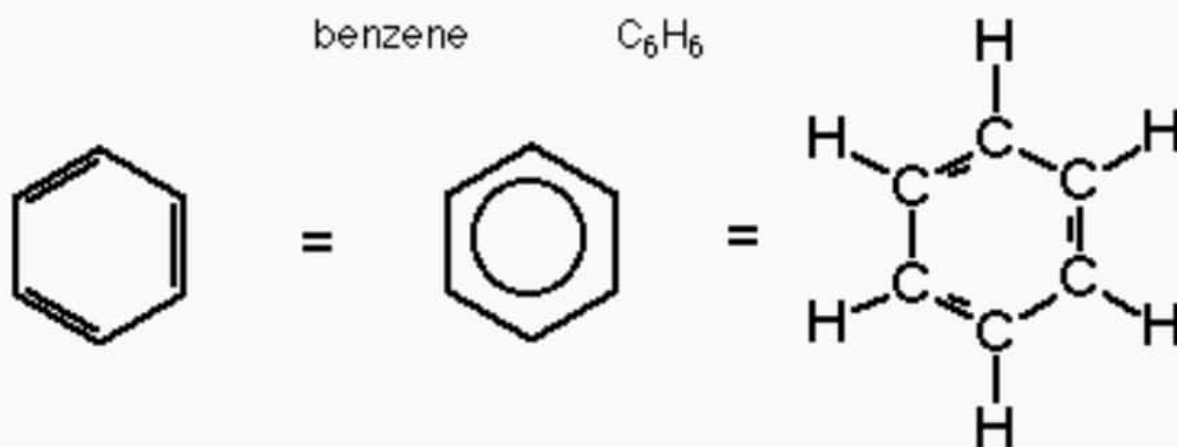


Benzene Structure and the Aromatic Ring

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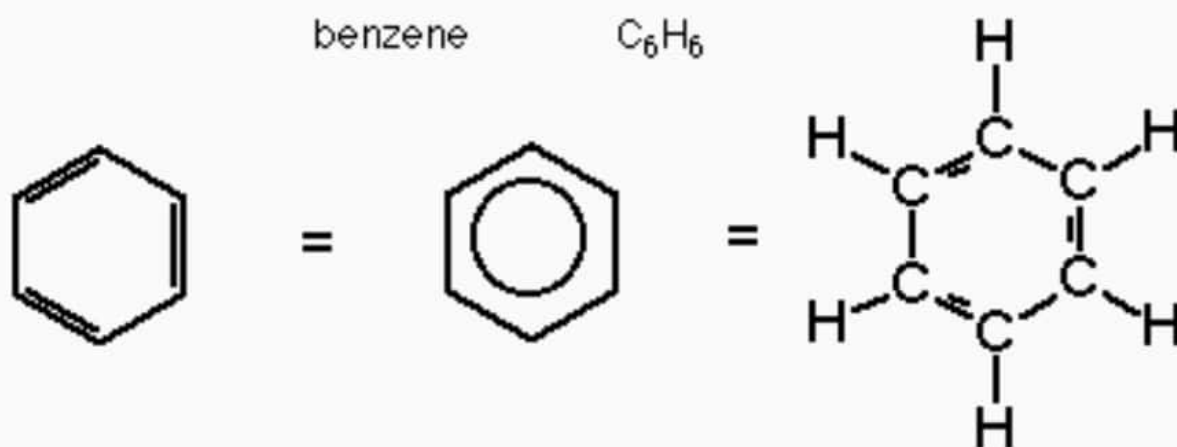
The most commonly encountered aromatic compound is benzene. The usual structural representation for benzene is a six carbon ring (represented by a hexagon) which includes three double bonds. Each of the carbons represented by a corner is also bonded to one other atom. In benzene itself, these atoms are hydrogens. The double bonds are separated by single bonds so we recognize the arrangement as involving conjugated double bonds. An alternative symbol uses a circle inside the hexagon to represent the six pi electrons. Each of these symbols has good and bad features. We'll use the three double bond symbol simply because it is also routinely used in the text.



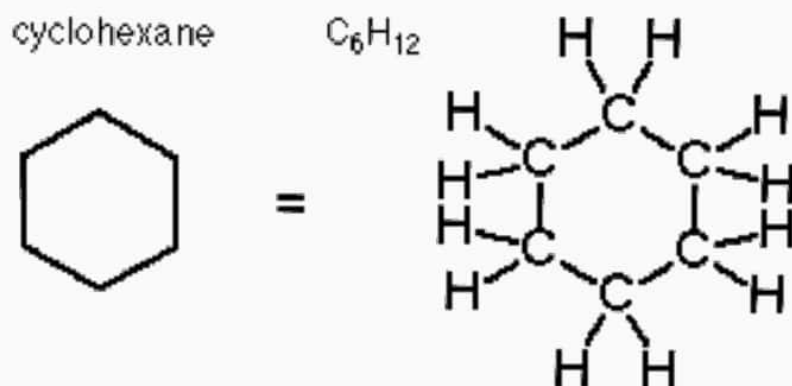
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Keep in mind that if the hexagon contains neither the three double bonds nor the circle, the compound is not aromatic. It is simply cyclohexane and there are two hydrogens on each carbon atom. This is easy to mistake when hurrying, so be careful when you are interpreting any structural formulas which include hexagons.



The structure with three double bonds was proposed by Kekule as an attempt to explain how a molecule whose molecular formula was C_6H_6 could be built out of carbons which make four bonds. The ring and the three double bonds fit the molecular formula, but the structure doesn't explain the chemical behavior of benzene at all well. Each of the double bonds would be expected to show the characteristic behavior of an alkene and undergo addition reactions, but this is not how benzene reacts.

In particular, we would expect a carbon-carbon double bond to react quickly with bromine to make a dibromo compound. This is what alkenes do very readily, and in fact it is a useful test for alkenes in the laboratory. Benzene does not react with bromine unless a very bright light or a strong catalyst is used, and then the reaction is not an addition reaction. We conclude that there is something quite unusual about the double bonds in benzene.

Kekule (thinking about this problem before bonds were understood as pairs of electrons) suggested that there are two forms of benzene which differ in the locations of the double bonds. His idea was that these were in rapid equilibrium, so rapid that there was never a fixed location for the double bond. One could say that an approaching bromine molecule could not "find" a double bond to react with.

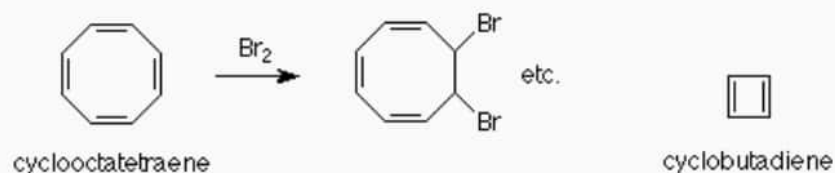
There were several other structures proposed for benzene, but a much more satisfactory approach became possible when we began to understand that covalent bonds consist of pairs of electrons shared between atoms. The difference between the two structures Kekule envisioned (called Kekule structures) is only the difference between the locations of three pairs of electrons. This is exactly the type of situation where resonance must be involved. The hybrid or "average" of the two Kekule structures has one sigma bond and one-half of a pi bond between each two carbon atoms. Thus each carbon is joined to each of its neighbors by a one-and-half bond. Each bond in

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Recall that resonance has another important feature: when resonance is involved, the real structure is more stable than we would expect from any of the structures we write using the one line = two electrons symbolism. This extra lowering of energy, which for benzene is about one-third as much as making a typical covalent bond, is quite important in the reactions of benzene and other aromatic compounds. As we will see, reactions of the benzene ring almost always result in products in which the benzene ring persists -- an outcome of its stability.

When resonance theory was first applied to understanding the structure of benzene, the key feature seemed to be a resonance hybrid of ring structures containing alternating single and double bonds. This immediately led to attempts to make and study compounds like cyclooctatetraene and cyclobutane. These compounds also have ring structures with alternating single and double bonds.

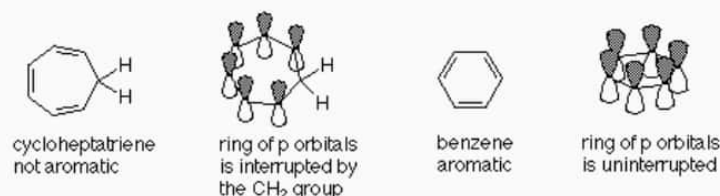


Cyclooctatetraene has been made, but it does not possess the properties of extra stability and resistance to addition reactions which distinguish aromatic compounds. It readily adds bromine, for example. Cyclobutadiene is extremely unstable -- one cyclobutadiene molecule reacts with another cyclobutadiene molecule instantaneously even at very low temperatures -- so it certainly does not act like an aromatic molecule and it has been called "antiaromatic" as a result.

alternating single and double bonds. After considerable development of the underlying theory, the pattern which has emerged is that aromatic characteristics are only expected when there is a ring of pi electrons in which the number of pi electrons is equal to $4n + 2$ (where n is an integer, 0, 1, 2, etc.). (This is known as the Huckel rule after its discoverer.) We can check this against the compounds we have considered so far: Benzene has 6 pi electrons (two for each pi bond) which is the number we get from $4n + 2$ if $n = 1$.

Cyclooctatetraene has 8 pi electrons, and there is no integer "n" which will make $4n + 2 = 8$. Cyclobutadiene has 4 pi electrons and also doesn't fit $4n + 2$. There are many other examples which support Huckel's rule.

It is important to be sure that the ring of alternating single and double bonds is complete. If there is an sp^3 hybridized carbon in the ring, the conditions for aromatic character are not present, and we do not worry about checking for $4n + 2$. Here's an example:



Another way to see this is to look at the p orbitals which combine to make the pi bonds. If these p orbitals combine to form an uninterrupted ring as is the case in benzene, then we can go ahead to use Huckel's rule to check for the proper number of pi electrons for aromatic character. If the ring of p orbitals is broken by a CH₂ (group or another tetrahedral carbon) with no p orbital, then the compound cannot be aromatic and we need not try to apply Huckel's rule.

The p orbitals which make up the unbroken p orbital ring can be associated with other atoms than carbon. Two examples are furan and pyrrole, in which two of the six electrons needed come formally from unshared electron pairs on oxygen.

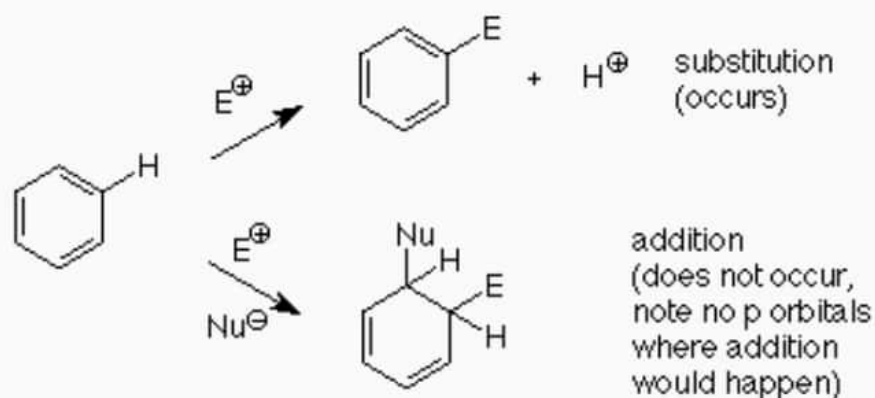


Such an unshared pair can also come from a carbon atom, which will have to have a negative charge. An example of this is the cyclopentadienide ion which can be made by treating cyclopentadiene with a moderately strong base. Cyclopentadienide ion is sufficiently stabilized by its aromatic character that cyclopentadiene (its conjugate acid) has a pK_a of 16, close to that of water. Cyclopentadiene is a remarkably strong acid for a hydrocarbon because its conjugate base has the extra stability of an aromatic compound.

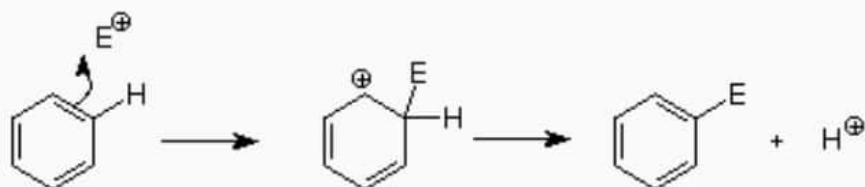


Notice that here the formally positively charged carbon atoms are sp^2 hybridized and have an empty p orbital which completes the cyclic arrangement of p orbitals.

Let's finish up today by looking at the general mechanism for the characteristic reactions of aromatic compounds -- electrophilic aromatic substitution. The most important characteristics of these reactions follow directly from the stability of the aromatic ring. First, these reactions are typically catalyzed by strong electrophilic (Lewis acidic) catalysts like H_2SO_4 , $AlCl_3$, and $FeCl_3$ which are required to overcome the stability of the aromatic ring. Second, these are substitution reactions since addition reactions would interrupt the p orbital ring and destroy the aromatic stability.



Even though the outcome of the attack of electrophiles on benzene is substitution rather than addition, the first step is the same as in electrophilic addition to alkenes -- attack of the electrophile on a pi bond and the formation of a new sigma bond between a carbon atom and the electrophile. The carbocation which is formed undergoes loss of the H^+ from the carbon which was attacked. The electrons from the C-H bond are returned to the aromatic pi electron ring and aromatic stability is restored.



Notice that the intermediate here is a carbocation, but it is not aromatic. The carbon bearing the hydrogen and the electrophile is sp^3 hybridized and has no p orbital to contribute to a cyclic p orbital system. The carbocation intermediate is somewhat resonance stabilized, though, by a resonance arrangement which is very similar to the one we saw in the addition of electrophiles to conjugated dienes.