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Chapter 12 Arenes and Aromaticity

Arenes

Arenes are hydrocarbon derivatives of benzene. They are called aromatic systems due to their special stability (not due to their aroma!). The special stability results from the highly conjugated system with the electrons delocalized all the way around the ring.

The name benzene comes from the Arabic *luban jawi* or "incense from Java" since it is isolated as a degradation product of gum benzoin. This is a balsam obtained from a tree that grows in Java and Sumatra. This degradation product is benzoic acid, which can be decarboxylated by heating with calcium oxide, CaO.



And tolu balsam from the South American tolu tree, when distilled, produces toluene or methylbenzene.

The term aliphatic hydrocarbons, given to alkanes, alkenes, alkynes and benzene derivatives, comes from the Greek word *aleiphar* which means oil or unguent.

Benzene

Benzene has three double bonds that are conjugated and in a circular arrangement. Due to this conjugation and circular arrangement, the double bonds are much less reactive than normal, isolated alkenes. For example, benzene will not react with bromine or hydrogen gas in the presence of a metal catalyst, reactions that alkenes undergo readily.

$$CH_{3}-CH=CH-CH_{3} \xrightarrow[rt]{Br_{2}} CH_{3}-C$$

$$CH_{3}-CH=CH-CH_{3} \xrightarrow{H_{2}, Pd} CH_{3}CH_{2}CH_{2}CH_{3}$$

$$(H_{2}, Pd) Ko Reaction$$

$$(H_{2}, Pd) Ko Reaction$$

If we examine the structure of benzene we do not see a series of alternating double and single bonds as we would expect from the Lewis structure. We see that all the C-C bonds and all the C-H are exactly the same. The bond order for the C-C bond is 1.5, so it is a one and a half bond.

We can see this if we compare the bond lengths in benzene with 1,3-butadiene.



In benzene we have a series of conjugated dienes for which we can draw two resonance structures that are of the same energy.



There is a special stability that is associated with a cyclic conjugated system. We can get a measure of this special aromatic stability by looking at the heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, and benzene. It is much more difficult to hydrogenate benzene than alkenes or alkyne. Rhodium and platinum catalysts are more reactive than palladium catalysts and it is possible to hydrogenate benzene under moderate pressure at room temperature using rhodium or platinum catalysis. Using the less active nickel catalysts, high temperatures are needed (100-200°C) and high pressures (100 atmospheres).



So, for cyclohexadiene, we find that the ΔH is 9 KJ less than for two isolated double bonds due to the extra stabilization provided by the conjugation.



Expect $\Delta H = 2 \times -120 = -360 \text{ KJ/mol}$ Find $\Delta H = -208 \text{ KJ/mol}$

So, benzene is more stable than expected by 152 KJ/mol.

So, the circular arrangement of the three conjugated double doubles gives a very large amount of stabilization to the system. We find that the three conjugated double bonds have a lower heat of hydrogenation than two conjugated double bonds.

The reason for this extraordinary stability is that the six π -electrons are delocalized over all of the six carbon atoms and in fact are circulating around the ring to make a ring current.



There is continuous circular overlap of p-orbitals around the ring. This is, in fact, the definition of aromaticity. The electrons can flow in a circel around the ring in these contiguous orbitals. Note that there is a region of electron density above and below the plane of the ring.

Note that in order for this delocalization of the electrons to occur there must be a continuous overlap of the p-orbitals and in order for this overlap to be effective all of the sp^2 carbon atoms must be in the same plane. Benzene is a flat molecule and there is a region of circular electron density both above the ring and below the ring.

The Π-Molecular Orbitals

It is useful to look in more detail at the actual orbitals that contain the 6π -electrons. As we saw with ethene and 1,3-butadiene, the six p-orbitals can be combined to give six molecular orbitals (M.O.'s). Three of these will be bonding and three of these will be non-bonding. We see that the lowest energy molecular orbital has no nodes. All of the p-orbitals overlap constructively. The next highest molecular orbital has one node and we

see that there are two molecular orbitals with one node. They therefore have the same energy. All of the six π -electrons all go into these low lying bonding molecular orbitals. This molecular orbital picture provides a good explanation of why benzene is so stable.



The delocalization provided by the cyclic conjugation in benzene causes it π -electrons to be held more strongly than they would be in the absence of cyclic conjugation.

Nomenclature

Substituted benzene derivatives are named as derivatives of benzene.



There are, however, several substituents that change the parent name. We need to learn these, since they are in common use. The official systematic name is given in brackets.



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Disubstituted benzenes have a special nomenclature that describes the relation between the substituents. The term *ortho* describes two substituents that are in a 1,2-relationship. Note that there are two *ortho* positions. If one of the substituents is one that defines the parent name (i.e. the –OH for phenol, the –CO₂H for benzoic acid, etc.) then this substituent gets the number one position and dominates the numbering. The term *meta* describes two substituents in a 1,3-relationship and *para* describes a 1,4-relationship. There are two *meta* positions and one *para* position. These terms are abbreviated as *o*-, *m*-, *p*-, respectively.



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Dimethyl derivatives of benzene are called xylenes. There are three possible isomers. We use the *ortho*, *meta*, *para* terms to describe them.



If there are three or more substituents use numerical locants. If there is a substituent that determines the parent name, this substituent gets number one. Then choose the direction of numbering so as to give the next substituted position the lowest number. List the substituents in alphabetical order. When there is no parent name other than benzene, number the positions so as to give the lowest locant at the first point of difference, just like in substituted cyclohexanes.



When the benzene ring is a substituent, use "phenyl".



We use the term "aryl" to refer to any benzene ring derivative. The "benzyl" group is a $C_6H_5CH_2$ - group. Biphenyl is two benzene rings joined directly together.



We can have polycyclic aromatic rings. Many of these are known and found in coal tar, which is produced when coal is converted to coke by heating to $\sim 1000^{\circ}$ C.



Naphthalene has a resonance energy of 255 KJ/mol. This is more than the resonance energy of benzene (152 KJ/mol) but it is less that twice the benzene resonance energy. The second benzene ring does not quite have the same amount of stabilization as the first. This can be seen from the resonance structures. In general, the most stable resonance structure for a polycyclic aromatic hydrocarbon is the one with the greatest number of rings that that correspond to Kekule formulations in which there are six π -electrons delocalized around the ring. For naphthalene only resonance structure **B** fits this criteria. It is therefore the most stable structure and is most representative of the actual structure of the molecule.



Only the ring on the left corresponds to the Kekule formulation in which there are 6 π -electrons fully delocalized.

Most stable form since both rings have the fully aromatic sturcture with the 6 π - electrons fully delocalized.

Only the ring on the right corresponds to the Kekule formulation in which there are 6 π -electrons fully delocalized.

Note that phenanthracene has a larger stabilization energy than anthracene, even though both have three aromatic rings joined together and both have 14 π -electrons. This is because the arrangement of π -electrons is more favorable in phenanthracene than anthracene in that anthracene has no Lewis structure in which all three rings are fully aromatic with the 6 π -electrons fully delocalized around all three rings but phenanthracene does. This is the one shown above.

Reactions of Arenes

There are two types of reaction of arenes:

(1) Reactions of the ring itself. These include: (a) reduction of the double bonds and (b) electrophilic aromatic substitution.

(2) Reactions of the side chain. The aryl group acts as a substituent and affects the reactivity of the side chain to which it is attached.

We will discuss reduction of the ring and reactions of the side chain in this chapter and electrophilic aromatic substitution in the next chapter.

A carbon that is next to a benzene ring is called a benzylic carbon. These are similar to allylic carbons but even more highly stabilized by the adjacent π -system.







benzylic carbocation

benzylic radical

Reduction of the Benzene Ring

A mild way to reduce the benzene ring without having to use high pressures of hydrogen gas is to use the Birch reduction. This is a dissolving metal reduction using sodium in liquid ammonia containing an alcohol as a proton source. The product is a 1,4-diene.



This is a radical anion mechanism and it accounts for the fact that the more stable conjugated 1,3-system is not form but the less stable 1,4-diene. When sodium is dissolved in liquid ammonia (b.p. -38°C) it forms a solution of free electrons. (It is a beautiful azure blue color!) One of these electrons adds to the electron deficient π -system of the benzene ring to form a radical anion. The lone pair and the single unpaired electron experience electron-electron repulsion and so align themselves as far apart as possible. The anionic lone pair abstracts a proton from the alcohol and then a second electron adds to make

another anion, which in turn abstracts a second proton from the alcohol to complete the reduction.



In the Birch reduction there is good regio-control over where the double bond forms in substituted benzene derivatives. If there is an electron donating substituent, such as alkyl or methoxy or an amine, the electron-donating substituent ends up attached to the double bond. The reason for this is that the initial radical anion intermediate is more stable if the negative charge and free radical end up on a carbon that is away from the negative charge. Electron donating groups destabilizing negative charges.



Conversely, electron-withdrawing substituents direct the double bonds to be away from the substituent.



Free Radical Halogenation

A benzylic C-H bond is weaker than a C-H bond of a tertiary alkane or allylic alkane. This can be determined by comparing bond dissociation energies.



The benzylic radical is stabilized by resonance, just like the allylic radical. Note that the odd electron is delocalized on the benzylic position and the *ortho* and *para* carbon.



Most stable Lewis structure since the ring retains its aromaticity.

In free radical halogenations there is excellent selectivity for the benzylic position because the benzylic C-H bond is the weakest bond due to the fact that it forms a resonance stabilized radical.



The mechanism is a free radical chain reaction.

Inititation: CI-CI hv 2 CI ·

Propagation



A good reagent for benzylic bromination is NBS. This provides a low level concentration of Br_2 . Again, only the benzylic position is brominated



Oxidation of Alkylbenzenes

The side chains of alkylbenzene, alkenyl and alkynyl derivatives can be oxidized by strong oxidizing reagents such as chromic acid or potassium permanganate. The oxidizing agents do not react with the benzene ring itself but react at the benzylic position to fully oxidize the benzylic carbon. The result is a benzoic acid derivative in which a carboxylic acid attached directly to the benzene ring.



In order for this reaction to occur there must be at least one benzylic hydrogen. Tertiary alkyl groups do not react.

$$\begin{array}{c} & \overset{CH_3}{\underset{l}{\leftarrow}} & \overset{Ra_2Cr_7O_7, H_2SO_4}{\underset{l}{\leftarrow}} & \overset{No Reaction}{\underset{l}{\leftarrow}} \\ \end{array} \\ \end{array}$$

It does not matter what functional groups are contained in the side chain; the end result of the oxidation is the benzylic carboxylic acid. If there are two alkyl groups on the benzene ring both will react, providing that they each have at least one benzylic hydrogen.



Nucleophilic Substitution of Benzylic Halides

Primary benzylic halides are very reactive in bimolecular nucleophilic substitution ($S_N 2$) reactions. The partial positive charge that develops in the transition states is stabilized by the adjacent benzene ring, accelerating the reaction. And they cannot undergo competing substitution reactions.



Secondary benzylic halides are very subject to elimination reactions since the resulting double bond is stabilized by conjugation with benzene ring.



 $S_N 1$ reactions are also very favorable because the highly stabilized carbocation. A tertiary benzylic carbocation is much more stable than a tertiary carbocation. For example, in a solvolysis reaction in aqueous acetone, chlorodimethylphenylmethane reacts six hundred times faster than 2-chloro-2-methylpropane.



This is because the tertiary benzylic carbocation is stabilized by resonance with the benzene ring. The carbocation is partially delocalized over the benzene ring.



But note, although the positive charge is spread out over both *ortho* and the *para* position, the nucleophile the nucleophile attacks only at the benzylic position. If attack occurred at the ring itself, the aromatic stability of the ring would be largely lost.

Triphenylmethyl cation is stable enough to be isolated as the perchlorate salt.



Preparation of Alkenylbenzenes

Dehydrogenation is a favorable reaction at very high temperatures since the entropy term is temperatures and becomes the dominant factor as the temperature increases.



Dehydration and dehydrohalogenation are also very favorable. When the double bond forms it always goes into conjugation with the benzene ring.



Addition Reactions

The modern formulation of Markovnikov's rule states the electrophile adds to an alkene so as to give the more stable carbocation intermediate. In systems where the alkene is conjugated with the benzene ring, this will be the benzylic carbocation. The nucleophile then becomes attached to the benzylic carbon.



Since the side chain double bond is much more reactive than the benzene ring, it can be selectively reduced.



In the presence of peroxides, HBr will add so as to form the more stable benzylic radical (also in accordance with Markovnikov's rule).



The reaction follows a free radical chain mechanism in which the weak O-O bond of the peroxide breaks homolytically when heated



The Polymerization of Styrene

Polystyrene or styrofoam is a very important material that has many uses as packing material, insulation, beverage cups, etc. It is very light and very strong. There are several ways to polymerize styrene including free radical polymerization, cationic polymerization with acid, Ziegler-Natta polymerization and other methods.

Free radical polymerization is what is called a head-to-tail polymerization. We need a radical initiator, RO, which adds to the terminal end of the styrene to start the radical chain process. The ensuing benzylic radical then adds to another molecule of styrene to give a benzylic radical, which in turn adds to the terminal carbon of another styrene molecule.

This process repeats itself thousands of times until the desired chain length is produced. Then a radical terminator, X, is added to stop the reaction. In a final purification process, the radical initiator and radical terminator are removed to give polystyrene. The length of the chains has a large effect on the properties of the final material and the chain lengths can be tailored to the desired application.



Aromaticity

As we have seen, benzene with its circular arrangement of six π -electrons, is very stable due to the delocalization of the π -electrons over all of the six carbons of the benzene ring. There literally is a small electric current flowing around the ring.

When we examine other systems that might also have this special aromatic stability, we find some interesting results. For example, look at cyclobutadiene, a molecule that on first glance looks as if it should be aromatic. It is a cyclic molecule and has two π -bonds that are conjugated. It looks as if it should be particularly stable in the same way that benzene is particularly stable but in fact it is not. It has never actually been isolated in pure form since it decomposes immediately on formation so in effect it is not a known molecule. It turns out that 1,3-butadiene is destabilized by the circular arrangement of π -electrons. It is less stable than expected.

This is also true of cyclooctatetraene. This molecule can be isolated and heats of hydrogenation experiments have been done to determine that the circular, conjugated arrangement of double bonds is less stable than isolated double bonds.



We see that cyclooctatetraene is less stable than expected by 26 KJ/mol. The circular arrangement of electrons, rather than adding stability, as it does in benzene, actually makes cyclobutadiene and cyclooctatetraene less stable. These compounds are called anti-aromatic. We can account for this using an empirical rule developed by Huckel, called Huckel's Rule.

Huckel's Rule: among planar, monocyclic, fully conjugated polyenes, only those having $4n+2\pi$ -electrons, where n is a whole number (n = 0, 1, 2, 3, ...) will be aromatic.

This is an empirical rule, meaning that Huckel developed the rule simply by looking at many, many cyclic conjugated polyenes and grouping those are aromatic and looking for a common property. He found that only certain number of π -electrons lead to Aromaticity and other numbers lead to anti-aromatic compounds. The number n has no physical significance. Using Huckel's rule we can predict that compounds having two π -electrons (n = 0), six π -electrons (n = 1), ten π -electrons (n = 2) and so on will have the special stability associated with aromaticity but those that have four π -electrons (cyclobutadiene), eight π -electrons (cyclooctatetraene), etc. do not have this special stability and are anti-aromatic.

We can explain the underlying theoretical basis for Huckel's rule by looking at the π -molecular orbitals that are present in these monocyclic, planar, conjugated polyenes. To do this we use a device known as Frost's circle, another empirical device. For a particular ring size, (3, 4, 5, 6, etc.) inscribe a polygon for that ring size inside a circle so that one of its vertices lies at the bottom of the circle. The points where the polygon touches the circle give the energy levels of the π -molecular orbitals. The number of p-orbitals involved equals the number of sixes of the polygon. For example, for cyclobutadiene, there are 4 p-orbitals (and it is a four-membered ring) so we inscribe a square inside a circle with one corner of the square at the bottom of the square. The center of the circle represents the non-bonding energy level.



There are two orbitals of the same energy so that the electrons will not pair. There will be one electron in each orbital, making cyclobutadiene a di-radical and hence very reactive and very unstable.

Cyclobutadiene is inscribed inside a circle; one corner of the square is put at the bottom of the circle. The four points where the square touches the circle define the relative energies of the four π -molecular orbitals.

For cyclobutadiene, we see that there are four π -molecular orbitals, one low lying bonding orbital and two non-bonding orbitals with the same energy and one high energy anti-bond orbital. As we feed in the four π -electrons, two electrons go into the low energy bonding orbital in accordance with Hund's rule, but then the next two electrons will not pair up and will go into the two equal energy non-bonding orbitals. This makes cyclobutadiene into a di-radical species. It is highly reactive and therefore very unstable.

If we do the same exercise with cyclooctatetraene, we get a similar result.

Frost's Circle for planar Cyclooctatetraene



Cycloctatetraene has eight π -electrons; if cyclooctatetraene were planarthe last two go into the equal energy non-bonding orbitals to make a di-radical. The actual structure of cyclooctatetraene is nonplanar, tub-shaped so as to avoid this.

If cyclooctatetraene were planar the last two π -electron would have to go into the two equal energy non-bonding orbitals, making it into a diradical like cyclobutadiene. To avoid this, cyclooctatetraene bends from planarity to form a tub-shaped molecule. This bending of the molecule changes the energy levels of the π -orbitals and keeps it from being a diradical.



Annulenes

Annulenes are completely conjugated monocyclic hydrocarbons that have more than six carbons. They are named as [X]annulene where X is the number of carbons. For example, [10]annulene is cyclodecapentane. Look at the *cis, trans, cis, cis, trans* isomer. The angles are close to 120° , the normal sp² value but there is a great deal of steric hindrance

between the internal hydrogens on the *trans* double bonds. They are in very close contact and to relieve this van der Waals strain, the molecule adapts a non-planar configuration. This relieves the steric hindrance but also decreases the π -overlap and decreases the π -electron delocalization.



cis, trans, cis, cis, trans [10]annulene - There is steric repulsion between the two H's.

The all *cis*-[10]annulene has angles of 144° versus the normal sp² values of 120°.



[14]annulene is also destabilized by steric hindrance between the internal hydrogens. In order to minimize this bad van der Waals interaction, it adopts a non-planar conformation.



Some steric strain due to the close contact of the four internal hydrogens.

[18]Annulene is nearly planar. It is large enough to accommodate the six internal hydrogens. All of the carbon-carbon bonds are between 1.37 - 1.47 A°, similar to those of benzene. This indicates that there is a lot of aromatic character to the ring system. It is believed to have a resonance stabilization of 418 KJ/mol. But it is much more reactive than benzene. It is easily hydrogenated and undergoes addition rather than substitution with bromine and it also under goes Diels-Alder reactions with maleic anhydride.



Aromatic Ions

We can also have aromatic stabilization of certain anions or cations, provided they have the continuous, circular overlap of p-orbitals and they have the requisite $4n+2\pi$ -electrons.

For example, there is the cycloheptatrienyl cation, the so-called tropylium ion, is aromatic. It is completely conjugated and it has six π -electrons spread out over seven carbon atoms.



Cyclopentadienyl anion is also resonance stabilized and is aromatic. Counting the two lone pair of the anion and the four electrons in the two double bonds it has six π -electrons spread out over five carbon atoms.



We can see the very large amount of resonance stabilization of cyclopentadienyl anion by looking at the pKa of 1,3-pentadiene. It is very acidic (pKa 16) when compared to cyclopentane (pKa > 60). This is due to the resonance stabilization of the resulting anion.



We also see resonance stabilization for cyclopropylium cation and cyclooctatetraene dianion. These are not stable species but are more stable than would be expected due to their resonance stabilization.



Heterocyclic Aromatic Compounds

We can also have aromatic compounds that have a heteroatom in the ring. In organic chemistry a heteroatom is any atom other than carbon. The most common heteroatoms are nitrogen, oxygen and sulfur. Many of these molecules are important building blocks in biochemical systems.

They may be monocyclic five or six-membered rings.



Many bicyclic heterocycles are known.



Many heterocycles contain two or more heteroatoms.





oxazole

imidazole

thiazole





These systems are all aromatic but they all have less aromatic stabilization than benzene itself since the heteroatom distorts the equal distribution of the π -electrons since, in all of the examples presented, it is more electronegative than carbon.

Pyridine, for example, has six π -electrons, not counting the lone pair on the sp²-nitrogen ring.



The six π -electrons come from the two electrons in each of the three π -bonds. The lone pair is not part of the aromatic system.

pyridine

But in pyrrole, the lone is part of the aromatic system. The lone pair of pyrrole, therefore, is partially delocalized around the pyrrole ring and is therefore less available for sharing. Pyrrole is a much weaker base than pyridine.



The lone of of electrons is partially delocalized around the ring and not available for sharing.

sp² nitrogen

Lone pair is part of the aromatic system.

