Arenes

An arene is a molecule that meets the following criteria:

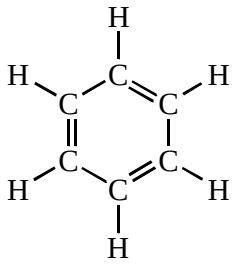
i) It is cyclic, planar, and all atoms must have at least one unhybridized *p* orbital.

ii) It contains at least 2, usually carbon-carbon, double bonds.

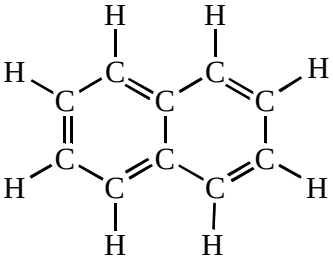
iii) The double bonds must occur on sequential pairs of atoms.

iv) It must contain 4n + 2 electrons in its π-system, where n is any positive integer.

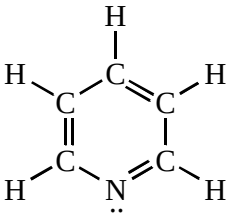
A few examples include:



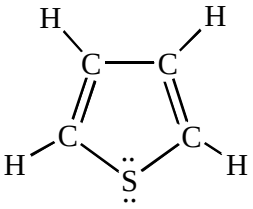
benzene



naphthalene



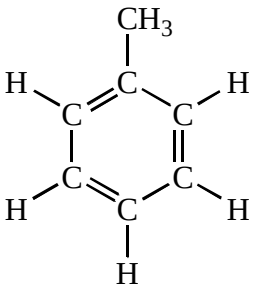
pyridine



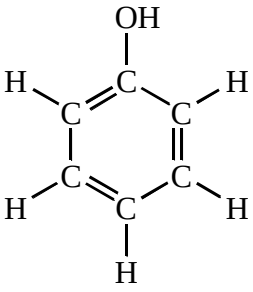
thiophene

All of these examples have distinctive odors (e.g. mothballs are made of naphthalene) and so these compounds were initially called *aromatic compounds*. Before going into the naming of these compounds a little bit of background may help you. All of these compounds have the same phonetic ending, -ene (pyridine is pronounced peer-id-een), which indicates the presence of a double bond. For example, $CH_3–CH=CH_2$ is propene and $Br–CH_2–CH=CH_2$ is 3-bromopropene (one of your unknowns). [N.B. Not all aromatic compounds end it "-ene" and, ironically, many are now known not to have an odor.]

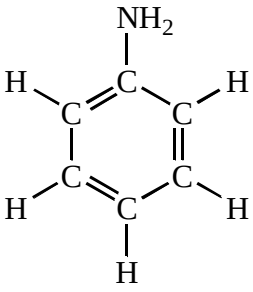
An important facet to naming arenes is that **all** simple, unsubstituted arenes have non-systematic names (e.g. molecules illustrated in the previous paragraph). Furthermore, a few substituted benzenes have unique names as well. In this context, substituents are atoms or groups attached to the rings; rather than heteroatoms within the rings. Substituted arenes with unique names include:



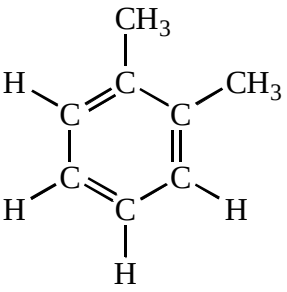
toluene



phenol



aniline



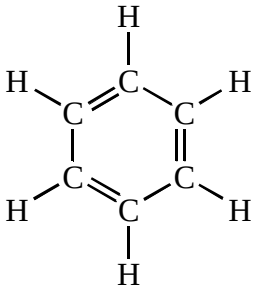
o-xylene

Historical reasons have caused this confusing situation. Aromatic compounds frequently exhibit high stability, making them relatively easy to isolate from their naturally occurring source. As a result, they represent some of the earliest organic compounds isolated in pure form. At the time, neither atoms nor chemical composition had been postulated, much less demonstrated; so <u>all</u> compounds were given unique names by their discoverer. The unique names you must learn are the ones that have survived over the centuries.

A result is that *toluene* is the correct name for $C_6H_5CH_3$, not methylbenzene or phenylmethane. The examples used thus far represent all of the uniquely named arenes you will encounter in this module.

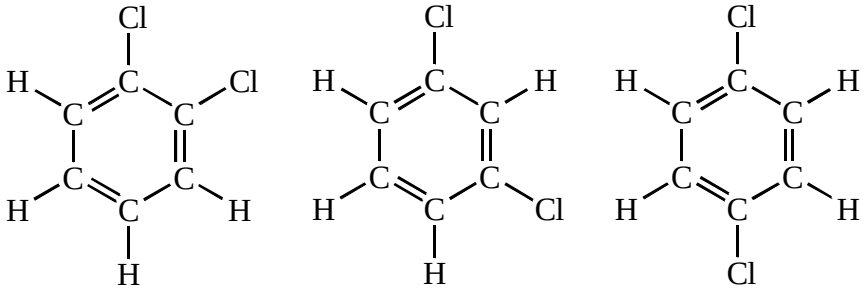
<u>New Nomenclature System for Substituted Arenes</u>

Naming arenes usually requires one to indicate the location of the substituent(s) on the ring. The only exception to this rule occurs when no ambiguity exists. Two examples illustrate this point: C_6H_5Cl and $C_6H_4Cl_2$. First, write down the parent benzene molecule, C_6H_6,

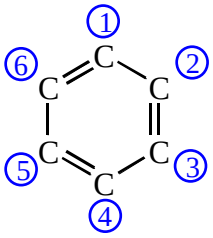


As you can see, all six positions are identical, so the chlorine atom can replace any of the hydrogens and yield the same compound, chlorobenzene. In contrast, in chlorobenzene three

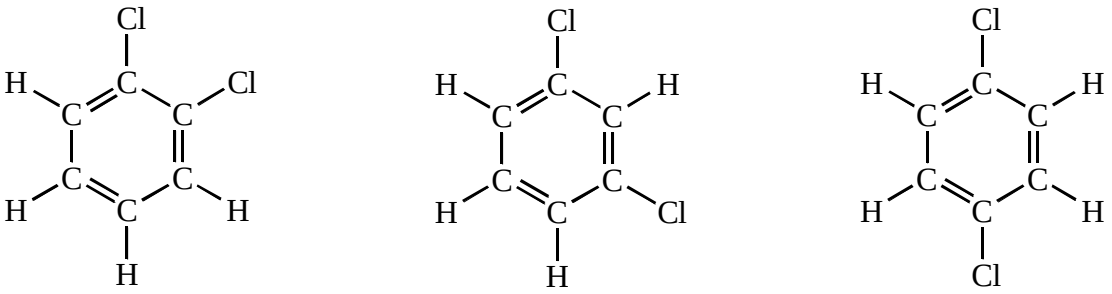
different types of hydrogen are present and replacing the second hydrogen with a chlorine can yield 3 different compounds.



The compounds are named by using a numbering system. The first substituent is always

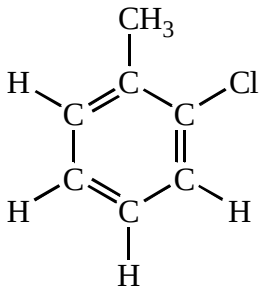


placed in the number 1 position and the remaining substituents are named relative to the first substituent. Thus, for the $C_6H_4Cl_2$ example, we have the names:

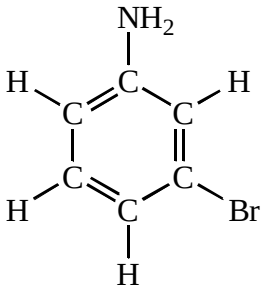


1,2-dichlorobenzene 1,3-dichlorobenzene 1,4-dichlorobenzene

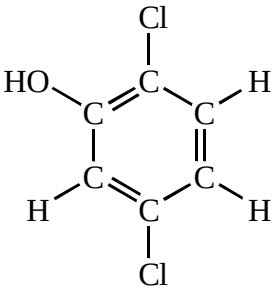
When the substituents are different, we must choose the one assigned to the #1 position. In the case of uniquely named compounds (e.g. toluene), that substituent always occupies the first spot. Thus, we have:



2-chlorotoluene

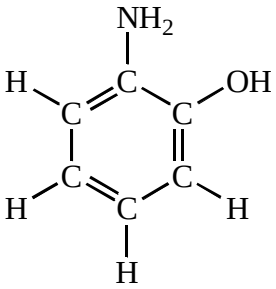


3-bromoaniline

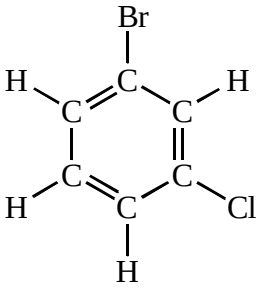


2,5-dichlorophenol

Finally, how do we chose when either two (e.g. $C_6H_4(NH_2)(OH)$) or no (e.g. $C_6H_4(Br)Cl$) unique names are possible. In each case, the #1 position goes to the attached atom with the higher atomic number. Like alkanes, the substituents are named alphabetically and, so, these compounds are named:



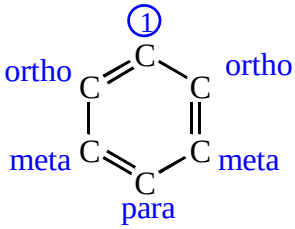
2-aminophenol



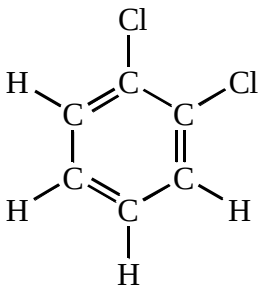
1-bromo-3-chlorobenzene

<u>Old Nomenclature System for Substituted Arenes</u>

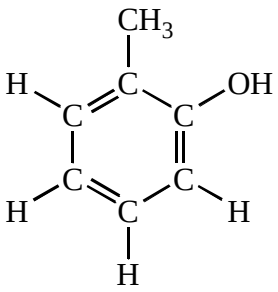
The older system of naming substituted arenes applies to doubly substituted benzenes.



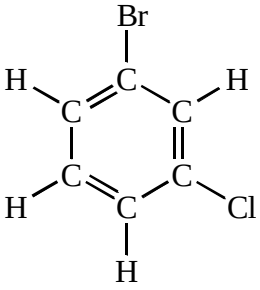
Thus, from our previous examples:



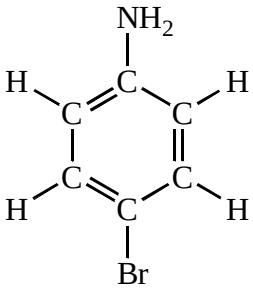
ortho-dichlorobenzene
o-dichlorobenzene



ortho-methylphenol
o-methylphenol

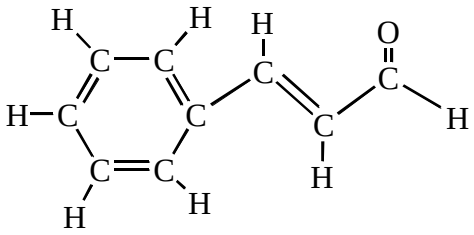


meta-bromochlorobenzene
m-bromochlorobenzene



para-bromoaniline
p-bromoaniline

Finally, in complicated molecules, the benzene ring is sometimes named as the substituent. For example, since a chlorine atom is simple, we name C_6H_5Cl as chlorobenzene, but the active ingredient in cinnamon, $C_6H_5CHCHC(O)H$, is most easily named with the benzene ring as a substituent. Substituent benzene rings are called <u>phenyl</u> groups.



trans-3-phenyl-2-propenal (common names: cinnamaldehyde, oil of cinnamon)