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Aromatic compounds

These are compounds based on benzene rings.

What are arenes?

Arenes are aromatic hydrocarbons. The term "aromatic" originally referred to their pleasant smells, but now implies a particular sort of delocalised bonding (see below).

The arenes you are likely to meet at this level are based on benzene rings. The simplest of them is benzene itself, C₆H₆. The next simplest is methylbenzene (old name: toluene) which has one of the hydrogen atoms attached to the ring replaced by a methyl group - C₆H₅CH₃.

The structure of benzene

The structure of benzene is covered in detail in two pages in the organic bonding section of this site. It is important to understand these thoroughly to make sense of benzene and methylbenzene chemistry. Unless you have read these pages recently, you should spend some time on them now before you go any further on this page.

What you need to understand about benzene is:

Benzene, C₆H₆, is a planar molecule containing a ring of six carbon atoms each with a hydrogen atom attached.

The six carbon atoms form a perfectly regular hexagon. All the carbon-carbon bonds have exactly the same lengths - somewhere between single and double bonds.

There are delocalised electrons above and below the plane of the ring.

The presence of the delocalised electrons makes benzene particularly stable.

Benzene resists addition reactions because that would involve breaking the delocalisation and losing that stability.

Benzene is represented by this symbol, where the circle represents the delocalised electrons, and each corner of the hexagon has a carbon atom with a hydrogen atom attached.

Methylbenzene just has a methyl group attached to the benzene ring - replacing one of the hydrogen atoms.

Attached groups are often drawn at the top of the ring, but you may occasionally find them drawn in other places with the ring rotated.

Physical properties

Boiling points

In benzene, the only attractions between neighbouring molecules are van der Waals dispersion forces. There is no permanent dipole on the molecule.

Benzene boils at 80 °C - rather higher than other hydrocarbons of similar molecular size (pentane and hexane, for example). This is presumably due to the ease with which temporary dipoles can be set up involving the delocalised electrons.

Methylbenzene boils at 111 °C. It is a bigger molecule and so the van der Waals dispersion forces will be bigger.

Methylbenzene also has a small permanent dipole, so there will be dipole-dipole attractions as well as dispersion forces. The dipole is due to the CH₃ group's tendency to "push" electrons away from itself. This also affects the reactivity of methylbenzene (see below).

Melting points

You might have expected that methylbenzene's melting point would be higher than benzene's as well, but it isn't - it is much lower! Benzene melts at 5.5 °C; methylbenzene at -95 °C.

Molecules must pack efficiently in the solid if they are to make best use of their intermolecular forces. Benzene is a tidy, symmetrical molecule and packs very efficiently. The methyl group sticking out in methylbenzene tends to disrupt the closeness of the packing. If the molecules aren't as closely packed, the intermolecular forces don't work as well and so the melting point falls.

Solubility in water

The arenes are insoluble in water.

Benzene is quite large compared with a water molecule. In order for benzene to dissolve it would have to break lots of existing hydrogen bonds between water molecules. You also have to break the quite strong van der Waals dispersion forces between benzene molecules. Both of these cost energy.

The only new forces between the benzene and the water would be van der Waals dispersion forces. These aren't as strong as hydrogen bonds (or the original dispersion forces in the benzene), and so you wouldn't get much energy released when they form.

It simply isn't energetically profitable for benzene to dissolve in water. It would, of course, be even worse for larger arene molecules.

Reactivity

Benzene

It has already been pointed out above that benzene is resistant to addition reactions. Adding something new to the ring would need you to use some of the delocalised electrons to form bonds with whatever you are adding. That results in a major loss of stability as the delocalisation is broken.

Instead, benzene mainly undergoes substitution reactions - replacing one or more of the hydrogen atoms by something new. That leaves the delocalised electrons as they were.

Methylbenzene

You have to consider the reactivity of something like methylbenzene in two distinct bits:

The tendency of the CH₃ group to "push" electrons away from itself also has an effect on the ring, making methylbenzene react more quickly than benzene itself. You will find this explored in other pages in this section as well.

The structure of chlorobenzene

There is an interaction between the delocalised electrons in the benzene ring and one of the lone pairs on the chlorine atom.

This delocalisation is by no means complete, but it does have a significant effect on the properties of both the carbon-chlorine bond and the polarity of the molecule.

IIT-JEE Chemistry by N.J. sir ORGANIC chemistry



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