Aromatic chemistry

The birth of benzene

The history of benzene began in London. But the path from its discovery to its structure was an extraordinarily long one…

The discovery

The installation of a gas lamp in Berlin, 1890

On the first of April 1814 the first gas lamp was brought into service in London. The common oil lamps were replaced successively because the new lamps were so convenient: The used coal gas is a byproduct of the coking process and easily obtainable. Furthermore, the new lamps are so efficient that they can illuminate whole parts of town. The gas lamp conquered the main cities of Europe like Berlin, Paris and Madrid.

In 1825, the chemist **Faraday** (1791-1867) compressed this coal gas and isolated a colourless, pleasant smelling liquid. Quantitative analysis showed that this compound had as many carbon as hydrogen atoms.

First syntheses

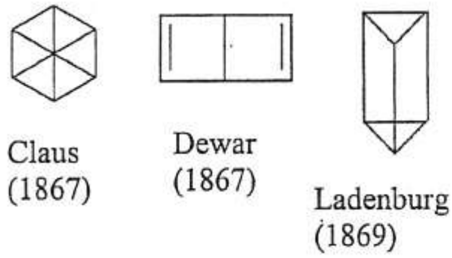
In 1834, **Mitscherlich** (1794-1863) successfully synthesized this compound and concluded the correct chemical formula of **C_6H_6**. So, it had to be an unsaturated compound with multiple double bonds! Because of its similarity to benzoic acid, Mitscherlich called this substance „Benzin", his scientific rival Justus **Liebig** (1803-1873) named it „Benzol", which still is its correct name in German.

Benzene - an aromatic compound

Chemical research show that the benzene part plays an important role in many good-smelling compounds, such as vanillin (vanilla), 2-phenylethanole (roses) and cinnamic aldehyde (cinnamon). Therefore, benzene belongs to the so-called „aromatic compounds". In chemical reactions, the benzene part remains unchanged.

Unanswered questions

Which structure belongs to this molecule, which is particularly stable, unreactive and - seemingly - unsaturated? The common knowledge of carbon's ability to form four bonds is not enough. In the following years, scientists such as **Claus** (1838-1900), **Dewar** (1842-1923) and **Ladenburg** (1842-1911) proposed several possible structures which do not fully explain benzene's special properties.



Until the final revelation, 40 more years would pass. In 1865, August **Kekulé** (1829-1896) postulated his version of benzene's structure.

<u>Task:</u>

Why did the scientists conclude that benzene is an unsaturated molecule? Note down structures for hexane, hexyne, hexene and cyclohexane.

Aromatic chemistry

A ring structure for benzene

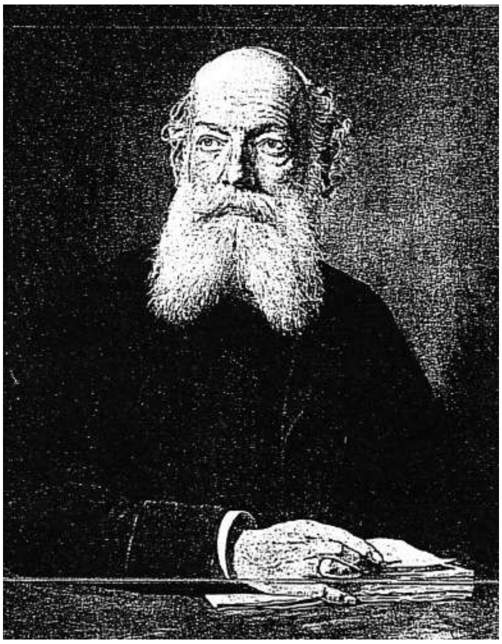
The name of the German scientist August **Kekulé** (1829-1896) is forever connected with the benzene formula. Here you can read how he came up with his structure for benzene.

<u>Task:</u>

Please construct a molecule consisting of 6 carbon and 6 hydrogen atoms. Draw the structures you come up with on a sheet of paper. Take into account the different bond lengths. Exchange your constructed molecules with other groups and note down remaining questions.

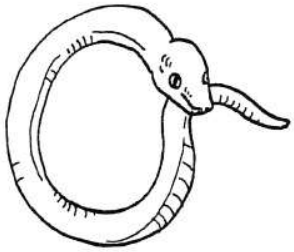
The solution to the riddle…

Kekulé and the snake



In his speech to the 25th anniversary of the discovery of the benzene formula in 1890, Kekulé reported about his daydream of a snake biting its own tail, just like the alchemist symbol of the Ourobouros snake.

"*Once again, the atoms danced before my eyes, long chains, everything in motion, turning and twisting like a snake. The snake bit its tail and continued to twist. I spent the rest of the night thinking of the consequences."*



In 1865, Kekulé postulated his ring structure for benzene with alternating single and double bonds: each of the 6 carbon atoms has a single as well as a double bond to the two neighbouring carbon atoms.

Not everything is explained!

Although Kekulé's formula with three double bonds had become widely accepted, it couldn't explain all of benzene's special properties. It was only possible with the development of quantum mechanics at the beginning of the 20th century to explain the structure of benzene and the extraordinary stability of aromatic systems.

Aromatic chemistry

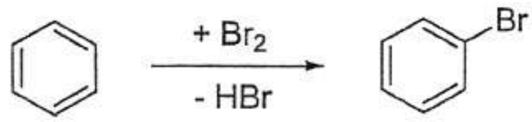
Something can't be right - a molecule with strange properties

In 1865, **Kekulé** proposed a ring structure for the benzene molecule, in which each of the six carbon atoms forms a single and a double bond to the neighbouring carbon atoms. But can this formula be correct?

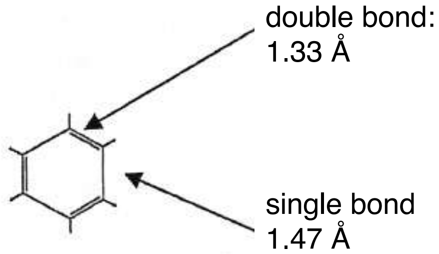
Chemical findings in opposition to benzene's formula

1. Because of its unsaturated character (formula **C_6H_6**) benzene should behave like an alkene, resulting in an addition reaction with bromine:

However, bromine does not bond with benzene's double bond, but rather replaces a hydrogen atom in the presence of an iron catalyst in a **substitution reaction**. So, benzene behaves rather like a saturated carbohydrate. The products are bromobenzene and HBr:

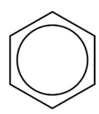


2. Because of the different lengths of single and double bonds, benzene molecules should have the shape of an irregular hexagon. The picture on the right shows the expected shape of benzene:



First X-ray structure analyses however show that benzene's bonds all have the **same length of 1.39 Å**, which lies in between the length of a single and double bond. Furthermore, all bonds have angles of **120°**, resulting in a perfect hexagon.

So, <u>all bonds between carbon atoms in benzene are equal</u>.
We speak of "delocalised double bonds" since their electrons do not stick to one place.

Therefore, benzene rings are often depicted like this: 

<u>Tasks:</u>

1. *Why could Kekulé's structure with localised double bonds not be right? Please summarise the scientific findings in your own words.*

2. *Can the scientific results explain the extraordinary stability of benzene? Please name Kekulé's structure using the IUPAC nomenclature.*

Aromatic chemistry

Hückel's rule or: 4n+2 = aromatic!

Back in the day, "aromatic" was the name given to compounds with an aromatic, pleasant smell.

After the discovery of benzene, the term "aromatic" was applied to all cyclic compounds with a benzene ring (delocalised double bonds). Furthermore, also compounds with more than one ring (polycyclic compounds) or other atoms than carbon (heteroatoms) in the ring (heterocyclic compounds). Moreover, compounds with a certain number of π-electrons (electrons in the ring are aromatic by definition, having a special stability - just like benzene.

In order to identify aromatic compounds, chemists still use **Hückel's rule**, developed in 1931:

Any cyclic compound consisting of (4n+2) π-electrons (2, 6, 10, etc.) is aromatic and particularly stable. Compounds with 4n π-electrons are anti-aromatic and particularly unstable. This rule does not rely on the number of carbon atoms in the ring.

<u>Tasks:</u>

1. *Cyclobutadiene and cyclobutaoctene have a cyclic structure. Cyclobutadiene is a compound which is extremely unstable and could only be detected at very low temperatures. Are the two compounds aromatic?*

cyclobutadiene

cyclooctadiene

2. *Fill in the missing items:*

   According to Hückel's rule, a cyclic molecule is only aromatic, if the number of π-electrons in the ring(s) can be described as (4n+2), n being a small natural number.

   So, molecules with _____ (n=0), _____ (n=1), _____ (n=2), _____ (n=3), etc. π-electrons are aromatic.

Aromatic chemistry

Aromatic memory game

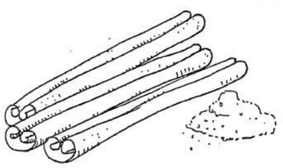
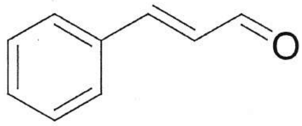
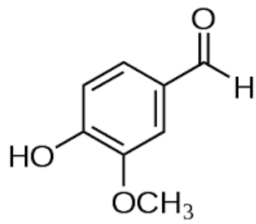
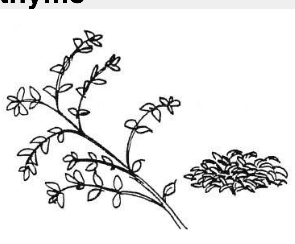
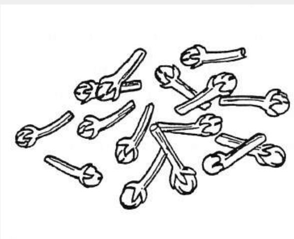
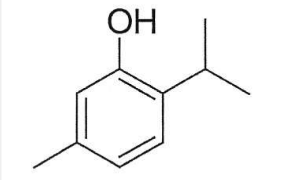
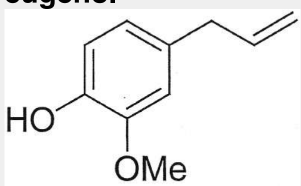
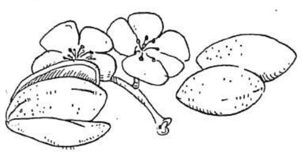
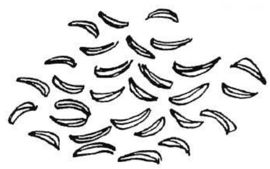
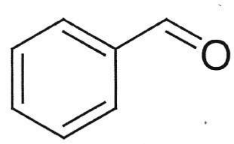
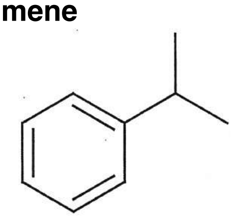
Which chemical ingredients are responsible for the scent of cloves? Which ones for cinnamon? Nowadays, a lot of modern flavouring substances are chemically synthesized, using benzene as starting material. You can find some examples here.

In this game, you will also find out why aromatic compounds are named like this.

Game rules

You have got six cards with certain natural scents and six cards with the aromatic compound responsible for the smell. First of all, cut them out!

Each player in your group turns around two cards. If they match, you have got a point and may take the cards. You may pick up two more cards. If the cards don't match, it's another player's turn. The winner is the player with the most matching cards.

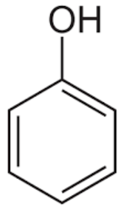
cinnamon (from the bark of the cinnamon tree) 	**vanilla** (from vanilla beans) 	**cinnamic aldehyde**  	**vanillin** 
thyme 	**cloves** 	**thymol**  	**eugenol** 
bitter almonds 	**caraway** 	**benzaldehyde**  	**cumene** 

Aromatic chemistry

Functional groups in organic and aromatic compounds

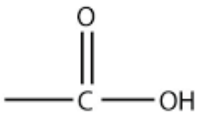
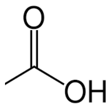
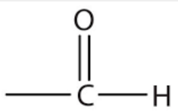
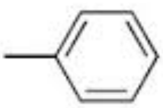
Just like other organic substances, aromatic compounds can have functional groups attached to them which lead to special physical and chemical properties and reactions.

The easiest example might be the compound phenol, which has a **hydroxyl (-OH) group** attached to a benzene ring.

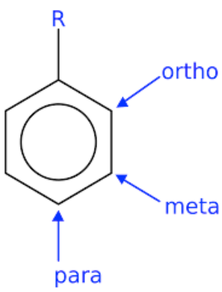


As a consequence, phenol is much more soluble in water than benzene and it has an acidic character because it can release hydrogen ions (H^+) from the hydroxyl group.

Here are other examples of functional groups:

Functional group	Name
—CH_3 / —Me	methyl
—COOH /  / 	carboxyl
—CHO / 	aldehyde
—O—R (alkyl rest) / -OMe	ether / methylether
—NH_2	amine
	phenyl

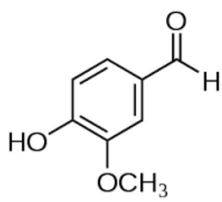
Aromatic compounds such as phenol can have more than one functional group attached to the benzene ring. Their exact location in relation to the first functional group “R” is labelled with the Greek terms “ortho” (*next to*), “meta” (*in the middle*) and “para” (*in opposition to*).



R = first functional group giving the compound its root name.

<u>Task:</u>

Look at the vanillin molecule again.



Try to describe this compound considering it as phenol with more functional groups. In this case, “R” is the hydroxyl group of phenol. Use the terms “ortho”, “meta” and “para”.