

UNDERSTANDING BENZENE STRUCTURE

WEEK 2 CONSIDERING POSSIBLE STRUCTURES

From last week, we have discovered that the **molecular formula of benzene is C₆H₆**

At the end of the last activity, I asked you to consider **possible structures for benzene** that could fit with this molecular formula.

The first question that you should always ask yourself when you look at any organic formula is,

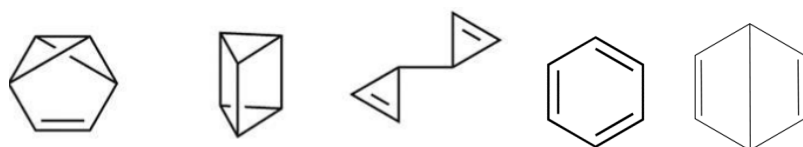
“Does it look unsaturated?”

Well, does it? Think about the C:H ratio compared to alkanes.

Also, remember that **carbon must always form 4 bonds** in organic compounds.

Sketch some structures below.

Draw 4 possible structures that could have the formula **C₆H₆**. Displayed formulae maybe best for this so that you can count the bonds to each C atom. There is a huge number of isomeric possibilities!



Amazingly, these are just 5 possibilities out of at least 217 isomers of C₆H₆! See below.

Benzene and its Isomers

In the May 2001 issue of *Resonance* the article with this title was subtitled, “How many structures can we draw for C₆H₆?” The 217 structures set out in the poster are basic framework structures drawn according to valency rules. If one takes into consideration the enantiomeric, geometric and other stereoisomeric forms, wherever possible, the total number of isomers would increase significantly. For instance, *trans, trans, trans*-1,3,5-cyclohexatriene (all-*trans*-benzene), Dewar benzene with *trans* ring junction or the two double bonds with *cis, trans* or *trans, trans* configuration etc. are in principle conceivable isomeric structures. But they would be so distorted that it would be difficult even to draw them! The basic frameworks turn out to be only 217 as listed here.

(Note: The bond angle around sp hybridized (acetylenic and allenic) carbon in acyclic compounds and exocyclic substituent in mono- and bi-cyclic structures is 180 degrees (i.e. linear). In the poster this angle is shown as bent for reasons of convenience in drawing them and aesthetics. When the triple bond or allene is part of a ring system, the linearity cannot obviously be maintained.)

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Resonance
June 2001

Structure	Name	Source	Properties
	Benzene	Petroleum, coal tar, trimerization of acetylene, natural products, etc.	Colourless liquid, b.p. 80°C, m.p. 5.5°C. Stable. Has relatively pleasant odour. (Carcinogenic). Industrially a very important compound.
	Dewar benzene; Bicyclo[2.2.0]hex-2,5-diene	van Tamelen and Pappas (1963)	Unstable, t _{1/2} = 2 days. Rearranges to benzene. (Stable in pyridine soln).
	Benzvalene; Tricyclo[3.1.0.0 ^{1,3}]hex-3-ene	Wittbach and others (1967) Kutz and others (1973)	Stable in solution. Explosive in pure state. Foul smelling.
	Prismane; Tetracyclo[3.1.0.0 ^{1,3} .0 ^{2,4}]hexane	Katz and Acton (1973)	Odourless liquid. Explosive. Stable at RT in toluene, at 90°C isomerizes to benzene, t _{1/2} = 11 hours.
	Bicyclopropenyl (2,2); (3'-cycloprop-1-enyl)-3-cycloprop-1-ene	Billups and Haley (1989)	Stable below 10°C, above that, decomposes to an unknown solid.

ACYCLIC

MONOCYCLIC

BICYCLIC

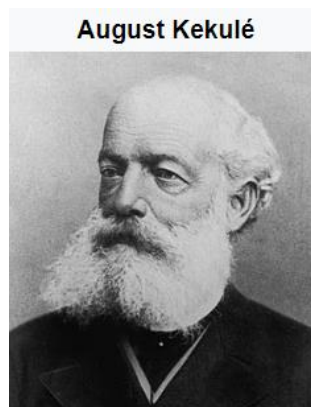
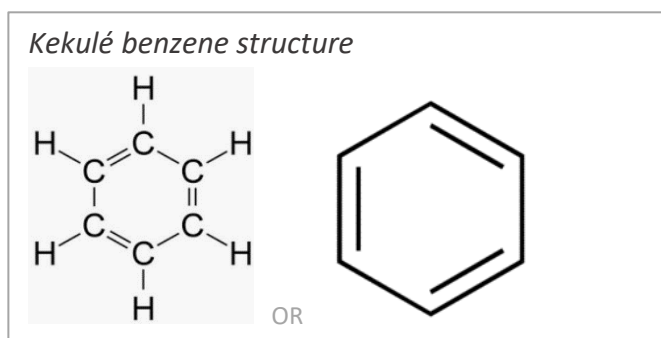
TRICYCLIC

TETRACYCLIC

Many chemists worked hard to propose a structure (including *Dewar**, *Armstrong* and *Claus*)

One structure that gained most favour was propose by ***Kekulé*** in 1865.

Find out his structure (***Kekulé benzene***) and draw it in the box below.



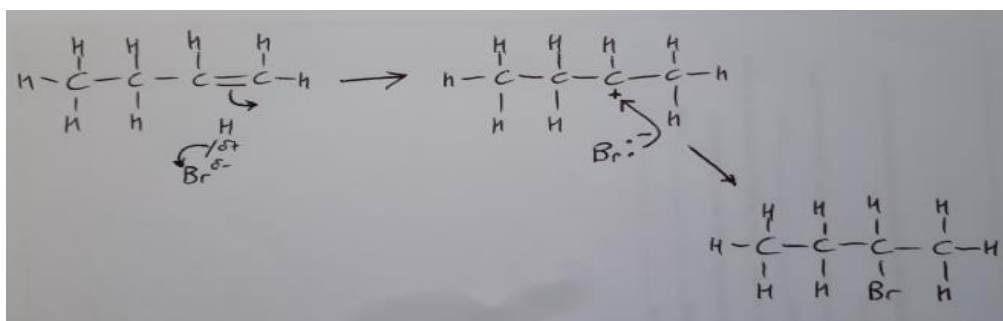
The next bit of this work on benzene will consider how well the **experimental evidence** supports the ***Kekulé benzene structure***

* Dewar was a Scottish chemist and inventor of the Thermos/vacuum flask.

1. Reactivity of Benzene with Bromine water.

The *Kekulé benzene structure* appears to have alkene double bonds.

1. Give the systematic name for *Kekulé benzene* **cyclohex-1,3,5-triene**
2. What is the main *reaction type* that alkenes undergo? **addition**
3. What is the main *mechanism type* that alkenes follow when they react? **electrophilic addition**
4. Draw the mechanism for the reaction between **but-1-ene** and **HBr** that gives the **major product**.



The major product can be predicted by applying a rule.

5. What is this rule called and why do these addition reactions to **unsymmetrical alkenes** give a major product?

Markovnikov rule.

More substituted carbocations produced in the mechanism are more stable than less substituted ones.

6. If this reaction in Q4 gives a **75% yield** of the major product, calculate the mass of product that would be produced if 11.2g of **but-1-ene** reacted with excess HBr.

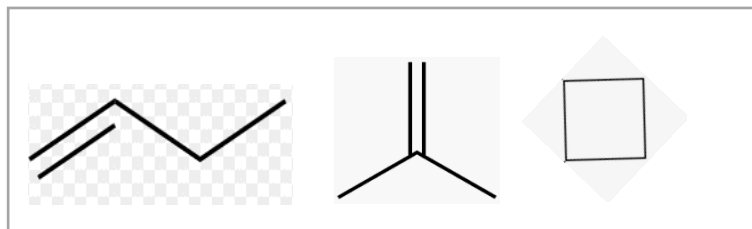
Reaction produces one mole of 2-bromobutane for each mole of but-1-ene (limiting reactant) consumed.

moles of **but-1-ene** consumed = $11.2\text{g}/56.0\text{g mol}^{-1} = \mathbf{0.200\text{ mol}}$

moles of **2-bromobutane** produced = $0.200\text{ mol} \times 0.75 = \mathbf{0.150\text{ mol}}$ (only 75% yield)

mass of **2-bromobutane** (major product) = **20.6g**

7. Does **but-1-ene** exhibit *E/Z* isomerism? **NO**
8. Using **skeletal formulae**, draw the **structural isomers** of **but-1-ene**



9. Describe the simple chemical test for the presence of an alkene.

Add a few drops of bromine water and the colour should change from orange/yellow to colourless (not clear!)

When bromine water is added to a sample of benzene, there is no obvious reaction.

This strongly suggests that benzene is not a typical alkene and it casts doubt on *Kekulé benzene structure*.

2. Bond Length Evidence

Atoms have different radii.

10. As one progresses across a period of the periodic table, from left to right, what are the trends in **atomic number** and **atomic radius**?

- i) Trend in atomic number **INCREASES**
- ii) Trend in atomic radius **DECREASES**

11. What is the reason for the trend in question 10 (ii)?

Increasing nuclear charge as you go from left to right. Each additional electron added as you cross the period goes **into the same shell**. **Greater attraction for outer shell electrons** pulls outer shell in therefore reducing radius.

12. Given that atoms have different sizes, the covalent bonds that hold atoms together in molecules must have different lengths. These can be found out using an analytical technique called **x-ray diffraction** which establishes where nuclei are in the solid state.

Find the length of the following bonds:

C-C	bond length = 154 pm
C=C	bond length = 134 pm

The x-ray diffraction of benzene derivatives* was carried out in 1929, the results of which finally proved the structure of benzene. It showed that benzene was

- i) flat (planar)
- ii) all the bonds between carbons were the same length
- iii) The **C to C** bond lengths were all **139 pm**

You should consider this evidence and compare it to the bond lengths that would have expected to see in **Kekulé benzene**

So, in conclusion,

1. benzene does not react with bromine water, like an alkene would.
2. benzene has bonds between carbon atoms that are all the same length AND the length is in-between that of a single C-C and a double C=C.

You should now be feeling even less confident about Kekule's proposed structure for benzene.

* This 'game-changing' work was actually done on *hexamethylbenzene*.

It was carried out by **Dame Kathleen Lonsdale, DBE, FRS**. Just like **Dorothy Mary Crowfoot Hodgkin OM FRS HonFRSC**, another legend in the world of x-ray crystallography, Lonsdale had very strong political and ethical views. Interestingly, Hodgkin was Margret Thatcher's chemistry teacher at Oxford! Thatcher has a portrait of Hodgkin in her office in Downing Street because she held her in such high regard! Hodgkin was a lifelong supporter of the Labour Party!

Stretch & Challenge

Please feel free to attempt this but don't be put off if you struggle with it!

a) Define *enthalpy of atomisation for an element* $\Delta_a H$

the enthalpy change that accompanies the formation of **1 mol of gaseous atoms from the element** in its **standard state**. For carbon, this is $C_{(s)} \rightarrow C_{(g)}$ For hydrogen, this is $\frac{1}{2} H_{2(g)} \rightarrow H_{(g)}$

b) Define *enthalpy of atomisation for a compound* $\Delta_a H$

the enthalpy change that accompanies the formation of **gaseous atoms from 1 mol of the compound** in its **standard state**. For benzene, this is $C_6H_6(l) \rightarrow 6C_{(g)} + 6H_{(g)}$

c) Define *mean bond enthalpy*

The **energy change** that accompanies the breakage of **1 mol of bonds** when **averaged** over all compounds that contain that type of bond.

Look up values for the following

$$\Delta_a H (\text{hydrogen}) = 218 \text{ kJmol}^{-1}$$

$$\Delta_a H (\text{carbon}) = 715 \text{ kJmol}^{-1}$$

$$\text{mean bond enthalpy } C=C = 610 \text{ kJmol}^{-1}$$

$$\text{mean bond enthalpy } C-C = 346 \text{ kJmol}^{-1}$$

$$\text{mean bond enthalpy } C-H = 413 \text{ kJmol}^{-1}$$



Using these *mean bond enthalpies*, calculate $\Delta_a H$ (benzene)

$$\Delta_a H (\text{benzene}) = (3 \times 346) + (3 \times 610) + (6 \times 413) = 5346 \text{ kJmol}^{-1}$$

d) Why is there often (but not always) a very significant* difference between the **enthalpy of atomisation of a molecular substance** and the **sum of the mean bond enthalpies within the molecule**. This is tied into the definitions in 2 and 3 and **not** because of the mean nature of bond enthalpies. (Clue: states!)

Because the use of *mean bond enthalpies* assumes that the compound being atomised is in a **gaseous state**. **BUT** The *enthalpy of atomisation* of a compound involves atomisation of the compound in its **standard state**. Benzene is a liquid in its standard state and therefore there will be a significant difference in values, bigger than could be due to the discrepancy caused using *mean bond enthalpies*.

e) You have already calculated the $\Delta_f H$ for benzene from experimental (real) $\Delta_f H$ data. This was done in WEEK 1

What value did you obtain?

$$\Delta_f H (\text{'real' benzene}) = 48.6 \text{ kJmol}^{-1}$$

Now let's assume that Kekulé's structure for benzene is correct, i.e. a structure that is the triene cyclohexa-1,3,5-triene. If so, the $\Delta_f H$ (benzene) should be the same, according to *Hess's Law*

We will recalculate the $\Delta_f H$ using *mean bond enthalpies* benzene and the *enthalpy of atomisation* $\Delta_a H$ for carbon and hydrogen. Surely the $\Delta_f H$ (benzene) should be the same, according to *Hess's Law*.

* the English that I used there is poor. You can't say *very significant* in the same way you can't say *very black* or *very unique*. (Black, unique and significant are **non-gradable adjectives**)

- f) To do this you will need to draw another Hess Cycle for $\Delta_f H$ (benzene). This has been started for you. **BUT** there is another enthalpy change that you need to complete the cycle. What is this enthalpy change? You can describe this in words.

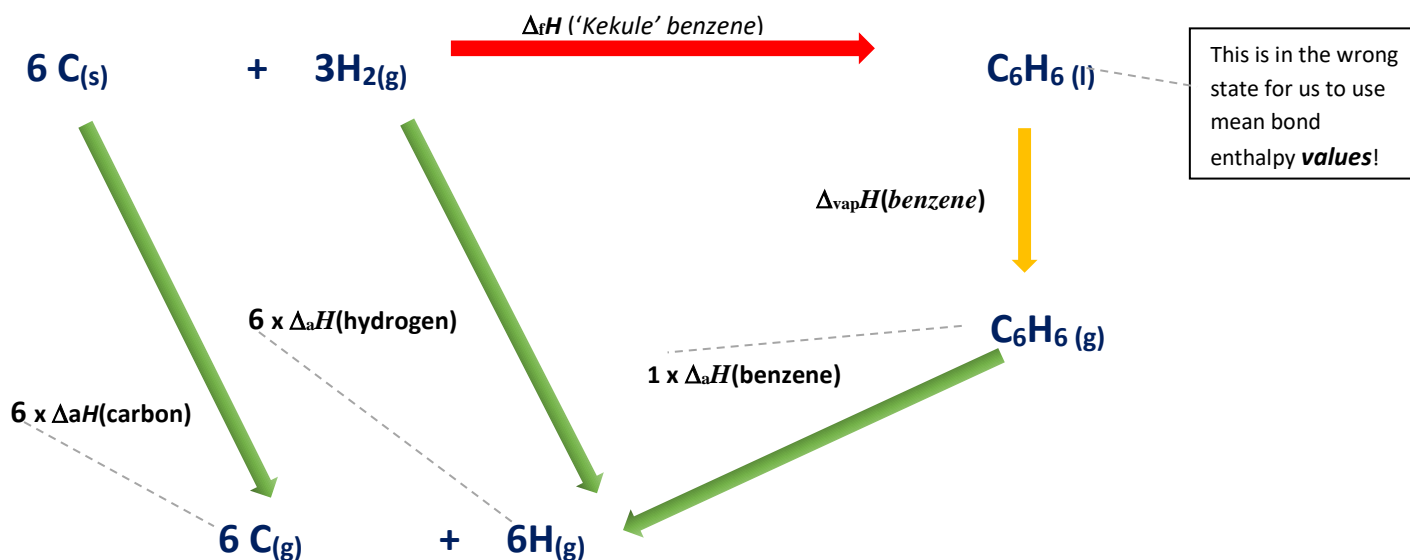
You need to convert benzene from its standard state to the gaseous state. This is called the **enthalpy of vaporisation**, $\Delta_{\text{vap}} H$

The enthalpy change that you need is the enthalpy change that will convert $\text{C}_6\text{H}_6(\text{l})$ into $\text{C}_6\text{H}_6(\text{g})$. It's only when it is in the gaseous phase that we can break all the bonds and then use the mean bond enthalpy values (according to the definition!)

This missing enthalpy change is the **enthalpy of vaporisation**, $\Delta_{\text{vap}} H(\text{benzene})$

- g) Look up a value for this.

$$\Delta_{\text{vap}} H(\text{benzene}) = +33.9 \text{ kJ mol}^{-1}$$



Remember, $\Delta_a H$ for **elements** are based upon **1 mol of gaseous atoms** being **produced** in the process.

$\Delta_a H$ for **compounds** are based upon **1 mol of gaseous molecules** being **consumed** in the process.

- h) Calculate the $\Delta_f H$ ('Kekule' benzene)

$$\begin{aligned} \Delta_f H(\text{benzene}) &= (6 \times \Delta_a H(\text{carbon})) + (6 \times \Delta_a H(\text{hydrogen})) + (-\Delta_a H(\text{benzene})) + (-\Delta_{\text{vap}} H(\text{benzene})) \\ &= (6 \times 715) + (6 \times 218) + (-5346) + (-33.9) = 218 \text{ kJ mol}^{-1} \\ \Delta_f H(\text{'Kekule' benzene}) &= 218 \text{ kJ mol}^{-1} \end{aligned}$$

backwards along arrow!

Now you have $\Delta_f H$ for the theoretical Kekule benzene, you can compare it to $\Delta_f H$ for the real benzene (a value that was obtained by doing experiments with the real stuff).

- i) What is the numerical value for this difference? Difference = $218 - 48.6 = 169 \text{ kJ mol}^{-1}$

The significant discrepancy between the **real** value and the **theoretical** value that you just calculated suggests that Kekule's structure can't be correct. It is too large to blame the average nature of bond enthalpies!

- j) Assume that the universe seems to favour processes that have negative a $\Delta_{\text{reaction}} H$ (or as small a positive value as possible) because it leads to **more stable** compounds being formed. What does this suggest about the **stability** of real benzene compared to the theoretical one?

'Real' benzene must be different to 'Kekule' benzene and be around 169 kJ mol^{-1} **more stable** than the 'Kekule' benzene

Next year, we will learn that there is more to the **feasibility** of a process than is associated solely with the enthalpy change of a reaction/process. **But**, the exothermicity of a process is a big contribution and is usually helpful hint about feasibility.