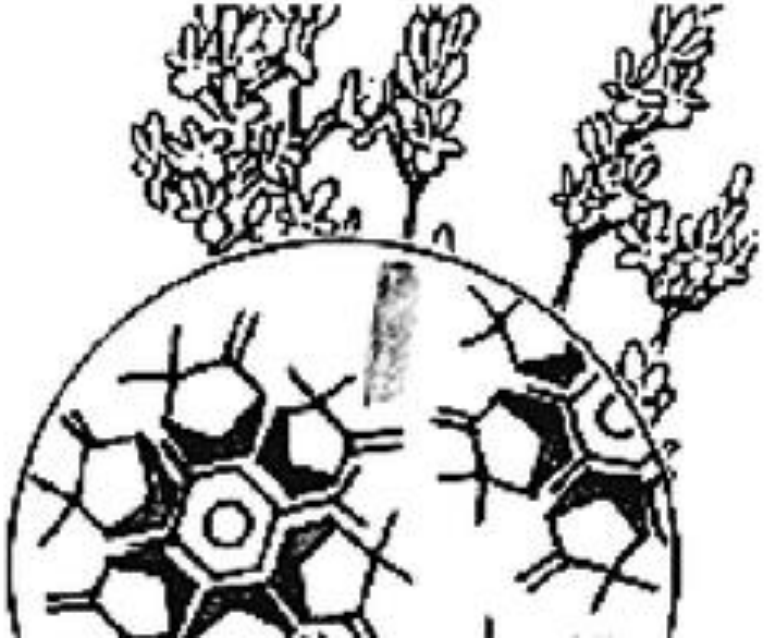
DR JOY'S WEBINARS

REFRESHING CHEMISTRY!

SET 2



ESSENTIAL OIL CHEMICAL FAMILIES

Dr E. Joy Bowles, PhD, BSc Hons.

COURSE OVERVIEW

- SET1- Foundational Chemistry Concepts – 5 modules
- **SET2 - Essential Oil Chemical Families – 12 modules**
- **Wed 9:30 pm UTC +11: 28 Feb, 7, 14, 21, 28 Mar, 4 April**

  EASTER break and change from Daylight Saving time to Australian Eastern Standard Time (same as QLD)
- **Wed 9:30 pm UTC +10: 25 April, 2, 9, 16 May**

  ITALY trip
- **Wed 9:30 pm UTC +10: 6, 13 June**
- SET3 - Clinical Evidence – 10 modules starting on Tues 13 Mar at 11:00 am UTC +11, and preceding the SET 2 Wednesday classes in the same week, thus ending on Tues 12 June.

LEARNING OUTCOMES EO CHEMISTRY.1 – HOW PLANTS MAKE ESSENTIAL OILS

Students will be able to:

- Explain why plants make essential oils
- Understand the photosynthesis equation
- Distinguish between isoprenoid and phenolic compounds
- Understand that environmental factors impact on EO quality

EO CHEMISTRY.2 – TERPENES

Activities

- Lecture – Isoprene units, carbon skeletons and terpenes
- Lecture – Distinguishing features of monoterpenes and sesquiterpenes
- Lecture - A special case: Benzene rings

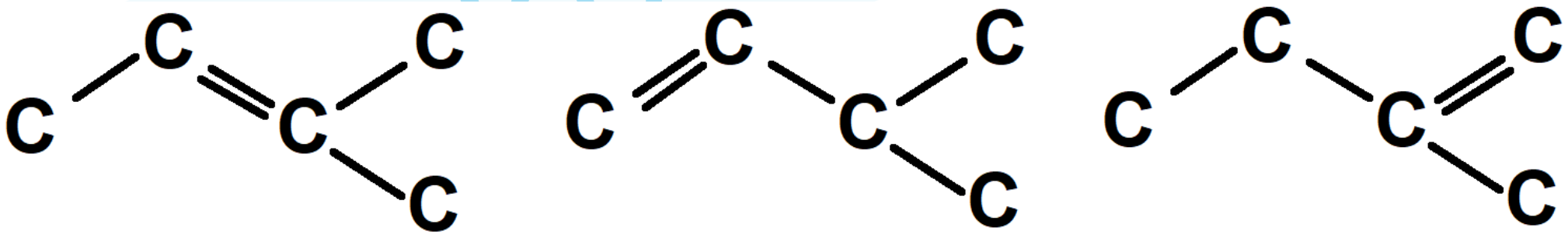
Learning Outcomes

Students will be able to:

- Explain how terpenes are made up of isoprene units
- Distinguish between mono- and sesqui-terpenes
- Explain the bonding of benzene rings
- Explain how the physical features of terpenes affect their therapeutic function

ISOPRENE UNITS

- 5 carbon atoms
- Branched structure (2-methyl-1but-2-ene)
- At least 1 C=C (-ene ending)



EARLY DAYS IN TERPENE RESEARCH

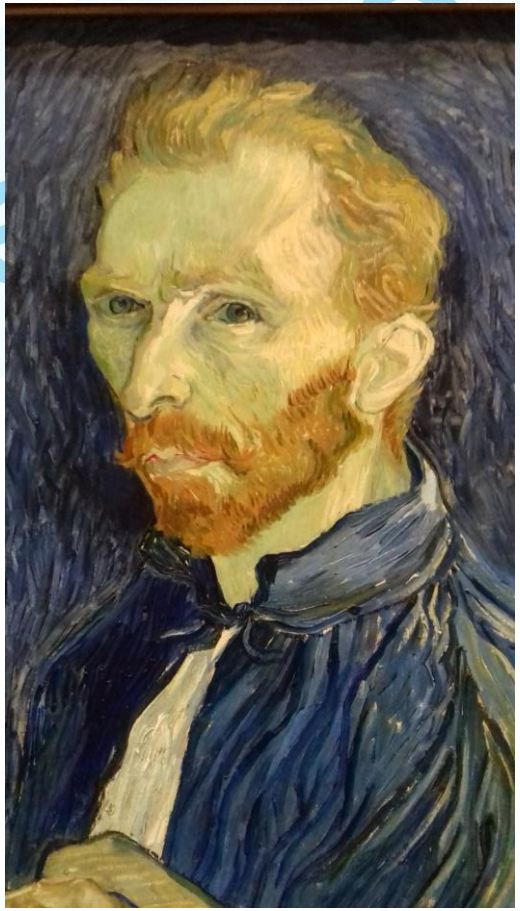
Discovery of solvent and lacquer properties of turpentine oils – painters doing oil painting

Early chemists managed to work out the structure of so-called monoterpenes first – $C_{10}H_{18}$ or $C_{10}H_{20}$ or $C_{10}H_{22}$

No alkane monoterpenes (that I know of) would be $C_{10}H_{24}$

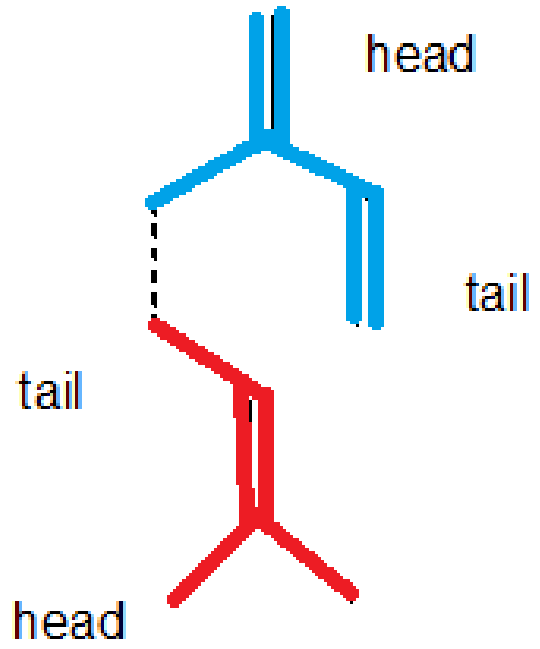
Can refer to whole class of molecules with TERPENOID structure

(Do terpenoids dream of scented sheep?)



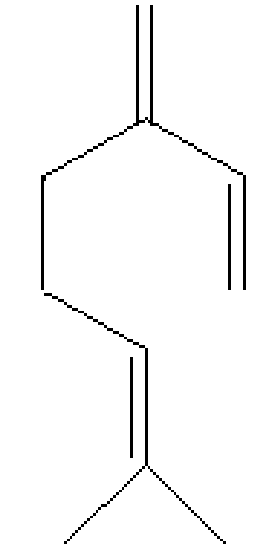
MONOTERPENES

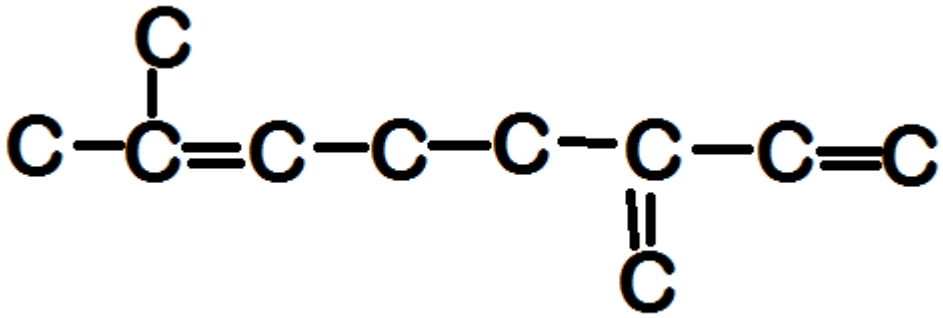
- 10 Carbon atoms
- 2 isoprene units joined head-to-tail
- At least one double bond
- Can be linear, mono-cyclic or bi-cyclic
- Monocyclic structure usually hexagonal
- No Oxygen atoms



WHY THE TYPICAL SHAPE?

Due to the double bonds and the head-to-tail joining rule, most EO monoterpenes have the characteristic crook shape with little 'feet' at the bottom (iso-propanoid or iso-propenoid tail)





7-methyl-3-methylideneocta-1,6-diene

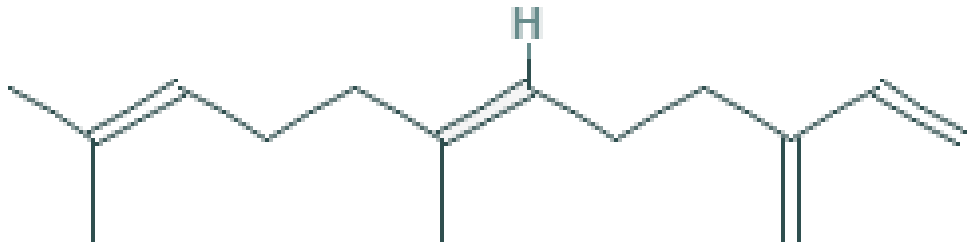
MODULAR BUILDING BLOCKS – MORE LEGO

All constituents were initially purified out of essential oils using very careful fractional distillation, and then crystallised (e.g. menthol and thymol), which aims to produce a pure substance.

As research continued, chemists found more molecules in the volatile plant oils that were heavier than the monoterpenes, and had higher boiling points.

They had 15 C atoms, not 11, 12, 13, 14 or 16…

(6E)-7,11-dimethyl-3-methylidenedodeca-1,6,10-triene



WHY CALL THEM SESQUITERPENES?

The reason that the name sesquiterpenes arose, is because they hadn't realised that the plants make isoprene units. These C5 moleules are usually so volatile, they are gases at room temperature, and are not found in the essential oils.

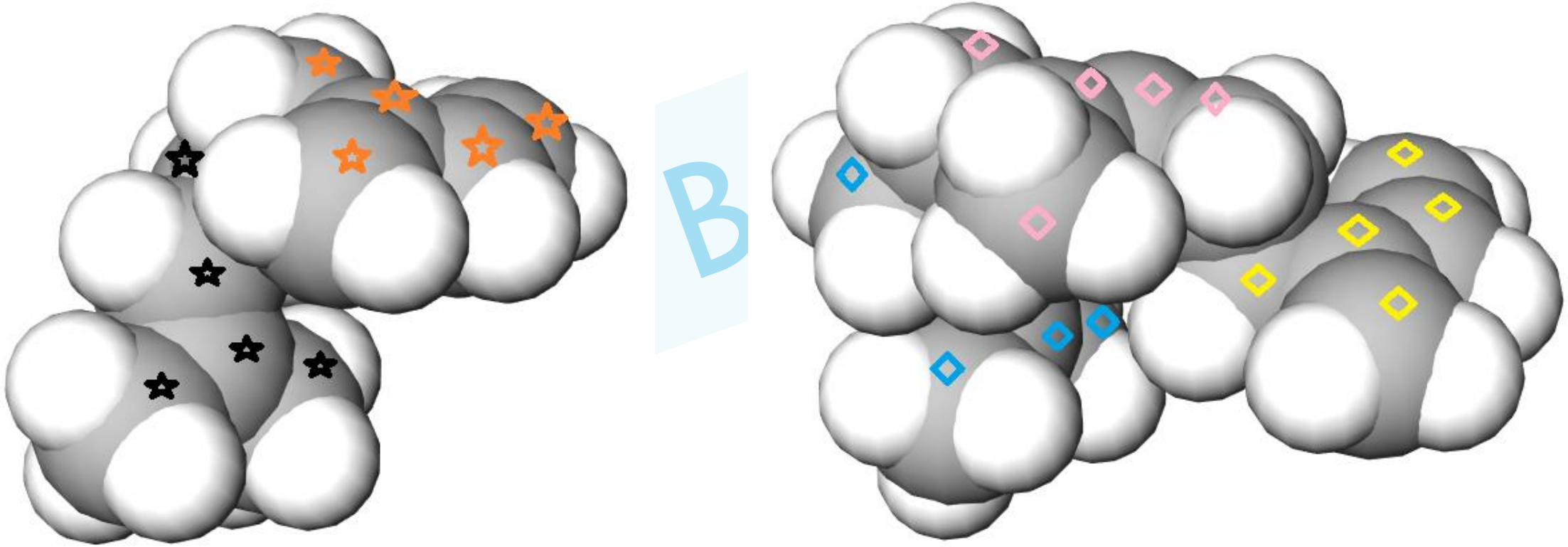
SESQUI- is Latin for "one and a half"

They had found molecules with exactly one and a half the number of Carbon atoms…

Nobel Prize winners, Otto Wallach & Friedrich Kekulé, first systematised terpene structures.

https://en.wikipedia.org/wiki/Otto_Wallach

3D STRUCTURAL DIFFERENCES



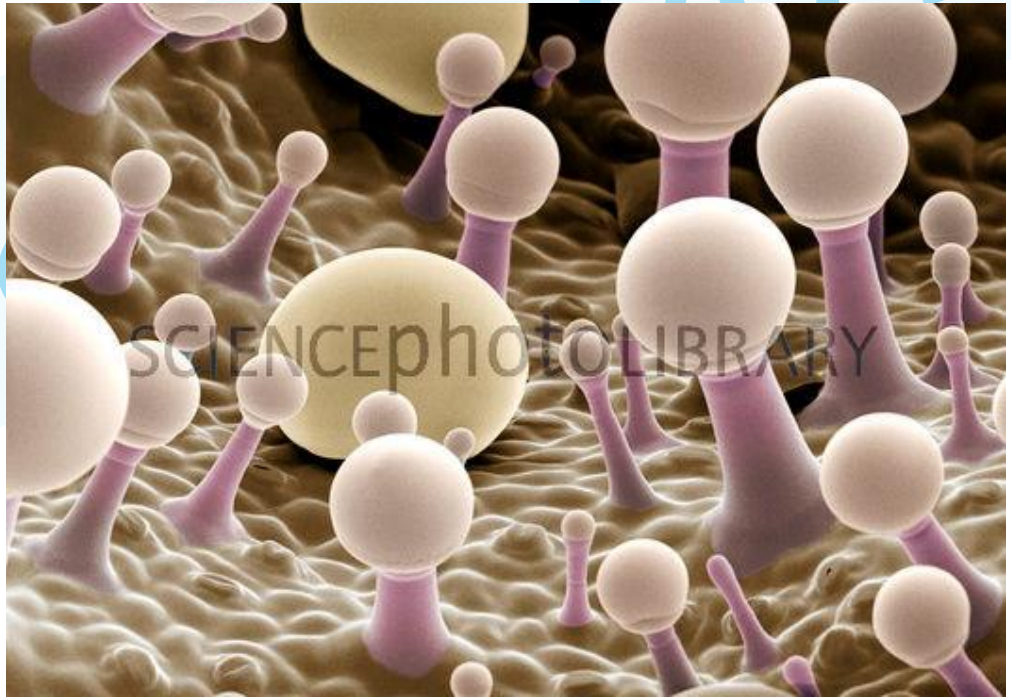
NOT ALL VOLATILE MOLECULES ARE ISPRENOID

Isoprenoid molecules are fashioned from the mevalonate synthesis pathway.

The other major synthesis pathway is the shikimic acid pathway. It makes benzene rings with propanoid tails and methyl group top-knots…

Sort of like cyclo-hexane, but different.

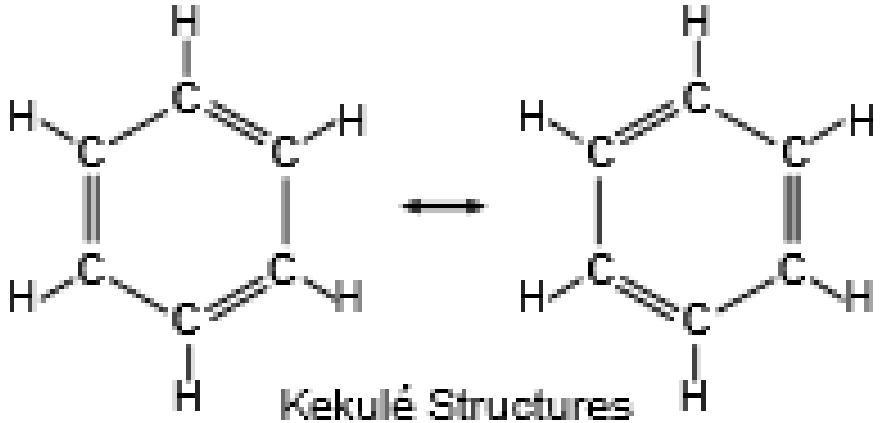
Manufacture of these molecules takes place in specialised glands or ducts in the plant, either flower, leaf, seed, wood or root.



Sage Leaf oil glands:
POWER AND SYRED/SCIENCE PHOTO LIBRARY

BENZENE RINGS

Also known as aryl or aromatic rings. The latter partly because the molecules tend to have an aroma if they have a benzene ring, but also because the special arrangements of bonds gives the molecule particular stability and resistance to metabolism which is known as ‘aromaticity’.

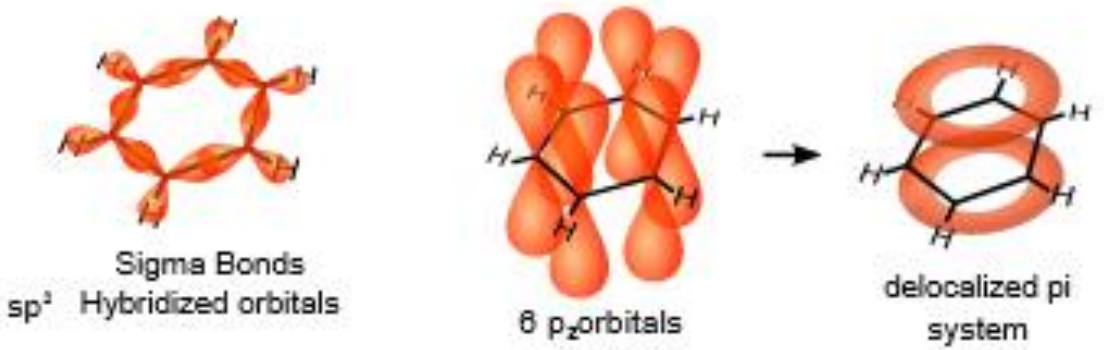


PROFESSOR KEKULE'S DREAM

Scientists are like artists and writers, they often get creative blocks, which then sometimes all of a sudden are resolved by a flash of inspiration or intuition.

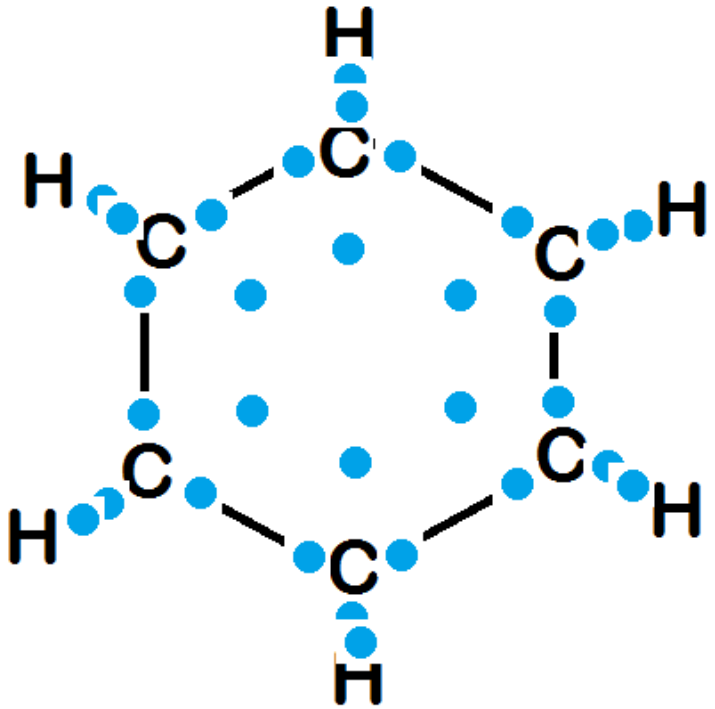
Kekulé had been dwelling on the seemingly illogical existence of States A and B of the benzene molecule, and dreamt that all the bonds were equal and were shared equally across the molecular surface of the benzene ring.

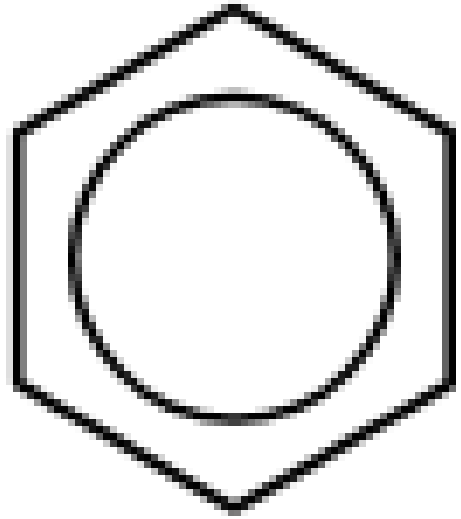
Kekulé's Nobel Prize was awarded in 1910.



By Vladsinger - Own vector drawing based on layout of en: File:Benzol trans.png., CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=7536474

ELECTRON SHARING IN THE BENZENE RING





FORMATION OF EO MOLECULES WITH BENZENE RINGS

The Shikimic Acid pathway in plants makes folate and the aromatic amino acids (i.e. that contain benzene rings).

It's complicated…
https://en.wikipedia.org/wiki/Shikimate_pathway

3D STRUCTURAL DIFFERENCES AFFECT INTERACTIONS WITH BODY MOLECULES

Terpenes

Mono- and sesqui-terpenes are more easily metabolised by the liver – the C=C can easily be attacked by liver enzymes, and have water-soluble molecular structures added to them.

Molecular shape can be wiggly (branched), fairly flat (mono-cyclic) or knobbly (bicyclic)

Phenyl compounds

Because of the delocalisation of the electrons across the ring, benzene derivatives don't have their C=C bonds easily broken – only substitution of their H atoms for other atoms. Quite a different reaction.

Molecule shape is like a flat pancake with a propeller at the back (isopropyl tail)