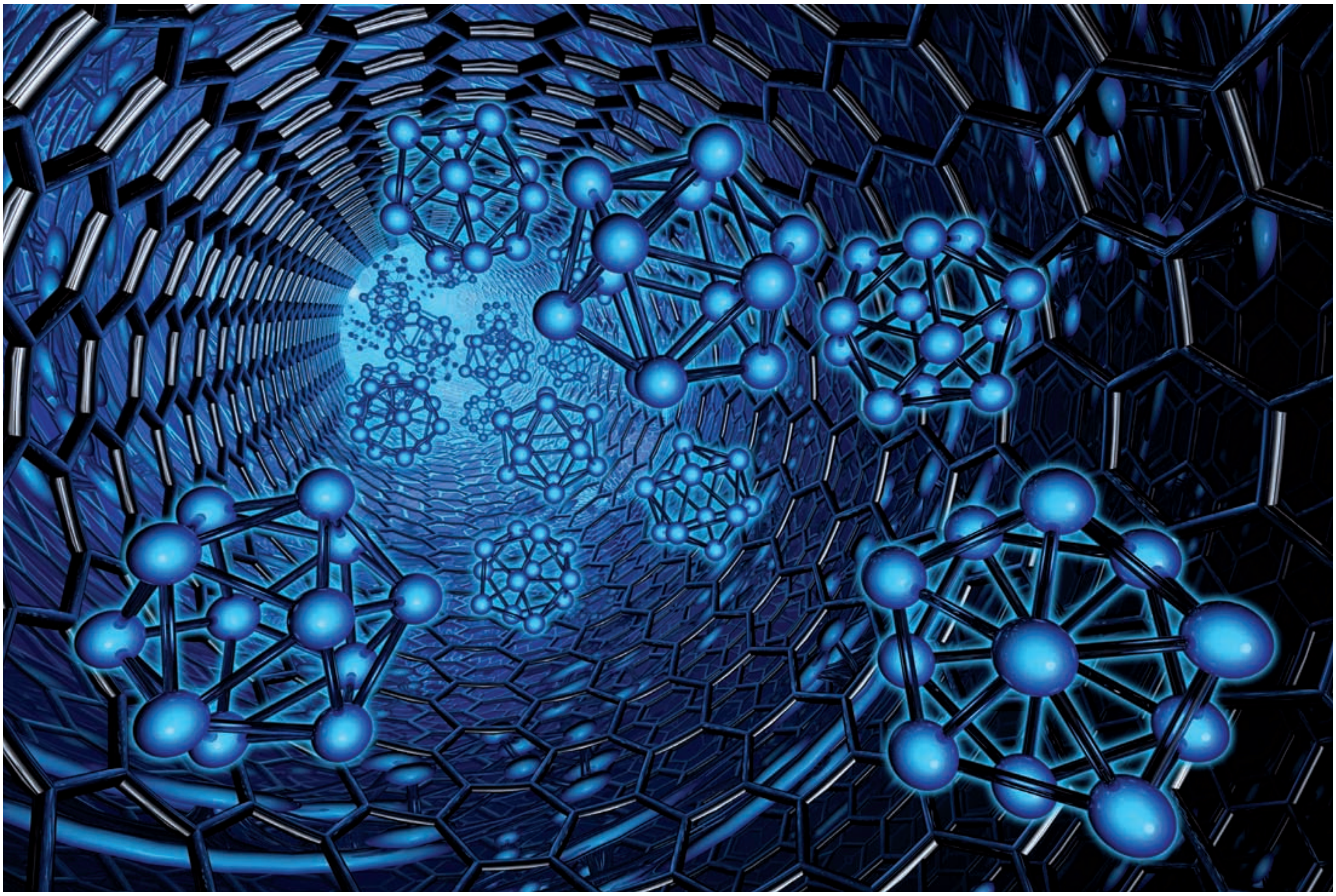
Structure and Bonding

Student Notes



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Activity 1: Lewis cubes

Bonding models

The person who is largely credited with developing the 'dot and cross' model of bonding was an American called Gilbert Newton Lewis (1875–1946). Dot and cross representations are also called Lewis structures, particularly in America.

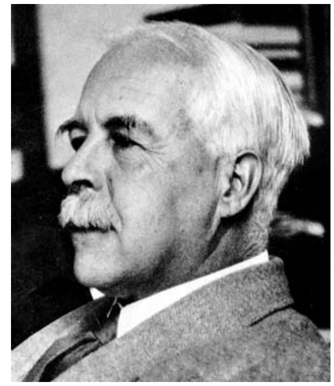
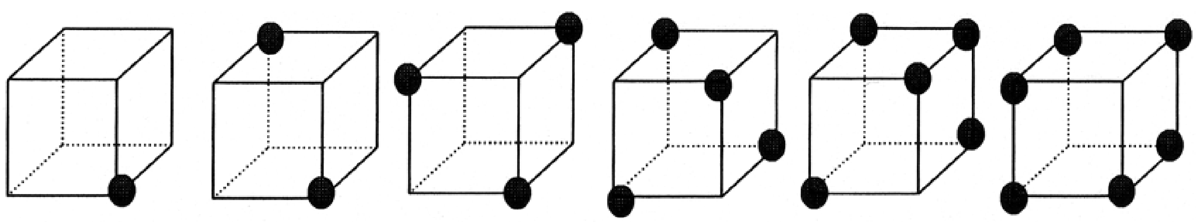


photo from http://dewey.library.upenn.edu/sceti/smith/scientist.cfm?PictureID=263&ScientistID=184 Used with permission of Edgar Fahs Smith Collection, University of Pennsylvania Library

Lewis' ideas developed over a long period of time, based on the observation that the periodicity of the properties of the elements seemed linked to the number eight. If you arrange the elements in order of increasing atomic number, the properties of the elements fall into a repeating pattern every eight elements (with some exceptions!). It follows from the work of Mendeleev on the Periodic Table.

He initially represented the 'electron shells' as cubes rather than the circles we use in the modern dot and cross model.



How Lewis represented the structure of atoms in 1916

His ideas can be expressed as follows:

- The electrons in an atom are arranged in concentric *cubes*.
- A neutral atom of each element contains one more electron than a neutral atom of the next smallest element in the period.
- The cube of eight electrons is reached in the atoms of the noble gases, and this cube becomes, in some sense, the core about which the larger cube of electrons of the next period is built. *(Lewis believed that helium had eight electrons).*
- The electrons of an outer, incomplete cube may be given to another atom, as in Mg^{2+} or enough electrons may be taken from other atoms to complete the cube, as in Cl^-, thus accounting for positive and negative ions.

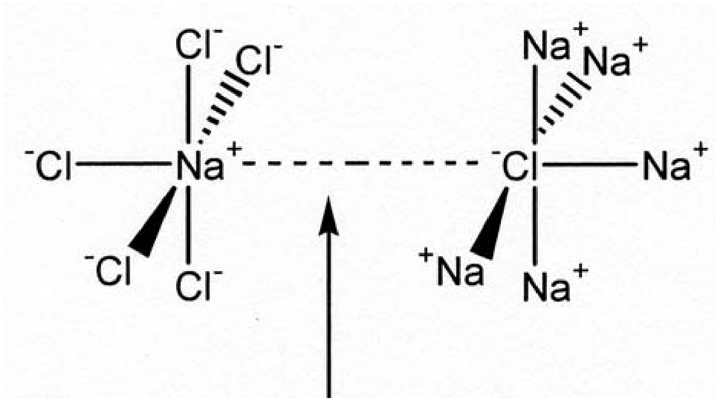
Questions

1. Can you suggest reasons why Lewis was attracted by the idea of the electrons occupying the corners of a cube?

2. Draw the electronic structure of neon using Lewis' ideas.

3. Draw the electronic structure of a sodium ion and a chloride ion.

4. Oppositely charged ions attract each other. This attraction gives rise to ionic bonding. The ions group together in a vast three dimensional array called a giant lattice. In the lattice of sodium chloride each ion has six nearest neighbours of the oppositely charged ion. Sodium chloride is said to have a coordination number of six.



This distance is exaggerated for clarity in the diagram

NaCl coordination number six. Note: the lines do *not* represent discreet bonds.

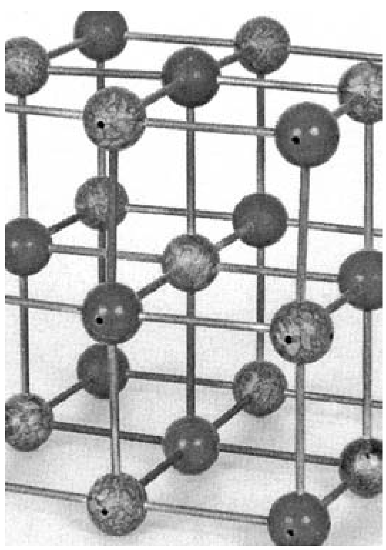


Photo of a NaCl model that is commonly used in schools

Explain how Lewis' cubic model would account for the coordination number of the sodium chloride. **Hint:** can you find some connection between the shape of cubes and a coordination number of six?

5. Lewis could account for covalent bonds as the sharing of electrons. The diagram below shows the structure of Cl_2. Draw similar diagrams for OF_2 and O_2.

6. Is it possible to draw a structure similar to the one in Question 5 showing a triple bond as in the molecule N_2?

Activity

1. Using two colours of Plasticine® and cocktail sticks, build models of O_2 and CCl_4. There are two ways of arranging CCl_4 – which do you think is best?

2. In a group, discuss the advantages and disadvantages of the cubic model compared with the circular dot and cross model.

3. Why do you think Lewis abandoned cubes for representing atoms?

Further research

Find out:

- What model of the atom was used before Lewis.
- What model Lewis introduced for acids and bases and which model it supplanted/refined.
- What role Lewis took in the famous Manhattan project to produce the first nuclear bomb.

For an introduction to bonding, visit:
www.chm.bris.ac.uk/pt/harvey/gcse/struc_bond_welcome.html

Activity 2: Extracting limonene from oranges by steam distillation

This experiment demonstrates the extraction of plant oils.

The peel of oranges is boiled in water and the oil produced (limonene) distilled in steam at a temperature just below 100 °C, well below its normal boiling point. The immiscible oil can then be separated. Direct extraction by heating would result in decomposition whereas steam distillation does not destroy the chemicals involved.

The experiment also links to tests for unsaturation, and at a higher level, chirality.

Apparatus and chemicals

Eye protection
Grater
Bunsen burner
Heat resistant mat
Tripod and gauze
Oranges, 2
110°C thermometer
Measuring cylinder (100 cm^3)
Measuring cylinder (50 cm^3)
Distillation apparatus
250 cm^3 round bottomed flask
Still head
Thermometer pocket
Condenser
Receiver adapter
Test tubes and bungs, 3
Dropping pipette
Anti-bumping granules
Bromine water, no more than 0.2% v/v (**Harmful**) CLEAPSS Hazcard 15B & CLEAPSS Recipe Book sheet 17
Potassium manganate(VII). 0.001 M, (solid – **Oxidising** & **Harmful;** solution – **low hazard**) See CLEAPSS Hazcard 81
Cyclohexene (**Highly Flammable & Harmful**) See CLEAPSS 45C
Cyclohexane (**Highly Flammable & Harmful**) See CLEAPSS 45B
Distilled water, 100 cm^3.

The apparatus should be assembled as shown in the diagram.

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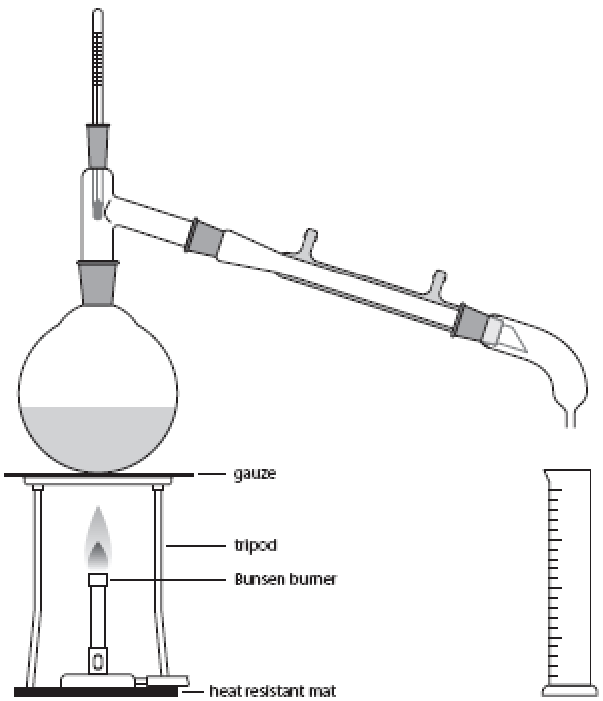
Apparatus



Procedure

HEALTH & SAFETY: Wear eye protection

Stage 1

a) Grate the outer orange coloured rind of two oranges and add to 100 cm^3 of distilled water in the 250 cm^3 round bottomed flask. Add anti-bumping granules to the round bottomed flask.
b) Set up the distillation apparatus as shown in the apparatus section.
c) Heat the flask so that distillation proceeds at a steady rate, approximately one drop per second of distillate. (Note: Take care not to let the liquid in the round bottomed flask boil too strongly).
d) Collect approximately 50 cm^3 of distillate in the measuring cylinder. The oil layer will be on the surface.
e) Using a dropping pipette carefully remove the oil layer into a test tube for the next stage.

Stage 2

Odour

f) Cautiously smell the extracted oil by wafting the fumes towards the nose. Do not breathe in directly from the test tube.

Action of bromine water

g) Measure out approximately 1 cm^3 of bromine water into each of three test tubes.
h) Add a few drops of the limonene oil to one test tube, a few drops of cyclohexane to another, and a few drops of cyclohexene to the third. Place in the bungs and agitate. If the bromine water is decolourised the molecule contains double bonds.
i) 0.001M potassium manganate(VII) can be substituted for the bromine water for class use. However, students need to know the action of bromine water.

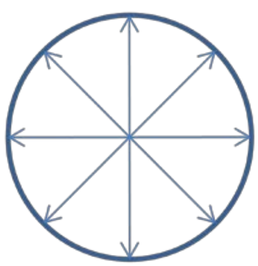
Activity 3: Chirality

Chirality, also referred to as optical isomerism due to the ability of the two enantiomers to rotate plane polarised light in different directions, describes the fact that a number of naturally occurring chemicals can exist as mirror images of each other, they are 'left or right handed'. A common example would be glucose. For this to happen it is necessary to have a carbon with four different groups attached. This can be easily illustrated using *Molymods*. The two forms are referred to as enantiomers. They are preceded by + and -, *D* and *L*, or *R* and *S*. It is a little confusing as there are several ways of expressing the same thing! The two different forms are chemically similar but biologically very different.

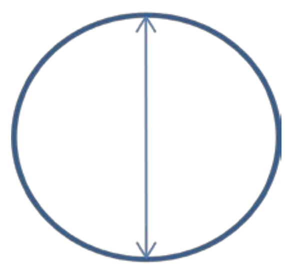
Asymmetric optically active molecules are often called chiral molecules, from the Greek word which means 'a hand'.

Chiral molecules and optical isomerism brings another higher level concept around structure and bonding that builds on the learning achieved to this point. It involves complex concepts such as mirror image molecules which are chemically similar but biologically very different, sometimes with disastrous results, hence the research exercise into thalidomide.

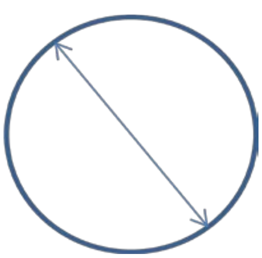
Optical isomerism occurs when there are four different atoms or groups of atoms joined to a central carbon atom. There are two possible arrangements, and each will be a mirror image of the other. The isomer structures will not be superimposable, one on the other, and each will interact with plane polarised light, twisting the light in either a clockwise or anticlockwise direction.



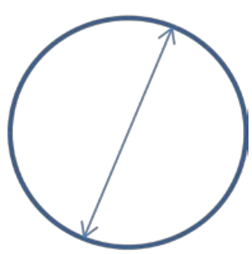
Normal light travelling in all directions



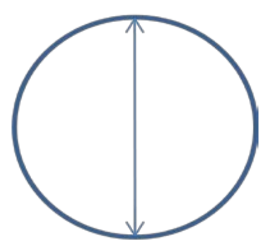
Plane polarised light travels in a single



(-) enantiomer
Anticlockwise rotation



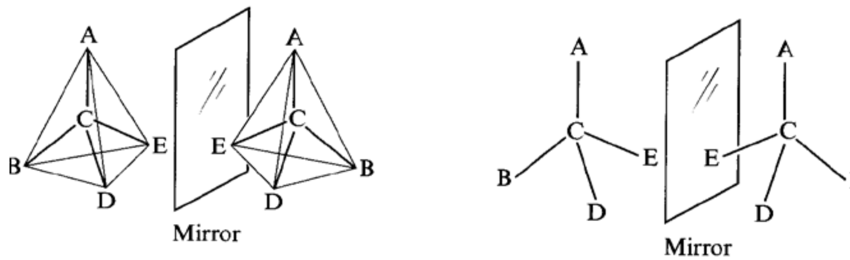
(+) enantiomer
Clockwise rotation



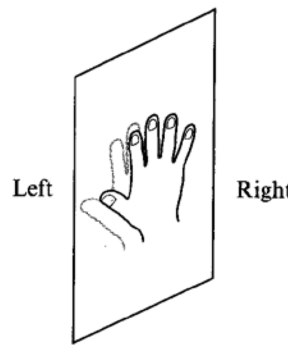
(±) racimate
No overall effect as each enantiomer cancels out the other

We say that such molecular structures, such as glucose, are asymmetrical, and it is the asymmetry around the carbon atoms which enables the formation of a pair of optically active isomers (enantiomers). The isomers are mirror images of each other.

Optical isomerism



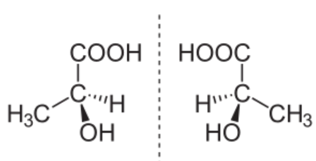
Isomers are mirror images of each other



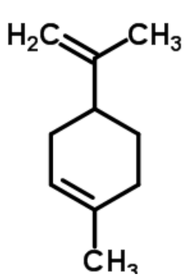
The two isomers are different, and a bit like your hands; if you put your hands flat together they are mirror images of each other. You cannot put your hands one on top of the other so that they match thumb on top of thumb. Neither can you place optical isomers one on top of the other. They are non-superimposable.

Try it with Molymods.

eg Lactic acid



Now attempt limonene



Activity 4: Research activities and questions

During the 1950s a new drug, thalidomide, was launched. Thalidomide was a sedative drug, often prescribed for morning sickness. It was widely sold between 1957 and 1961 before being withdrawn from the market.

1. Research the background of the development of thalidomide.
2. Draw the structure and identify any isomers.
3. Why was the drug withdrawn and what were the side effects?
4. Is the drug on sale again?
5. What processes are involved in the new method of production that ensure that the side effects are removed?

Guidance

Below are several websites that would form the starting point for any research. There are plenty of references in periodicals and texts.

Thalidomide is a chiral drug where one enantiomer acted as a teratogen causing severe birth defects when prescribed to pregnant women. At the time of development the identification of chiral enantiomers was difficult. It is now possible to isolate the two enantiomers using chromatography and the drug has been relaunched.

General information

http://en.wikipedia.org/wiki/Thalidomide

BBC report

http://news.bbc.co.uk/1/hi/uk/2031459.stm

Chiral drugs

http://www.chem.yale.edu/~chem125/125/thalidomide/thalidomide.html

General information

http://www.britannica.com/EBchecked/topic/589836/thalidomide

Activity 5: Question on chiral molecules

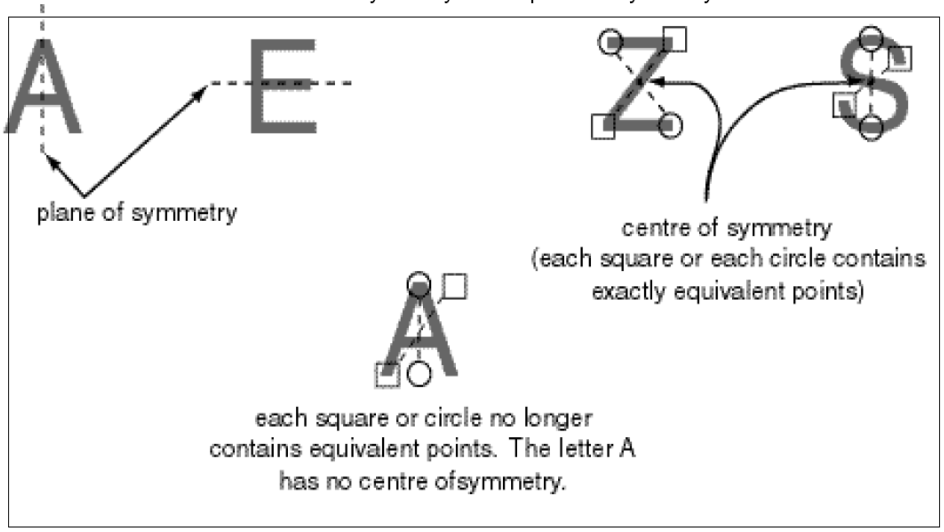
A carbon atom bonded to four different groups is called a chiral centre (asymmetric carbon, *C). For example, hexan-3-ol has a chiral centre:

$CH_3CH_2{}^*CH(OH)CH_2CH_2CH_3$

and can exist as two different optical isomers (enantiomers), which are nonsuperimposable mirror images. A molecule which contains just one chiral centre will always exist in two enantiomeric forms. However, some molecules with two or more chiral centres can be achiral, i.e. they *can* be superimposed on their mirror images. Such achiral molecules will have either a **plane** or **centre of symmetry**.

A **plane of symmetry** ('mirror plane') is one which cuts an object into two parts so that each part is the mirror image of the other. For example, the letters A and E both contain a plane of symmetry.

A **centre of symmetry** is a point from which lines, when drawn on one side and continued in the same direction an equal distance on the other side, will meet exactly similar points in the object. For example, the letters Z and S both have a centre of symmetry but no plane of symmetry.

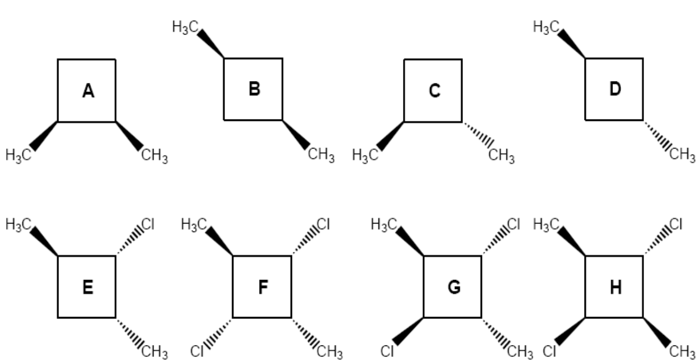


Compounds possessing a plane or centre of symmetry are always **achiral.**

a) Which of the molecules given below have a plane of symmetry?

b) Which molecules have a centre of symmetry?

c) Which molecules are chiral and therefore have nonsuperimposable mirror images?



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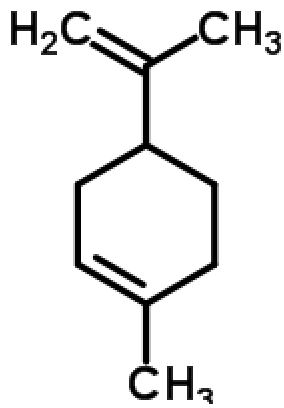
Glossary

Below are some of the terms used within this document:

Term	Definition
alkene	An unsaturated compound containing at least one C=C bond
asymmetrical carbon	A carbon atom attached to four different atoms or groups of atoms
centre of symmetry	The carbon atom attached to four different atoms or groups of atoms
chiral molecule	A molecule that does not have a plane of symmetry forming two mirror images
covalent bond	A bond formed by the sharing of pairs of electrons between two atoms
enantiomer	Stereoisomers of molecules that are mirror images of each other
hydrocarbon	A hydrocarbon is an organic compound consisting of hydrogen and carbon
isomer	Compounds with the same molecular formula but different structural formula
optically active	A chiral molecule that causes the rotation of plane polarised light
plane polarised	Light waves restricted to a single plane
polarimeter	An instrument used to measure the degree of rotation of plane polarised light through a chiral molecule
racemic mixture	A mixture, in equal proportions, of the left and right handed enantiomers
stereoisimer	Isomers that have the same molecular formula and bonded atoms but differ in the three-dimensional orientations of their atoms.
unsaturated	Unsaturated compounds are generally referred to as hydrocarbons that contain double bonds.

Limonene - data

Limonene is an organic (carbon based) molecule classed as a terpene. Its name is based on the fact that that it exists as a colourless oil at room temperature that can be extracted from the rind of lemons, and oranges. It has two isomers that have a distinct odour of lemon/orange or turpentine.



Limonene exists as two isomers with one form more common than the other. One form is more common than the other. This is common with naturally occurring molecules that exhibit this type of behaviour. The isomers of these molecules are referred to as enantiomers. The common enantiomer is the (+) enantiomer, sometimes referred to as the *D* or *R* form. These symbol reference the fact that these isomers are optical active and can rotate plane polarised light in either a clockwise (+) or anticlockwise (-) direction.

Uses of limonene include food flavouring, cosmetics, as a perfume in cleaning fluids and as a degreasing solvent. As a renewable product there have even been experiments for its use as a biofuel. The (+) enantiomer has the lemon/orange odour whereas the (-) enantiomer has the odour of turpentine.

Data

IUPAC name	1-methyl-4-prop-1-en-2-yl-cyclohexene
Molecular formula	$C_{10}H_{16}$
Molecular mass	136.24
Boiling point	176 ^{o}C
Density	0.8411 g/cm^3
Flash point	50^{o}C

Figures quoted at 25^{o}C and 100 kPa

For comprehensive data visit:

http://www.chemspider.com/Chemical-Structure.20939.html

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