LECTURE 1. ALKANES (PARAFFINS), ALKENES (OLEFINS), ALKYNES (ACETYLENES): GENERAL

Basic Nomenclature

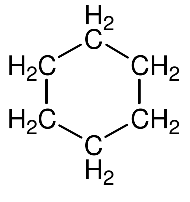
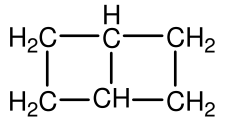
- a saturated hydrocarbon is denoted by the suffix –ANE
- an unsaturated hydrocarbon with one double bond is denoted by the suffix –ENE
- an unsaturated hydrocarbon with one triple bond is denoted by the suffix –YNE
- the number of carbons in the chain is denoted by the prefixes METH- (one carbon), ETH- (two carbons), PROP- (three carbons), BUT- (four carbons), PENT- (five carbons), HEX- (six carbons) etc.
- alkenes and alkynes with more than one double or triple bond are given the designations DI-, TRI-, TETRA-, PENTA- etc before the -ene and -yne according to the number of multiple bonds
- the position of multiple bonds and substituents are indicated by numbers along the chain, using the smallest set of numbers (see last example below which would be incorrectly named as 6-chloro-hept-2-ene).

Examples:

CH_3CH_3	Ethane
$CH_3CH{=}CH_2$	Propene
$CH_3C{\equiv}CCH_3$	But-2-yne or 2-Butyne
$CH_2{=}CHCH_2CH{=}CH_2$	Penta-1,4-diene
$CH{\equiv}C\text{-}C{\equiv}C\text{-}C{\equiv}CH$	Hexa-1,3,5-triyne
$CH_3CH(Cl)CH_2CH_2CH{=}CHCH_3$	2-Chloro-hept-5-ene

Units of Unsaturation (Double Bond Equivalents)

Let us take three hydrocarbons each with six carbon atoms to illustrate units of unsaturation (otherwise called double bond equivalents or DBE):

Straight Chain:	$CH_3CH_2CH_2CH_2CH_2CH_3$	C_6H_{14} (C_nH_{2n+2})
	$CH_3CH_2CH_2CH_2CH{=}CH_2$	C_6H_{12} (C_nH_{2n})
	$CH_3CH_2CH_2CH_2C{\equiv}CH$	C_6H_{10} (C_nH_{2n-2})
Monocyclic:		C_6H_{12}
Bicyclic:		C_6H_{10}

Hex-1-ene has two hydrogen atoms fewer than hexane and is said to have one unit of unsaturation. Hex-1-yne has four hydrogen atoms fewer than hexane and is said to have two units of unsaturation or two double bond equivalents

(DBEs). In the monocyclic case, cyclohexane, C_6H_{12} is the same formula as that for a straight chain compound with one double bond. Therefore, the monocyclic compound is said to have one unit of unsaturation or one DBE (even though it is not an unsaturated compound). The bicyclic compound has yet two hydrogens fewer than the monocyclic case and therefore has two DBEs.

DBEs can be applied to molecules functionalised with O, N or halogen substituents provided we follow some simple rules as follows:

Element	example	mol formula	action	CH formula	DBEs
O	$CH_3(CH_2)_4CH_2OH$	$C_6H_{14}O$	ignore O	C_6H_{14}	0
O	$CH_3(CH_2)_4CH{=}O$	$C_6H_{12}O$	ignore O	C_6H_{12}	1
N	$CH_3(CH_2)_4CH_2NH_2$	$C_6H_{15}N$	remove NH	C_6H_{14}	0
N	$CH_3(CH_2)_4CN$	$C_6H_{11}N$	remove NH	C_6H_{10}	2
Hal	$CH_3(CH_2)_4CH_2X$	$C_6H_{13}X$	add 1H, - X	C_6H_{14}	0

The use of DBEs is very helpful when we only have the molecular formula of an unknown compound since we can use them to make an initial guess as to the nature of the functional groups present in the molecule.

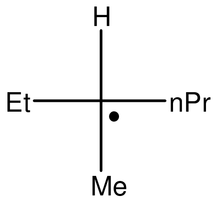
Isomerism

Isomers, i.e. compounds exhibiting isomerism, are defined as compounds with the same molecular formula but which differ in some other respect. There are a number of types of isomerism.

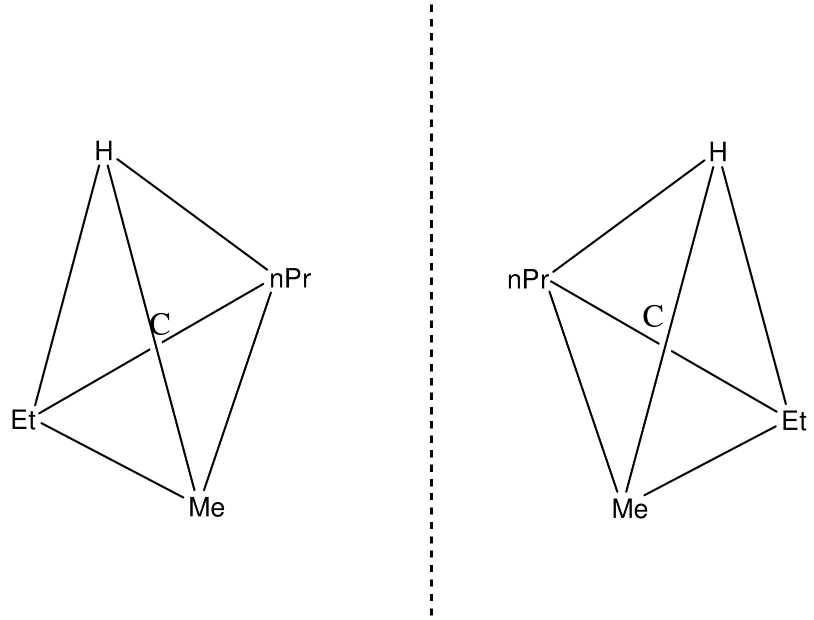
Structural or Positional Isomerism: Hex-1-ene and cyclohexene are both C_6H_{12} and they are structural isomers because their structures are different despite the same molecular formula. Likewise, 3-methylpent-1-ene ($CH_3CH_2CH(CH_3)CH{=}CH_2$) is a structural isomer of those two. Since it only differs in the position of the methyl group it is also known as a positional isomer of hex-1-ene.

Optical Isomerism (Enantiomerism): Now look at the following branched chain alkane:

$$CH_3CH_2\overset{\bullet}{C}H(CH_3)CH_2CH_2CH_3 \quad \equiv$$



This can exist as two separate molecules which have the same molecular formula, the same structural formula and only differ in the way we order the groups around the indicated carbon in three-dimensional space. Such isomers are called optical isomers or enantiomers. If we put the indicated carbon at the centre of a tetrahedron then we see that they are related as mirror images:

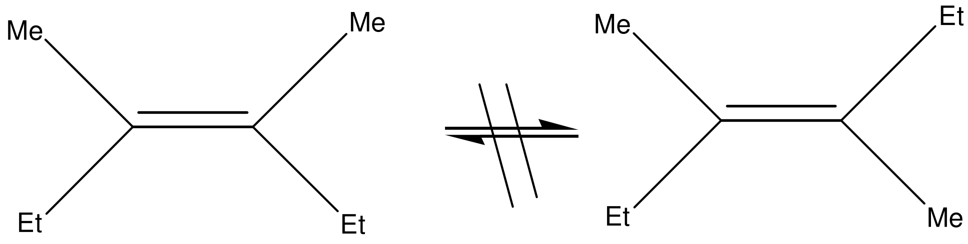


Mirror plane

No matter how we rotate these two molecules in space, they cannot be superimposed one upon the other so that **ALL** the groups line up i.e. they cannot be the same molecule and must have separate existences. Clearly, they are isomers and they are called optical isomers because the only way to distinguish between them is to measure their optical rotation i.e. the rotation of the plane when plane polarised light is passed through them. One of them rotates the plane clockwise and the other anti-clockwise.

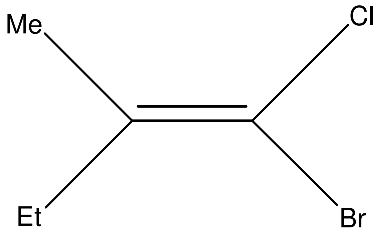
One test to see whether a new compound can exist as enantiomers is to look for a carbon atom within the molecule which bears four different groups, a so-called asymmetric centre. However, some molecules can exist as optical isomers even though they do not have an asymmetric centre and a more fundamental test for optical isomerism is to look for the **absence** of a mirror plane within the molecule. We shall see later how we can apply this latter test.

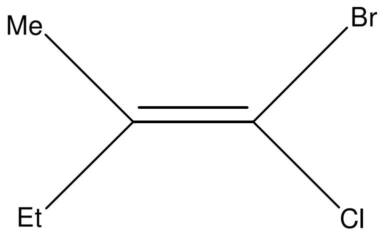
Geometrical Isomerism: E/Z Notation: A double bond does not allow rotation about itself (we shall see why soon). This phenomenon of zero rotation leads to the independent existence of two isomers, called geometrical isomers, which are NOT interconvertible by rotation at normal temperatures:



CIS TRANS

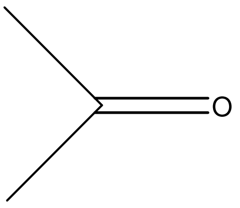
These two isomers are usually designated cis and trans in order to distinguish them. When similar groups are on the same side of the double bond the isomer is cis and when they are on opposite sides the isomer is trans. However, this system of naming is no good when the groups are unlike one another, as in the following pair:



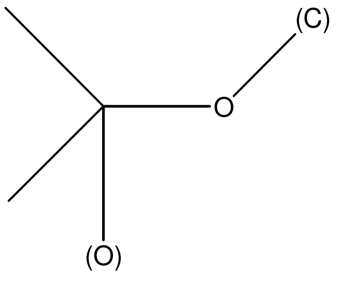


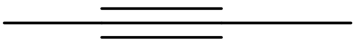
For such cases we need the E/Z-Notation. In this notation we first assign an order of priority to the atoms of the groups **directly** attached to the double bond carbons. To do this a few simple rules apply:

1. Atoms of higher atomic number take precedence over those of lower atomic number:
   I > Br > Cl > F > O > N > C > H
2. For isotopes, those of higher atomic weight take precedence:
   $^3H > ^2H > ^1H$
3. Where two or more of the atoms attached to the double bond are the same (e.g. C in the Me and Et groups in the example above) we establish the order of priority of the next atoms along the chain:
   Et > Me because $H_3\mathbf{C}\text{-}CH_2 > \mathbf{H}\text{-}CH_2$
4. Groups containing π-bonds themselves e.g. C=O are converted into an equivalent saturated system by ghost atoms (indicated by brackets):

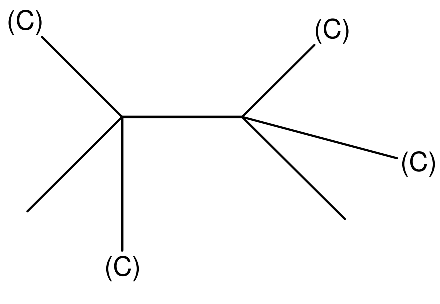


is equivalent to





is equivalent to



We then use the saturated system to decide upon the priority:

$CO_2Me > CO_2H > CONH_2 > COMe > CHO > CN > CCH > CHCH_2$

Thus in the example above the bromine and the ethyl groups have top priority on their respective double bond carbon atoms and the methyl and chlorine have second priority. The molecule on the left with the highest priority groups on the same side of the double bond is now designated the Z-isomer (from zusammen, German for together) and where they are on opposite sides the molecule on the right is the E-isomer (from entgegen, German for opposite).

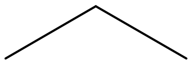
A general term which covers both optical and geometrical isomer(ism) is stereoisomer(ism) the term “stereo” meaning to indicate a spatial arrangement.

Line Notation

Notice how long it takes to write these structures down when we include all the atoms. A simpler and faster method is by line notation. In this a line represents a bond and the termini of the line represent carbon atoms and their associated hydrogens.

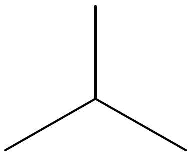
Thus,  is CH_3-CH_3

Where two lines meet they are joined at an angle to show that there are two bonds and a carbon between them. Thus the junction of two lines is a methylene (CH_2) group:



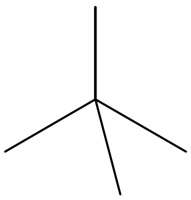
is $CH_3CH_2CH_3$

Notice this method of notation already has another advantage in that it indicates the shape of the molecule; propane is indeed not linear. A methine carbon (CH) is represented by the junction of three lines:



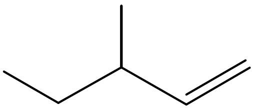
is $CH_3CH(CH_3)CH_3$

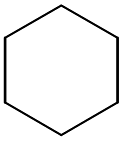
Finally, a carbon without any hydrogens attached to it is represented by four lines meeting:

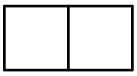


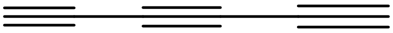
is $CH_3C(CH_3)_2CH_3$

Thus, some of the C6 compounds at the beginning of this lecture may be written as:

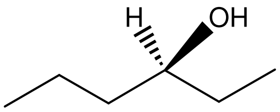


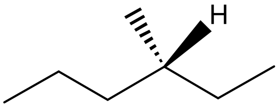






When we have stereochemical (i.e. for enantiomers) information to impart we use a wedged and dashed line notation, the wedge indicating a group pointing towards you and a dash indicating a group pointing away from you, the rest of the molecule being in the plane of the paper e.g.:

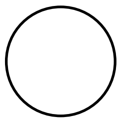




(Note in the right hand molecule the end of the dashed line shows no substituent and therefore a methyl group is present at that position). Normally we would not include hydrogens as substituents (see the C6 compounds) but where an asymmetric centre bears a hydrogen, as in the two examples above, the hydrogen is shown to give the sense of the tetrahedral nature of the asymmetric carbon i.e. we do not use:

Bonding and Hybridisation

The electronic configuration of carbon is $(1s)^2$ $(2s)^2$ $(2p_x)^1$ $(2p_y)^1$ $(2p_z)^0$. In order to explain the fact that it bonds to four groups (it is tetravalent) in its compounds the electronic configuration then becomes $(1s)^2$ $(2s)^1(2p_x)^1$ $(2p_y)^1$ $(2p_z)^1$. Electrons are in orbitals which define approximately their position in space, i.e. the probability of finding the electron in that volume outlined by the orbital is 1, and these orbitals have shapes as follows:



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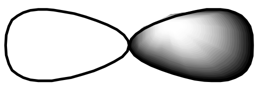
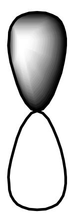
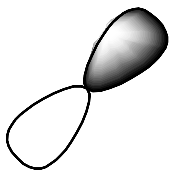


p_x

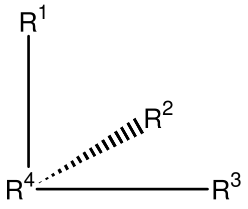


p_y

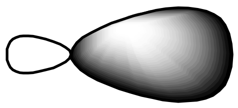


p_z

Alkanes: If the groups R^1 – R^4 bonded to the central carbon atom use these orbitals then a saturated molecule should have the following shape which is clearly NOT tetrahedral:

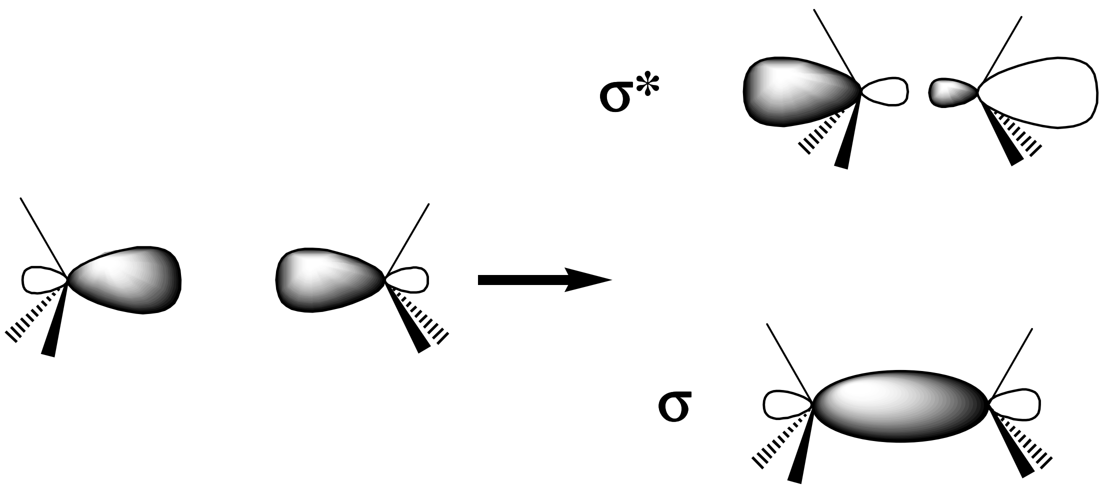


What we need is four equivalent bonds and this can be achieved by mixing the one s and the three p orbitals to make four new orbitals each containing one-quarter s character and three-quarters p character. These are called sp^3 hybrid orbitals and the process of mixing them is called hybridisation. The shape of these equivalent orbitals is now:

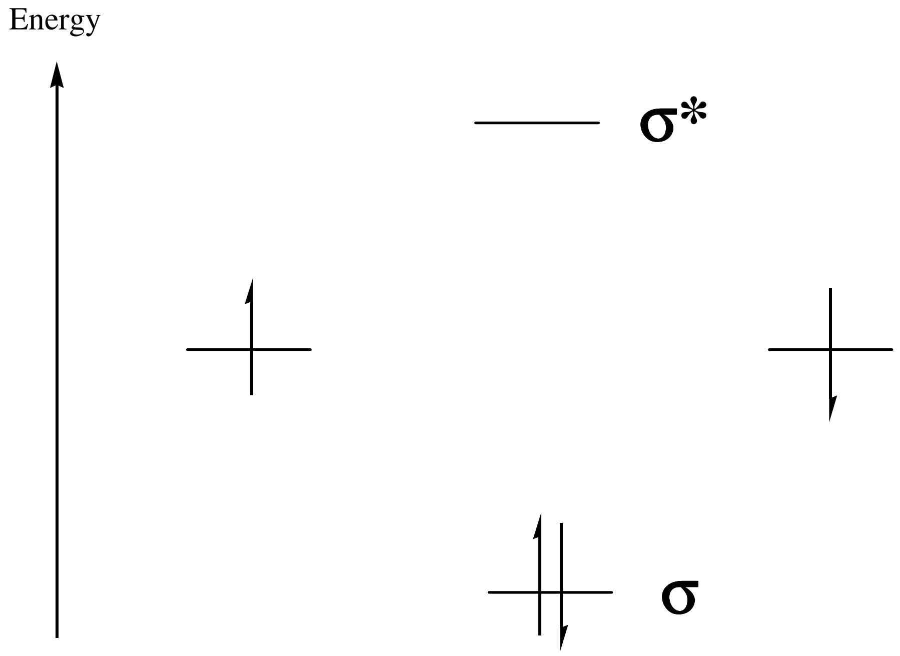


In order to minimise the electron-electron repulsion between the electrons in the four bonds these orbitals point towards the apices of the only geometrical shape which can achieve this, namely, a tetrahedron.

In saturated organic molecules we make bonds between carbon atoms by overlapping the sp^3 hybrid orbitals as follows:



The result is a sigma (σ) orbital which has most of the electron density associated with it between the two carbon atoms thereby bonding them, hence it is called a Bonding orbital. In addition, a second, empty orbital is created (by the Conservation of the Number of Orbitals, n molecular orbitals must result from the combination of n atomic orbitals). This is known as the σ* orbital and if it had electrons in it they would be concentrated away from the internuclear gap and this would prevent bonding, hence it is called an Anti-Bonding orbital (indicated by the asterisk). In energy terms the σ* orbital is much higher in energy than the σ-orbital because bonding is the favoured process reducing the internuclear repulsion. The two electrons in the original atomic orbitals, one from each carbon, fill up the σ-orbital by the Aufbau process:



Rotation about the central C-C bond in alkanes is generally very easy because the orbital is not broken by this process i.e. we do not break a bond on rotation.