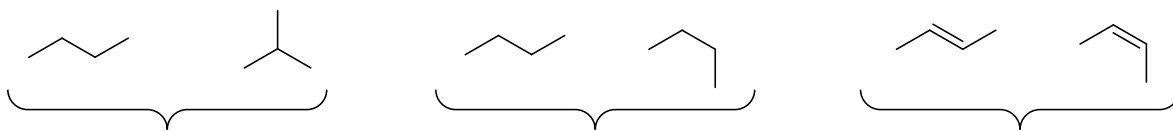


## CHEM1902/4 Worksheet 2: Isomerism and Structure Elucidation

### Model 4: Isomerism

There are three broad classes of isomers. Use the definitions below to help you decide the type of isomerism shown by each of these three pairs of compounds.

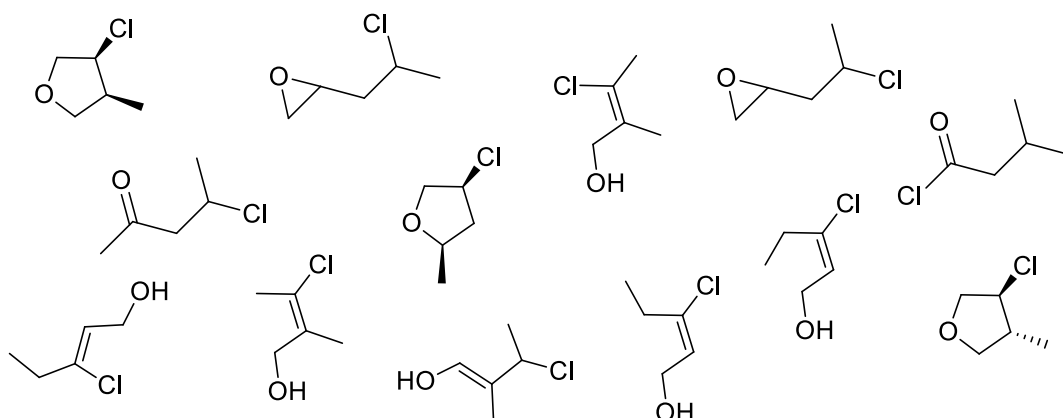


**Constitutional** isomers have the same formula but different connectivity.

**Conformational** isomers differ only by rotation about a single bond. They interconvert freely at all but extremely low temperatures (ie they are identical).

**Configurational** isomers (**Stereoisomers**) have the same connectivity but cannot be interconverted through single bond rotation. Bond breaking and bond formation are required for interconversion.

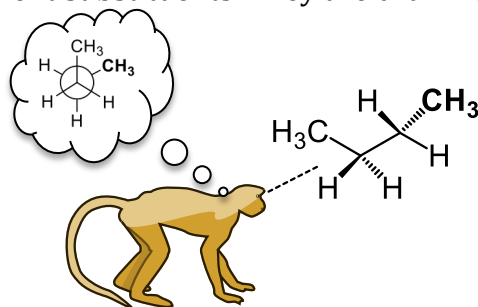
Here are some molecules all with the formula  $C_5H_9ClO$



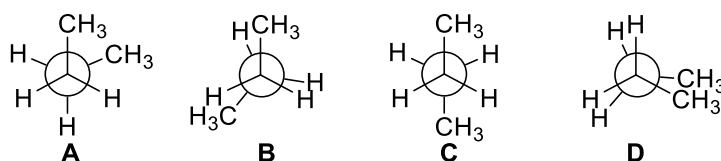
1. Circle at least 7 constitutional isomers
2. Identify two pairs of conformational isomers
3. Identify three pairs of configurational isomers. Assign them and *E/Z* or *cis/trans*.

**Extension:** How many different functional groups can you identify?

Newman projections are an effective way to draw conformers, as they allow us to see the relative positioning of the different substituents. They are drawn as if you were looking along one of the C-C bonds:



Here are some of the possible conformers of butane.



The electrons of each substituent (including the bonding electrons) exert a repulsive force on nearby groups. This is minimized when the groups are as far apart in space as possible (recall the tetrahedral shape of methane). The larger the group, the greater this **steric effect**.

4. Arrange the conformers from highest in energy to lowest in energy.
5. Can you usually observe single conformers? Why/why not? How might you isolate a single conformer?

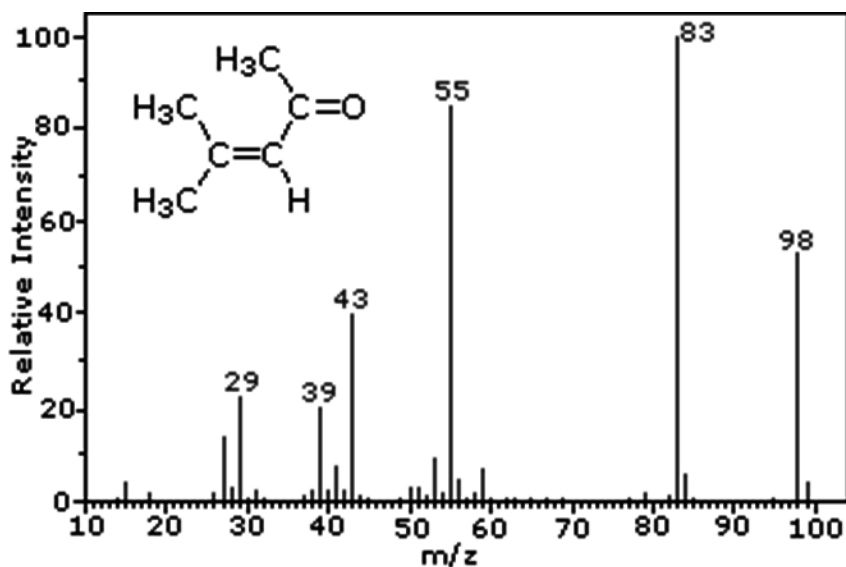
## Model 5: Structure Elucidation

### 1. Mass Spectrometry

Mass spectrometry allows us to determine the molecular weight of a compound. However, it is a highly destructive technique, and molecules will often break up into smaller fragments. These fragments can further help in the identification of the compound.

For example, a  $\text{CH}_2\text{CH}_3$  group has a mass of 29, so a peak at 29 might indicate the presence of a  $\text{CH}_2\text{CH}_3$  group. Alternatively, *loss of an ethyl group* could also be diagnostic – where would you look for this signal?

Identify as many peaks as possible in the mass spectrum of 4-methyl-pent-3-enone. Which peak is the molecular ion?



How would you expect the mass spectrum of 3-methyl-pent-3-enone to differ from the one shown above?

And 3,4-dimethylpent-3-enone?

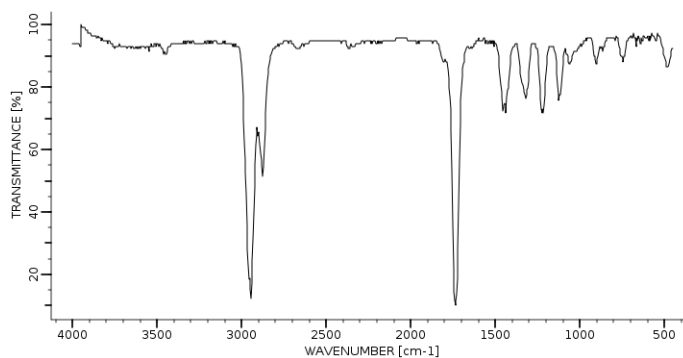
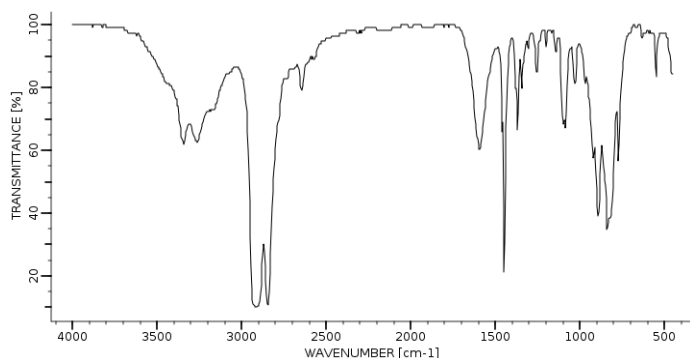
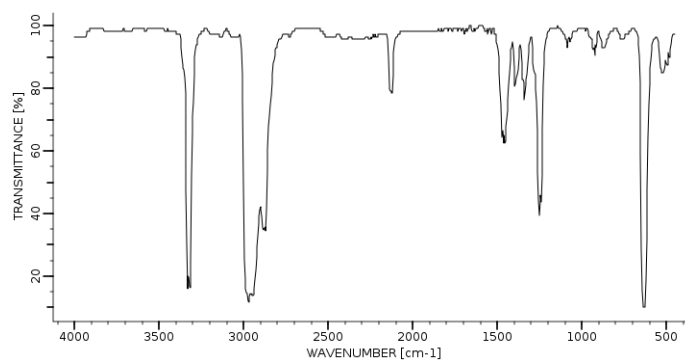
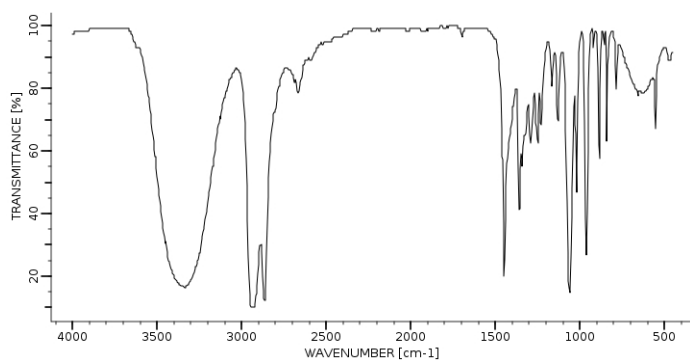
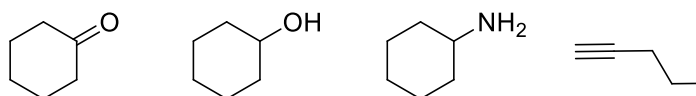
## 2. Infrared Spectroscopy (IR)

You have seen in lectures how bonds stretch, bend and rotate (or you will very soon). A light wave of the correct frequency will be in resonance with a bond in motion and transfer its energy to this motion, like a parent pushing a swing. Light absorbed by the molecule in this manner falls in the infrared range. As a result **IR spectroscopy can be used to identify bonds, and hence functional groups, in a molecule.**

Here is a table of characteristic IR absorption frequencies.

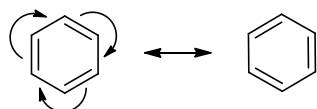
Bond Description	alcohol OH	alkane $C_{sp^3}H$	carbonyl C=O	amine NH	alkyne $C_{sp}C_{sp}$
Example	RO—H	$R_3C—H$	$\begin{array}{c} R \\   \\ C=O \\   \\ R \end{array}$	$R_2N—H$	$HC\equiv CH$
Absorption Range ( $cm^{-1}$ )	3200-3650 (strong, broad)	2840-3000 (strong)	1690-1760 (strong)	3100-3500	2100-2260



Use these to match these four compounds to their corresponding IR spectrum.



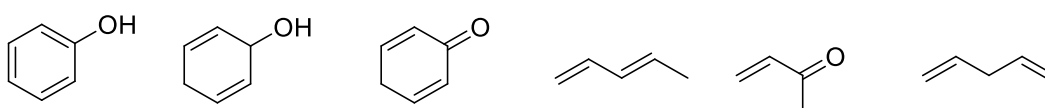
### 3. UV-Vis

A chain of double bonds, each separated by exactly one single bond gives rise to a pattern of double-single-double bonds that is called conjugation. Benzene is the classic example of a conjugated molecule. What is the hybridization at each carbon in benzene?



	These <b>curly arrows</b> show electron pairs moving.
	This arrow shows that these are <b>resonance structures</b> . The <b>only</b> difference between them is the <b>position of electrons</b> .

Here are a few examples of molecules containing more than one double bond. In which ones are the bonds conjugated?



For the last three molecules in the list above, draw the unhybridized p orbital on each atom that is  $sp^2$  hybridized. What do you notice in the conjugated compounds?

Last semester, you learned about molecular orbitals, specifically how electrons can be excited from the lowest occupied molecular orbital (LUMO) to the highest unoccupied molecular orbital (HOMO). The energy of the photon had to corresponded precisely to the LUMO-HOMO energy difference to cause this 'jump'.

For conjugated systems, this LUMO-HOMO energy difference falls in the UV-Vis range. Given this information, which of the above structures would show a peak in the UV-Vis spectrum?

How useful do you think a UV-Vis spectrum is in identifying organic molecules?

**UV-Vis is used to determine whether conjugation is present in a molecule.**

**(Model 5 continues next week)**

*Model 5 forms part of the 'Spectroscopy Problem Solving Assignment' which represents 10% of the assessment of this unit. You should use the support material on eLearning alongside this worksheet and your lecture notes. The assignment is assessed through online quizzes and must be completed by the end of week 7.*