Preparatory Material for Incoming Students

A summary of what you need to know before arriving in Oxford and for the first term is given below.

- The organic chemistry lectures in Michaelmas term are as follows:

  Introduction to Organic Chemistry (7 lectures)

  Introduction to Organic Spectroscopy (2 lectures)

  Orbitals and Mechanisms (7 lectures)

- The organic chemistry tutorials in SEH are given by Dr Paul Roberts.
- We will cover the following topics in tutorials in MT in parallel to lectures as much as possible): basic concepts (structure, shape); stereochemistry; acidity and basicity.
- Please buy a copy of 'Organic Chemistry', either the first edition by Clayden, Greaves, Warren and Wothers, or the second edition by Clayden, Greaves and Warren. Both editions will be fine and are available on Amazon for about £40-45 new (although used versions, particularly of the first edition, are substantially cheaper). This book will be invaluable throughout the whole of the course.
- The first lecture course and the first tutorial are specifically intended to bridge gaps between knowledge required for A-level and that required for the first-year course. The first tutorial sheet is appended below ***for your information only*** (i.e., you are ***not*** expected to start or complete this before arriving in Oxford). It is, however, a good idea for you to read over the tutorial sheet and "Foundations of Organic Chemistry" (Oxford Chemistry Primers, No. 9) by Hornby and Peach. College Grant funds are available to support purchases (up to £100 on books).
- Further information will be given at the start of term meeting when you arrive in Oxford.

Basic Concepts: Structure and Shape

Introduction

You need to understand the vocabulary which we use to describe the structure and bonding within molecules. Get into the habit of drawing clear diagrams which give good representations of the 3D structures of molecules, which will make life a lot easier. Cover the following topics in the form of concise revision notes. You must be able to give a definition and understand the differences between the terms mentioned. An illustrative example of each in your notes is a good idea. Then go on to answer the attached problems.

Make notes on the following topics

1. Atomic orbitals (s, p, etc) and ground-state electronic configuration of C; concept of hybridisation (sp, sp^2, sp^3); concept of molecular orbitals (and their shapes); bonding and anti-bonding orbitals; VSEPR theory; electronic structure of simple carbocation, carbanion and carbon-centred radical 'reactive intermediates'; definition of classification of species as electrophile and nucleophile; types of bond-breaking: homolytic or heterolytic.

2. Definition of conformation, conformer, and torsion (dihedral) angle (use ethane as an example); understand the use of Newman projections; definition of the terms: staggered, eclipsed, anticoplanar, antiperiplanar, syncoplanar, synperiplanar, gauche; energy profile diagram for rotation about the central C–C bond in ethane, energy maxima and minima.

3. Cyclic systems: hybridisation of cyclopropane (how can you have a three-membered ring comprised of tetrahedral, sp^3-hybrid carbon atoms?); conformations of cyclohexane (why is cyclohexane not flat?), limit to 'chair' and 'boat' forms (which is more stable and why);

nomenclature of 'axial' and 'equatorial' positions for chair form of cyclohexane; dihedral angles of axial/axial, axial/equatorial and equatorial/equatorial substituents (relevance?).

4. Geometric requirements arising from the necessity of orbital overlap; bond/angle strain, for example what (and more importantly *why*) is Bredt's rule?

5. Aromatic systems, e.g. benzene; shape, bonding; concept of Hückel aromaticity; Kekule structures and the concept of delocalisation.

6. Resonance forms: delocalisation of electrons/charge over a molecule *via* a conjugated π-system is stabilising relative to charge localisation (why?). Be able to draw resonance structures for such systems, interconverted by two electron transfers represented by curly arrows. Make sure you can define: resonance; resonance hybrid; mesomerism.

Tutorial Problems

1. State the shape and assign charges (where appropriate) to the following species.

BH_3, BH_4, NH_2, NH_3, NH_4, CH_2, CH_3, CH_4, OH, OH_2, OH_3

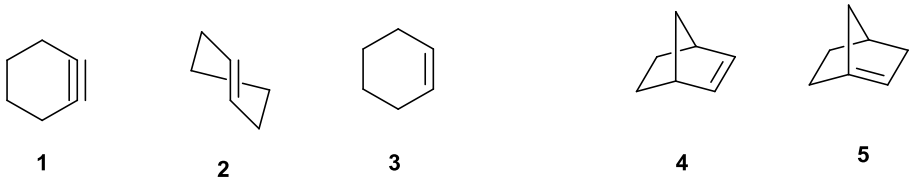
2. Using butane as an example, define the terms: torsion angle, anticoplanar (antiperiplanar), syncoplanar (synperiplanar), and gauche. Draw an energy profile diagram for rotation around the central C–C bond and identify the conformations that correspond to energy maxima and minima.

3. Explain why $CH_2{=}CH_2$ (ethene) and $CH_2{=}C{=}C{=}CH_2$ (cumulene) are planar, whereas $CH_2{=}C{=}CH_2$ (allene) is not.

4. Explain why:

(i) cyclohexyne **1** and *trans*-cyclohexene **2** are too unstable to be isolated at room temperature but *cis*-cyclohexene **3** is stable.

(ii) the bicycle **4** is stable whereas the isomer **5** is not.



5. Distinguish between the terms “inductive effect” and “resonance effect”, and give an illustrative example of each.

6. Rank the following species in order of stability and give a rationale for your choice:

(i). Me_3C^+, Me_2CH^+, $MeCH_2^+$, CH_3^+; (ii). Me_3C^-, Me_2CH^-, $MeCH_2^-$, CH_3^-.

7. Draw out all of the significant resonance forms for the following species, and show their interconversion using the curly arrow notation.

