Experiment 18

ORGANIC MOLECULAR MODELING

Objective

The purpose of this experiment is to use the molecular model kit MOLYMOLD® to assemble the ball-and-stick models of organic compounds and compare the spatial arrangements of conformers and isomers.

Lab techniques

- Constructing the ball-and-stick molecular models
- Operating the simulation software

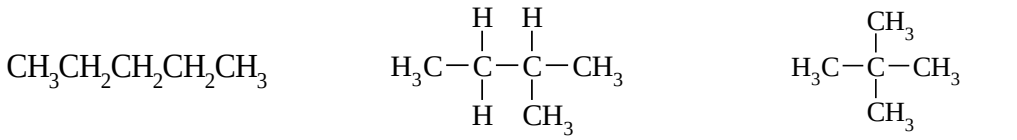
Introduction

I. Organic compounds

Organic compounds refer to carbon-containing compounds (except carbon monoxide, carbon dioxide, carbonic acid, carbonates, carbides, and cyanides, which are considered inorganic substances) and derivatives of hydrocarbons. A carbon atom has four valence electrons. It can use sp^3, sp^2, or sp hybrid orbitals to form single, double, or triple bonds with various structures. Some organic compounds have the same molecular formula but different structures and properties. These compounds are called isomers. There are two categories of isomers: structural isomers and stereoisomers.

II. Structural isomers

Structural isomers are compounds with the same molecular formula but different structural formulas. For example, *n*-pentane, 2-methylbutane, and 2,2-dimethylpropane have the same molecular formula, C_5H_{12}, but different structures and properties (Fig. 18-1).



n-Pentane (bp_{760}: 36.1°C) | 2-Methylbutane (bp_{760}: 30°C) | 2,2-Dimethylpropane (bp_{760}: 9.5°C)

Figure 18-1 Structural isomers of C_5H_{12}

III. Stereoisomers

Stereoisomers have the same molecular formula and connections of bonded

atoms but different three-dimensional orientations of their atoms in space. They are further distinguished into *cis-trans* isomers and enantiomers.

1. *Cis-trans* isomers

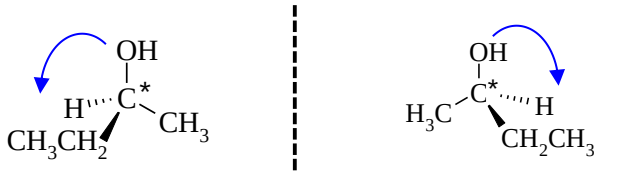
Alkenes are hydrocarbons that contain C=C double bonds, such as ethene, CH_2=CH_2. The two C atoms in a double bond are sp^2 hybridized. The π bonding of the C=C bond restricts its rotation and fixes the relative positions of the atoms bonded to it. This leads to a type of stereoisomerism, *i.e. cis-trans* isomers (previously called geometric isomers). For 1,2-dichloroethene, it has different orientations of substituents around a double bond as shown in Fig. 18-2. In general, the *cis* isomer has the larger substituents of the C=C bond (in this case, two Cl atoms) on the same side of the double bond, while the *trans* isomer has them on opposite sides. Cycloalkanes may also have *cis-trans* isomers due to the restricted rotation of the bonds in a ring.

Trans-1,2-dichloroethene (bp_{760} : 47.2°C) *Cis*-1,2-dichloroethene (bp_{760}: 60°C)

Figure 18-2 *Cis-trans* isomers of 1,2-dichloroethene

2. Enantiomers

A tetrahedral carbon with four different substituents is called a chiral carbon and is often marked as C^*. A molecule containing a chiral carbon has non-superimposable mirror images called enantiomers or optical isomers. The enantiomers show almost identical physical and chemical properties but rotate the plane of polarized light in opposite directions. One enantiomer that rotates the plane-polarized light clockwise is dextrorotatory, designated as *d*- or (+). On the contrary, the mirror image of the molecule that rotates the plane-polarized light counterclockwise to the same extent is levorotatory, designated as *l*- or (−). For example, 2-butanol is an optically active chiral molecule, as shown in Fig. 18-3. The absolute configuration of the chiral carbon is denoted by (*R*) or (*S*). However, it cannot be known from the structure whether the molecule is *d*- or *l*-; it must be determined experimentally.



(*S*)-(+)-2-Butanol
$[\alpha]_D^{25}$ +13.52

(*R*)-(−)-2-Butanol
$[\alpha]_D^{25}$ −13.52

Figure 18-3 The enantiomers of 2-butanol

1. (*R*): Absolute configuration describing the spatial arrangement of substituents on the chiral carbon when the observed order of decreasing priority of the substituents is clockwise
2. (*S*): Opposite of (*R*)
3. $[\alpha]_D^{25}$: Specific rotation at 25°C for sodium D line(2)

IV. Conformers

The C–C single bond allows the rotation of bonded groups, so the atoms in an alkane continually change their relative positions. For example, the six carbon atoms of cyclohexane, C_6H_{12}, are connected through sp^3 hybrid orbitals to form a six-membered ring structure. Because of the free rotation of C–C single bonds, there are two stable conformers of cyclohexane, *i.e.* the boat form and the chair form, as shown in Fig. 18-4. Since the chair form is lower in energy, 99.99% of cyclohexane exists as the chair form at room temperature.

Boat form Chair form

Figure 18-4 Conformers of cyclohexane

A lot of biomolecules are stereoisomers and show specific biological activity. For example, vitamin C is a dextrorotatory substance. In this experiment, we use the MOLYMOLD® model kit to build the ball-and-stick models of organic compounds and compare their spatial arrangements. You can also download free software, such as Chemsketch and Avogadro, to sketch the molecular structures or calculate the relative energies of molecules.

Apparatus

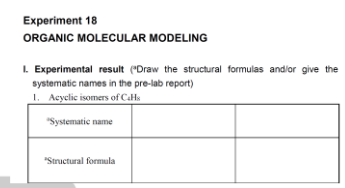
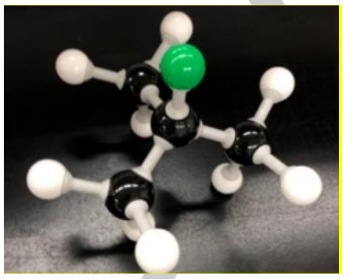
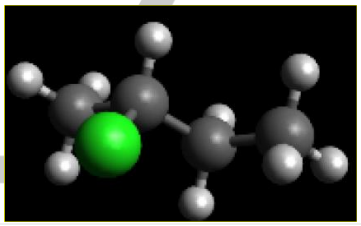
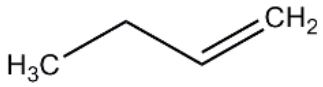
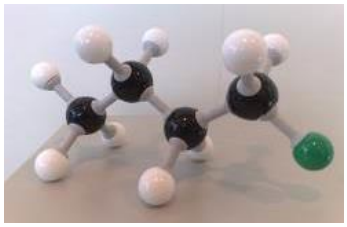
MOLYMOLD® model kit; notebook, tablet, or digital camera (self-prepared).

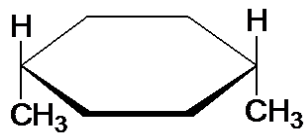
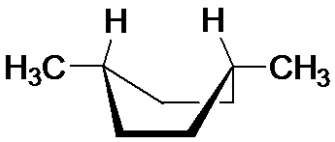
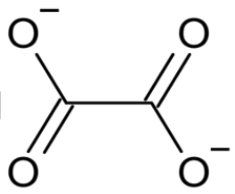
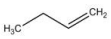
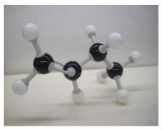
Free software for molecular simulation:

(1) Avogadro: https://avogadro.cc/

(2) Chemsketch: https://www.acdlabs.com/resources/freeware/

Procedure

	Procedure	Illustration
1	According to the data sheet in the lab report, draw the structural formulas and/or give the systematic names of the molecules in the pre-lab report.	 Experiment 18 ORGANIC MOLECULAR MODELING I. Experimental result (*Draw the structural formulas and/or give the systematic names in the pre-lab report) 1. Acyclic isomers of C_4H_8 *Systematic name *Structural formula
2.	Collect a box of MOLYMOLD® model kit and check the content. Replenish the missing ones before use.	
3.	(1) Use MOLYMOLD® model kit to construct the ball-and-stick models of the molecules and take pictures. (2) Optional: Use Chemsketch to draw the structural formula; use Avogadro to calculate selected molecules' relative energies, bond lengths, and bond angles. Note: You may install the software on your computer to complete the structure drawings and calculations, then combine the graphics into the lab report.	 
4.	Sketch and construct the ball-and-stick models of all acyclic isomers of C_4H_8 and indicate *cis-trans* isomers.	
5.	Sketch and construct the ball-and-stick models of all isomers of C_4H_9Cl and indicate enantiomers.	

6.	Sketch and construct the ball-and-stick models of the *cis-trans* isomers of 1,4-dimethylcyclohexane, $(CH_3)_2C_6H_{10}$, and indicate *cis-trans* isomers.	
7.	Show the boat and chair conformations of *cis*-1,4-dimethylcyclohexane and indicate which one is more stable according to the arrangements and crowdedness of their atoms.	
8.	Sketch and construct the ball-and-stick models of oxalate ion, $(COO^-)_2$, and ethylenediamine, $H_2NCH_2CH_2NH_2$. Rotate the orientation of atoms to realize that they are used as bidentate ligands in complexation.	
9.	After finishing the experiment, separate and check the components of the MOLYMOLD® model kit and return them to the lab instructor.	Black ball: 12 Blue ball: 4 Green ball: 4 Grey ball: 1 Purple ball: 1 Red ball: 6 White ball: 20 Yellow ball: 2 Short white link: 26 Long grey link: 12 Medium grey link: 26 Link remover: 1
10.	Combine the photos of molecules in your lab report. Summit the pdf file to NTUCOOL.	Systematic name: 1-Butene Structural formula:  MOLYMOD® Ball-and-stick model: 

References

1. Zumdahl, S. S. *Chemical Principles*; 6th ed., Houghton Mifflin Co.: New York, **2009**.
2. Brown, W. H. *Introduction to Organic Chemistry*; 2nd ed., Saunders College Publishing: New York, **2000**.