Experiment 23

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.

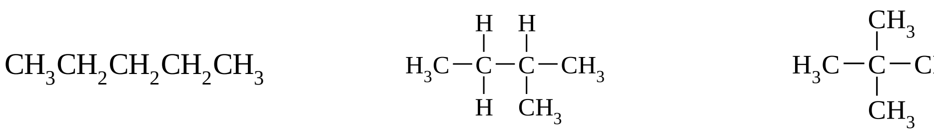
Principle

I. Organic compounds

An organic compound is a molecule that contains carbon. A few exceptions, such as CO, CO_2, carbonates, carbides, and cyanides are considered inorganic. Carbon atom has four valence electrons. It can use sp^3, sp^2, and 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 isomers. There are two types of isomers: structural isomers and stereoisomers.

II. Structural isomers

Structural isomers are compounds that have the same molecular formula but different arrangements of bonded atoms. For example, *n*-pentane, 2-methylbutane, and 2,2-dimethylpropane have the same molecular formula, C_5H_{12}, but different structures (Fig. 23-1) and properties.



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

Figure 23-1 Structural isomers of C_5H_{12}

III. Stereoisomers

Stereoisomers have the same molecular formula and sequence of bonded atoms but different three-dimensional orientations of their atoms in space. It is divided into *cis*-*trans* isomers, and optical isomers.

1. ***Cis-trans*** **isomers**

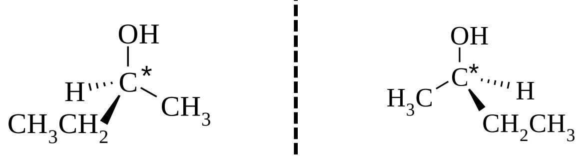
Alkenes are hydrocarbons that contains C=C bond, such as ethene, $CH_2{=}CH_2$. The two C atoms in a double bond are sp^2 hybridized. The π bonding of the C=C bond restricts its rotation and fixes the relative positions of the atoms bonded to it. This leads to a type of stereoisomerism, i.e. *cis-trans* isomers or geometric isomers. For 1,2-dichloroethene, it has different orientations of groups around a double bond as shown in Fig. 23-2. 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 23-2 *Cis-trans* isomers of 1,2-dichloroethene

2. Enantiomers

A tetrahedral carbon that has four different substituents is called a chiral carbon and designated as C*. A molecule containing a chiral carbon has nonsuperimposable mirror images called enantiomers or optical isomers. The enantiomers show similar physical and chemical properties, but they rotate the plane of polarized light to opposite direction. One of the enantiomers rotates the plane of polarized light clockwise that is dextrorotatory, designated as *d*- or (+). On the contrary, the mirror image of the molecule rotates the plane-polarized light counterclockwise to the same extent that is levorotatory, designated as *l*- or (−). For example, 2-butanol is a chiral molecule and optically active as shown in Fig. 23-3.



(*S*)-(+)-2-Butanol   (*R*)-(-)-2-Butanol

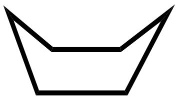
$[\alpha]_D^{25}$ +13.52 $[\alpha]_D^{25}$ -13.52

Figure 23-3 The enantiomers of 2-butanol

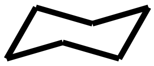
1. (*R*): Absolute term describing the spatial arrangement about an asymmetric carbon when the observed order of decreasing priority of the groups is clockwise
2. (*S*): Opposite of (*R*)
3. $[\alpha]_D^{25}$: Specific rotation at 25°C for sodium D line

IV. Conformational isomers

C-C single bond allows 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-member ring structure. Because of the free rotation of C-C single bond, there are two conformers of cyclohexane, i.e. the boat form and the chair form, as shown in Fig. 23-4. 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 23-4 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 MOLYMOLD® model kit to build the ball-and-stick models of organic compounds and compare the spatial arrangements of them. You can also download the free software Chemsketch and Avogadro to sketch the molecular structures and calculate the relative energies of molecules.

Apparatus

1. MOLYMOLD® model kit.
2. Digital camera, and USB (self-prepared).
3. Download the free software
   (1) **Avogadro**: http://sourceforge.net/projects/avogadro/files/
   (2) **Chemsketch**: http://www.acdlabs.com/resources/freeware/

Procedure

1. Collect a box of MOLYMOLD® model kit and check the content. Replenish the missing ones if necessary.

Black ball: 12	White ball: 20
Blue ball: 4	Yellow ball: 2
Green ball: 4	Short white link: 26
Grey ball: 1	Long grey link: 12
Purple ball: 1	Medium grey link: 26
Red ball: 6	Link remover: 1

2. According to the data sheet in the lab report, complete the followings:
   (1) Draw the structural formulas of the molecules.
   (2) Use MOLYMOLD® to construct the ball-and-stick models of the molecules and take pictures.
   (3) Optional: Use Chemsketch to draw the structural formula; use Avogadro to calculate the relative energies, bond lengths, and bond angles of selected molecules.
3. Sketch and construct the ball-and-stick models of the isomers of C_4H_8 and indicate *cis-trans* isomers.
4. Sketch and construct the ball-and-stick models of the isomers of C_4H_9Cl and indicate enantiomers.
5. 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.
6. Show boat and chair forms of *cis*-1,4-dimethylcyclohexane and indicate which one is more stable.
7. 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 using as bidentate ligands in complexation.
8. After finishing the experiment, separate and check the components of MOLYMOLD® model kit and return them to lab instructor.
9. Paste the drawing of chemical structures and pictures into the lab report.

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.