Chapter 5 Alkanes and Cycloalkanes

Contents

Hydrocarbons are composed solely from carbon and hydrogen atoms, and form one of the fundamental group of organic compounds. Hydrocarbons are widely used for practical purposes. For instance, methane, propane, and butane are used as fuels, and ethylene (ethene), propene and benzene are row materials for chemical industry.

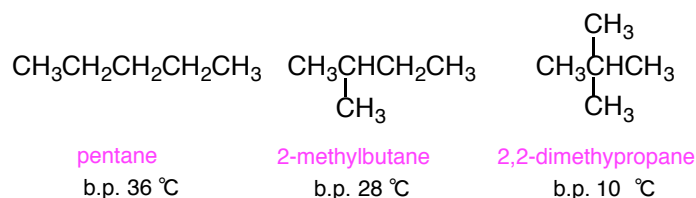You have already learned a little about the structure and nomenclature of hydrocarbons. In this chapter, you will learn saturated hydrocarbons that do not have double nor triple bonds, that is, alkanes and cycloalkanes. The three-dimensional structure of these compounds, particularly the change of structure caused by the rotation about the single bond, *i.e.*, conformational analysis, is particularly interesting.

5.1 Properties and nomenclature of alkanes

Alkanes are saturated and chain hydrocarbons. All carbon atoms are sp^3 hybridized and hence alkanes do not have any unsaturated bonds. Alkanes composed of less than four carbon atoms are gases at normal temperature and pressure, and they will become liquid as the molecular weight increases. If the molecular weight increases further, they will become solid, which are sometimes called **paraffin**.

Melting and boiling points of alkanes depend on the way of branching as well as molecular weights. Melting and boiling points of **straight chain alkanes** without branching will become high as the molecular weight increases (Table 5.2). When the molecular weights are equal, a certain amount of differences in melting and boiling points is observed between straight chain and branched alkanes. The difference is assumed to be due to the difference in the strength of intermolecular interaction.

A few examples of names of alkanes are given below. When there is no ambiguity, the locant can be neglected. Thus, 2-methylpropane can be named methylpropane. It is wise, however, not to omit locants when the structure is more complicated.

CH$_3$CH$_2$CH$_2$CH$_2$CH$_3$ CH$_3$CHCH$_2$CH$_3$ | CH$_3$ CH$_3$CH(CH$_3$)CHCH$_3$ with CH$_3$

pentane   2-methylbutane   2,2-dimethypropane
b.p. 36 ℃   b.p. 28 ℃   b.p. 10 ℃

Alkanes, or rather, hydrocarbons in general, are hardly soluble in water (**hydrophobic**), but are miscible with many other hydrocarbons and organic compounds with some functional groups (**lipophilic**). The specific gravity of alkanes is less than 1, and these float on the surface of water.

Alkanes are classified into chain- and branched ones, and a name is given to each of the former depending on the number of carbon atoms. To give a name to the latter, the name of side chain (alkyl groups) and the position where the side chains are bonded (**locants**) is required.

The outline of nomenclature of hydrocarbons is given below.

(1) Common (trivial) names are used for alkanes with less than four carbon atoms.

(2) For alkanes with more than five carbon atoms, a combination of numerals derived from Greek or Latin (Table 5.1) and a suffix –ane is used.

[Example] octane C$_8$H$_{18}$; octa = 8

Table 5.1 Numerals describing the number of atoms and substituents

number	numerals	number	numerals
1	mono	7	hepta
2	di	8	octa
3	tri	9	nona[*]
4	tetra	10	deca
5	penta	11	undeca[*]
6	hexa	12	dodeca

[*]numerals of lingua latina

In Table 5.2, representative alkanes are listed.

Table 5.2 Representative chain alkanes

name	molecular formula	structural formula	m.p. (b.p.) °C (°C)
methane	CH_4	CH_4	-182.8(-161.45)
ethane	C_2H_6	CH_3CH_3	-183.6(-89.0)
propane	C_3H_8	$CH_3CH_2CH_3$	-187.7(-42.01
butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	-138.3(-0.50
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	-129.7(36.1)
hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	-95.3 (68.7)
heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	-90.6(98.4
octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	-56.8(125.7)
nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	-53.5 (150. 8)
decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	-29.7(174.1)
undecane	$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$	-25.6(195.9)
dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$	-9.6(216.3)
icosane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$	36.8(343.0)
triacontane	$C_{30}H_{62}$	$CH_3(CH_2)_{28}CH_3$	66(449.7)
pentacontane	$C_{50}H_{102}$	$CH_3(CH_2)_{48}CH_3$	92

(3) For a branched alkane, it is named as an alkane of the longest chain (main chain) in the molecule. The side chains are named as alkyl groups.

[Example]

$CH_3CHCH_2CH_3$
  |
  CH_3

2-methylbutane

(not ethylpropane CH_3CHCH_3
                        |
                        CH_2CH_3)

Since there is no ambiguity, 2-methylbutane may be named as methylbutane.

(4) The position of alkyl groups is indicated by numbers (locants) given to the carbon atoms of the main chain. Care should be taken to make the number as small as possible.

[Example]

$CH_3CHCH_2CH_2CH_3$
  |
  CH_3

2-methylpentane

(not   4-methylpentane $CH_3CH_2CH_2CHCH_3$
 |
                                         CH_3)

(5) When the number of carbon atoms in the main chain is equal, the chain with more substituents is chosen as the main chain.

[Example]

$$CH_3CH_2CHCH_2CH_3$$
$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$
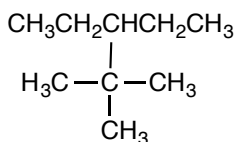
3-ethyl-2,2-dimethylpentane (not 3-*t*-butylpentane)

(6) For alkanes with two or more than two different alkyl groups, these groups will be arranged in alphabetical order before the name of the alkane. The locants are placed before the names of relevant substituents.
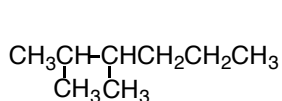
[Example]

$$CH_3CH\text{-}CHCH_2CH_2CH_3$$
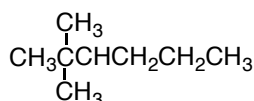$$CH_3CH_2CH_3$$
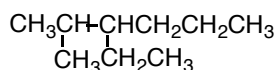
3-ethyl-2-methylhexane

(7) For alkanes with two or more than two identical alkyl groups, numerals such as di, tri and tetra, representing the number of substituents are placed in front of the name of alkyl groups.
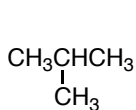
[Example]

$$CH_3CH\text{-}CHCH_2CH_2CH_3$$
$$CH_3CH_3$$

2,3-dimethylhexane

$$\overset{\displaystyle CH_3}{\overset{|}{CH_3CCHCH_2CH_2CH_3}}$$
$$CH_3$$

2,2-dimethylhexane

(8) The following common names are allowed to use only when the compound does not have substituents.

[Example]

$$CH_3CHCH_3$$
$$CH_3$$

$$CH_3CHCH_2CH_3$$
$$CH_3$$

$$\overset{\displaystyle CH_3}{\overset{|}{CH_3CCH_3}}$$
$$CH_3$$

$$CH_3CHCH_2CH_2CH_3$$
$$CH_3$$
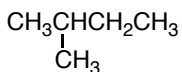
common name	isobutane	isopentane	neopentane	isohexane
IUPAC name	methylpropane	methylbutane	2,2-dimethylpropane	2-methylpentane
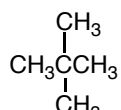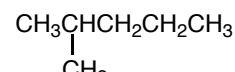
Exercise 5.1 Naming of alkanes

Name alkanes given below.

a) $CH_3CHCH_2CH_2CHCH_3$ (b) $CH_3CHCH_2CH_2CHCH_3$ c) $CH_3CH–CHCH_2CH_2CH_3$
     CH_3 CH_3 CH_3 CH_2CH_3 CH_3 $CH_2CH_2CH_2CH_3$
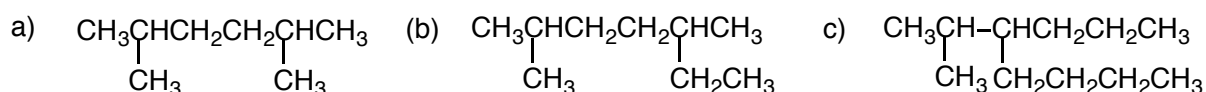
Answer

(a) 2,5-dimethylhexane

(b) 2,5-dimethylheptane

Care should be taken not to name the compound as 2-ethyl-5-methylhexane. In these simplified representations, the direction of bonds (vertical or horizontal) does not reflect the actual structure. Sometimes the main chain is folded to save space.

(c) 4-isopropyloctane. Do not name it as 3-butyl-2-methylhexane.

Alkyl groups are named based on the rules given below.

(1) monovalent groups: the end of the name of alkanes is changed from –ane to –yl.

[Example]

       methane CH_4 → methyl CH_3-

(2) divalent groups: the end of the name of alkanes is changed from –ane to –ylene.

[Example]

       methane CH_4 → methylene $–CH_2$-

When drawing simplified structures, you can use symbols for main alkyl and aryl groups. Table 5.3 summarizes representative alkyl and aryl groups including their symbols.

There are two compounds for an alkane with four carbon atoms, butane, without branching and methylpropane with branching. Since they have common molecular formulas, they are **isomers**.

Of isomers, those with different sequences of atoms in the molecule is called **structural isomers.** The larger the number of carbon atoms in alkanes, the larger the number of structural isomers. Decane, composed of only ten carbon atoms, has 75 structural isomers.

Table 5.3 Representative alkyl and aryl groups

name	simplified structural formula	abbreviation
methyl	CH_3-	Me
ethyl	C_2H_5-, CH_3CH_2-	Et
propyl	C_3H_7-, $CH_3CH_2CH_2$-	Pr
1-methylethyl (isopropyl)	iso-C_3H_7-, $(CH_3)_2CH$-	i-Pr
butyl	C_4H_9-, $CH_3CH_2CH_2CH_2$-	Bu
1-methylpropyl (s-butyl)	s-C_4H_9-, $CH_3C_2HCH(CH_3)$-	s-Bu
2-methylpropyl (isobutyl)	iso-C_4H_9-, $(CH_3)_2CHCH_2$-	iso-Bu
1,1-dimethylethyl (t-butyl)	t-C_4H_9-, $(CH_3)_3C$-	t-Bu
vinyl	C_2H_3-, $CH_2=CH$-	-
phenyl	C_6H_5-	Ph
benzyl	C_7H_7-, $C_6H_5CH_2$-	(Bn)

Exercise 5.2 Naming of alkanes

Draw simplified structural formulas of all possible isomers of hexane and name these.

Answer

You had better start from pentane, an alkane with one carbon atom less than hexane. Search all possible way to add one carbon atom to each of pentane isomers Give correct names to these isomers with six carbon atoms. Delete those you wrote in duplicate. To help understanding, locants of carbon atoms are given as superscript when appropriate.

There are three ways to add one carbon atom to pentane $CH_3CH_2C^3H_2C^2H_2C^1H_3$ (add one carbon atom to each of C^1, C^2 and C^3. Hexane, 2-methylpenane and 3-methylpentane are obtained.

Similarly, there are four ways to add one carbon atom to methylbutane $C^4H_3C^3H_2C^2H(C^1H_3)_2$ (add one carbon atom to each of C^1, C^2, C^3 and C^4). 3-methylpentane, 2,2-dimethylbuane, 2,3-dimethylbuane and 2-methylpentane are obtained. There is only one way to add one carbon atom to 2,2-dimethylproane $CH_3C(C^1H_3)_3$ (add one carbon atom to each of C^1). 2,2-dimethylbuane is obtained.

After removing duplications, you will obtain five isomers as shown below.

name	simplified structural formula
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
2-methylpentane	$CH_3CH_2CH_2CH(CH_3)_2$
3-methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$
2,2-dimethylbuane	$CH_3CH_2C(CH_3)_2CH_3$
2,3-dimethylbuane	$CH_3CH(CH_3)CH(CH_3)_2$

5.2 Structure of alkanes

(a) Structures of methane and ethane

The C-C **bond length** of ethane is 0.154 nm, which is the standard bond length of a bond formed by two sp³ hybridized carbon atoms. There is no difference between C-H bond length of methane and that of ethane. Figure. 5.1 shows the structures of methane and ethane as defined by the **bond length** and the **bond angle**. The H-C-H angle of methane is the tetrahedral angle, but the C-C-H angle of ethane is slightly larger than the tetrahedral angle. A larger C-C-H angle reduces the repulsion among hydrogens bonded to adjacent carbon atoms (C_A and C_B).
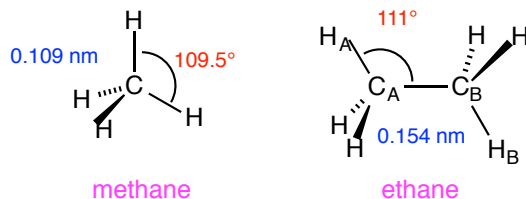
Figure 5.1 Structures of methane and ethane

The structure of methane is defined by two parameters completely, the bond length and the bond angle. However, that of ethane cannot completely be defined by these two parameters, because the interatomic distance between H_A proton belonging to C_A methyl group and H_B proton belonging to C_B methyl group (Figure 5.1) will change as the C-C bond of ethane rotates.

The 3rd parameter, in addition to the bond length and the bond angle, **torsion angle**, is to be defined which describes the change of the structure caused by rotation about the C-C bond. As indicated by Figure 5.2, torsion angle is an angle made by two planes A and B. Torsion angle has a sign and the sign is defined as below. Suppose you look the molecule through C_A-C_B bond from the C_A side. You rotate the plane A that contains C_A and H_A so that this plane overlaps the plane B that contains C_B and H_B. If the Plane A rotates clockwise, the torsion angle is defined positive (+). If it rotates anticlockwise, it is negative (-). In Figure 5.2, θ is positive.
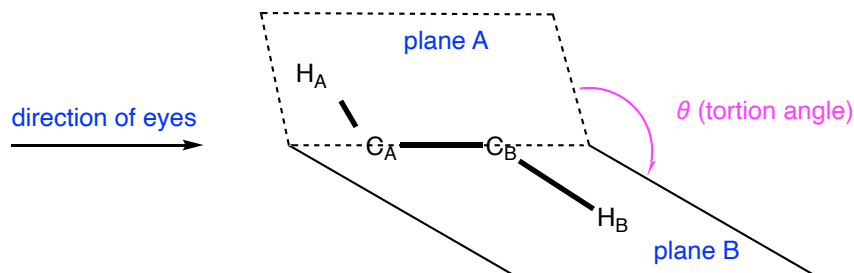

Figure 5.2 Torsion angle

(b) Conformational analysis
(1) Rotation about a single bond

Since the C-H bond of methane is formed by the overlap of sp^3 hybridized orbital of a carbon atom and 1s orbital of hydrogen atom, the electron is symmetrically distributed along the bond. Rotation about the axis of the bond is possible for symmetrical bond. This phenomenon is named **internal rotation**, and this rotation is common to all single bonds including these of a methane molecule.

The effect of rotation can be various depending on the type of the bonds or molecules. Suppose a methane molecule. Rotation about C-H bond does not affect the shape of C-H bond if we assume that the hydrogen atom is a sphere. Since no change of the structure is accompanied with the rotation, we need not take rotation into consideration.

The rotation of C-C bond of ethane is the next problem. Since this bond is formed by the overlap of two sp^3 hybridized orbitals of a carbon atoms from the longitudinal direction, rotation of the bond is possible. The result is, however, quite different from that for the C-H bond of methane. There accompanies no change of structure of molecule for methane, but the rotation of C-C bond of ethane is accompanied by the change of the structure of molecules every second. If we assume that ethane molecules are composed of two methyl groups, we can say the relation of two methyl groups changes every second, or, the torsion angle defined by Figure 5.2 changes. Actually the energy possessed by the molecule also changes every second.

The structure of ethane changes by rotation, and each of the resultant structures are named **conformation**. Study of the change of molecular structures (conformation) and molecular energy (conformational energy) is called **conformational analysis**.

Let us study conformational analysis of ethane as an example. The best way to deepen your understanding is use of molecular models to ascertain the structural change by your own eyes. One of the easily available molecular models is the **HGS** molecular model (distributed by Maruzen). This model is a type of ball-and-stick models, which use spheres as atoms and rods as bonds (Figure 5.3).

The **Dreiding** model uses only rods for bonds. This model is convenient to find out the skeleton of the molecule. The **space-filling** model uses only spheres with the diameters corresponding to the

van der Waals radii of atoms. This model is suitable to find out the extent of electron cloud in the molecule.

Dreiding model   HGS model   space-filling model
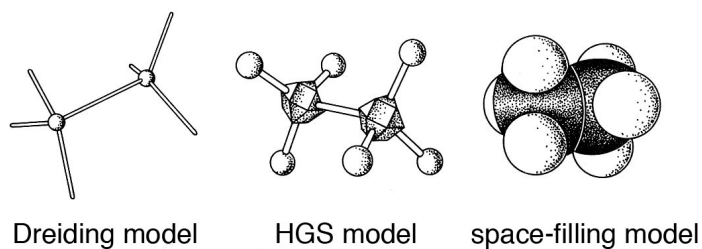
Figure 5.3 Some popular molecular models

Such a simple exercise as the conformational analysis of ethane, you can manage to do with tooth stick and a piece of clay even if you do not have a molecular model.

(2) Newman projection

Even if you use molecular model for conformational analysis, some device is necessary for recording the results. Though sketches of molecular models or drawing of perspective view are useful, care should be taken because the molecules look different depending on the direction of your eyes. The more complex the molecules, the larger the problem. A common understanding will be more and more difficult to obtain.

A method, named the **Newman projection**, was devised to solve this problem. In this method the molecule is projected from the direction of C-C bond to the wall behind, and the shadow obtained is rewritten so that the structural information is readily obtained. In Figure 5.4, the Newman projection of ethane is shown as an example.
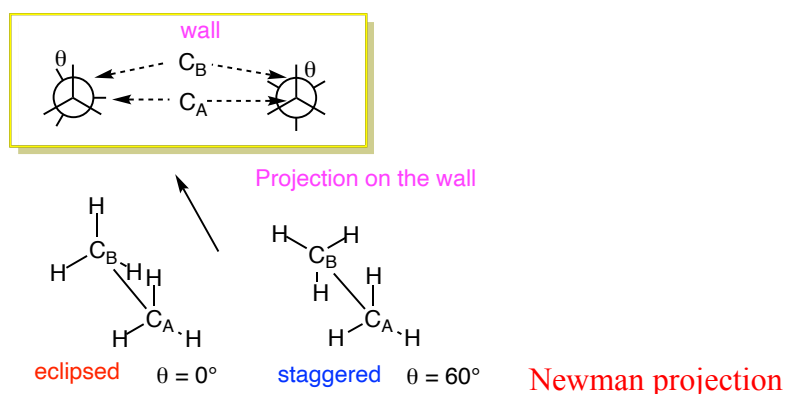
Figure 5.4 Newman projection of ethane. θ is torsion angle.

Care should be taken when you read the Newman projection.
(1) The front carbon is represented as a dot (*i.e.*, the intersection of three rods representing bonds)
(2) The bond angles are 120° though in fact these are tetrahedral angle.
(3) In the eclipsed form, the bonds connected to the back carbon are hidden by the bonds connected to the front carbon. To avoid this inconvenience, the bonds connected to the back carbon are slightly rotated.

(c) Conformational analysis of ethane

The change of structure of ethane caused by internal rotation of C-C bond can be defined by the **torsion angle** θ in the Newman projection. Since the torsion angle θ changes continuously from 0° to 360°, there are innumerable conformations of ethane. However, isomers with the maximum or minimum energy, that is, those with θ = 0°. 60°, 120°, 180°, 240° and 300°, are to be considered. Conformers with θ = 0°. 120°, 180° and 240° are named **eclipsed** conformers, and those with θ = 60°, 180° and 300°, are named **staggered** conformers. The energy difference between two conformers is 12.1 kJ mol^{-1}, which corresponds to the activation energy of rotation about C-C bond of ethane. Since eclipsed and staggered conformers have the same arrangements of atoms in the molecule, but their geometrical arrangements are different. Hence these are **stereoisomers** each other. The stereoisomerism of eclipsed and staggered conformers is due to the internal rotation, these two are called **conformational isomers** or simply **conformers** each other.
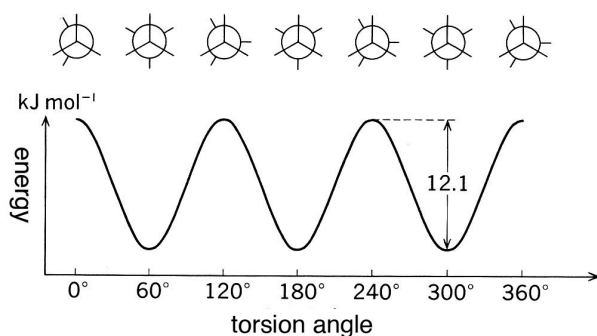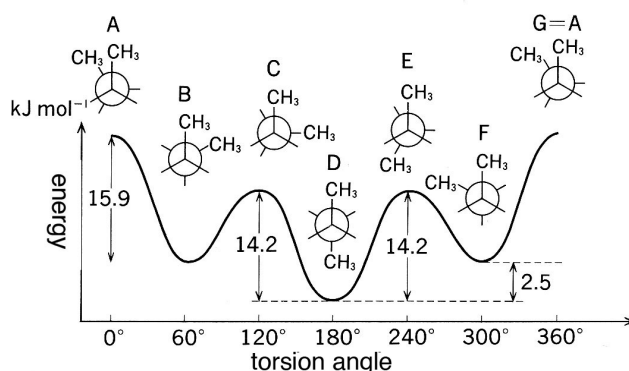

Figure 5.5 Torsion angle-energy diagram of ethane

(d) Conformational analysis of butane

The conformational analysis of the central C-C (C^2-C^3) bond of butane $CH_3C^2H_2C^3H_2CH_3$ is the basis of conformational analysis of substituted ethane. In the case of ethane, the three staggered and three eclipsed conformers have the same structure, and hence have the same energy. As is shown in Figure 5.6, there are two kinds of staggered and eclipsed forms in butane. There are two types of conformations in which the relative geometry of methyl groups is different: *i.e.*, D and B, F for staggered, and E and A, G for eclipsed conformations.

If two terminal methyl groups come close together, steric repulsion will be generated and the energy of butane will increase. Only two conformers are possible for ethane, but for butane four conformers are possible. The conformational energy associated with these is in the order:

$$D < B = F < C = E < A(=G)$$

Figure 5.6 Torsion angle-energy diagram of butane

Naming of conformers of butane is more complicated than that of ethane. Of the staggered isomers, conformer D is named **anti** or **trans**, conformers B or F are named **gauche** or **skew**, and conformer A is named **cis**. There is an alternative method of naming conformers of butane as shown in Table 5.4.

The energy differences between conformers of butane are also small as is the case with ethane. At room temperature, the rotation about the C-C bond is rapid, and it is impossible to isolate conformers as such.

<p align="center">Table 5.4 Naming of conformers of butane</p>

conformation	torsion angle (°)	name	symbol
A, G	0, 360	synperiplanar	sp
B, F	60, 300	synclinal	sc
C, E	120, 240	anticlinal	ac
D	180	antiperiplanar	ap

Point: Conformational analysis of butane

Stable conformation   *staggered* conformation ($\theta = 60°, 180°, 300°$)

                              most stable conformation: *anti* (*trans*) form ($\theta = 180°$)

Unstable conformation   *eclipsed* conformation ($\theta = 0°, 120°, 240°$)

                              least stable conformation: *cis* form ($\theta = 0°$)

Exercise 5.3 The Newman projection of ethane derivatives

Draw the Newman projection of the *staggered* and *eclipsed* conformations of the compounds shown below.

(a) propane, (b) 1,2-dichloroethane

Answer

eclipsed   staggered   eclipsed   staggered

(a)   (b)

Alkanes with chains longer than that of butane take a zigzag structure in which all four successive carbon atoms assume *trans* (*anti*) conformation.

all *trans* conformation

5.3 Reactions of alkanes

(a) Combustion

The most important use of alkanes is fuels for industry, automobiles and domestic purposes. The combustion reactions that accompany a large amount of heat of reaction are most important one for alkanes. The combustion of methane is expressed as below.
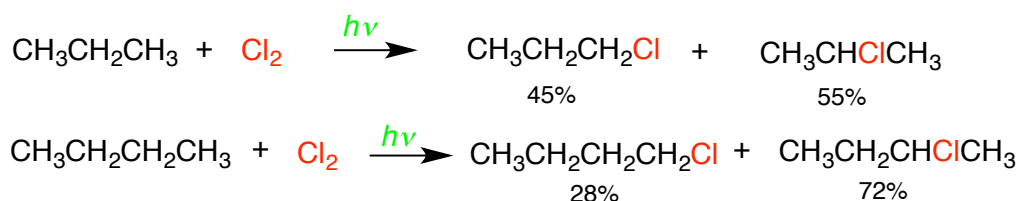
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l), \quad \Delta H (25 °C) = -890.3 \text{ kJ mol}^{-1}$$
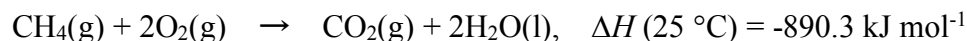
where ΔH is the enthalpy of reaction which corresponds to so called the heat of reaction.

By comparing the enthalpy of combustion of alkanes with different chain length, it can be estimated that the enthalpy of combustion increases by *ca.* 627-669 kJ mol^{-1} as one CH_2 unit increases.

(b) Radical reactions

Because of weak polarity of C-H bonds, ionic reactions involving this type of bonds are not easy to take place. Such standard reaction conditions as those with strong acids or bases or with halogens is not enough to cause reactions of alkanes. However, when radicals attack alkanes, reactions readily take place. Photochlorination of methane was already discussed in Ch. 4.1 (a).

By chlorination of alkanes, any hydrogen atom will be replaced by a chlorine atom. Hence, monochloroalkanes obtained in the 1st stage of the reaction are generally mixtures. The yield of branched monochloroalkanes is always higher than that of linear monochloroalkanes. This is due to the stability of intermediate radicals. (see Ch. 4.3)

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{h\nu} \underset{45\%}{CH_3CH_2CH_2Cl} + \underset{55\%}{CH_3CHClCH_3}$$

$$CH_3CH_2CH_2CH_3 + Cl_2 \xrightarrow{h\nu} \underset{28\%}{CH_3CH_2CH_2CH_2Cl} + \underset{72\%}{CH_3CH_2CHClCH_3}$$

Exercise 5.4 Radical chlorination

Draw the structures of all monochlorinated products of 2-methylpropane $(CH_3)_3CH$. Discuss the distribution of the products.

Answer

(a) $(CH_3)_2CHCH_2Cl$ (64%) and (b) $(CH_3)_3CCl$ (36%)

It is expected that the tertially isomer (b) is formed more than less-branched one (b).

The result is reverse to the expectation and seems contradictory. However, this result also shows the higher stability of tertiary radicals. There are two types of protons, one to form (a) $(CH_3)_3CH$ and the other to form (b) $(CH_3)_3CH$. The number of former type protons is nine while the other type only one. If the reactivity of two types of hydrogen is the same, the amount of (b) should be 1/9 of (a). The experiment shows the ratio is close to 1/2, indicating the higher reactivity of $(CH_3)_3CH$ proton.

5.4 Nomenclature of cycloalkanes

Compounds obtained by ring closure of aliphatic alkanes are called **cycloalkanes**. Species containing one double bond, or one triple bond, is called **cycloalkenes** and **cycloalkynes**, respectively.
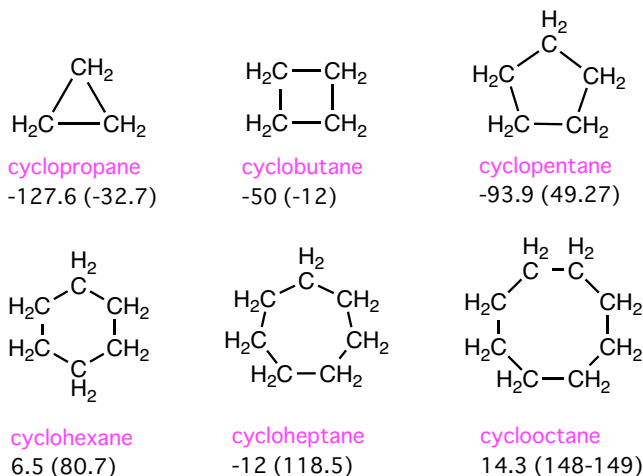
Cycloalkanes are cyclic hydrocarbons expressed by a general formula C_nH_{2n} in which all carbon atoms are sp^3 hybridized. Except cyclopropane, the chemical property of cycloalkanes is close to that of corresponding alkanes with the same number of carbon atoms.

Cycloalkanes are named based on the following rules.

(1) Prefix "cyclo" is added before the name of alkanes with the same number of carbon atoms.
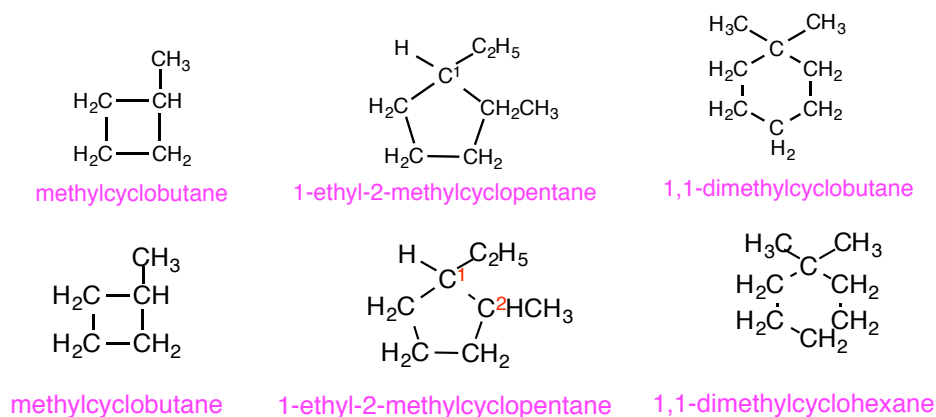
[Example]

Some important cycloalkanes are listed together with their melting points and (boiling points) (°C).

cyclopropane
-127.6 (-32.7)

cyclobutane
-50 (-12)

cyclopentane
-93.9 (49.27)

cyclohexane
6.5 (80.7)

cycloheptane
-12 (118.5)

cyclooctane
14.3 (148-149)

(2) Cycloalkanes with alkyl side chain(s) are named in a manner similar with that for the corresponding alkanes. Locants are chosen so that their numbers will be smaller.

[Example]

methylcyclobutane

1-ethyl-2-methylcyclopentane

1,1-dimethylcyclobutane

methylcyclobutane

1-ethyl-2-methylcyclopentane

1,1-dimethylcyclohexane

5.5 Structure of cycloalkanes
(a) Non-planar structure

In the cyclic structures each carbon atoms tend to keep the bond angle associated with their hybridization state. However, there is some restriction as for the possible structure for cycloalkanes as compared with that of alkanes. For instance, cyclopropane has a triangle structure (necessarily planar) and the C-C-C bond angle is 60° which will cause substantial strain. The molecular model

will indicate that this molecule is almost immovable. This is the reason why cyclopropane is very reactive and readily opens its ring.

Cycloalkanes larger than cyclopropane are non-planar. Cyclobutane and cyclopentane are of an envelope form and cyclohexane takes a chair form. Thus, these are non-planar (Figure 5.7) Hence the C-C-C bond angles deviate from the values of corresponding regular polygons.The bond angle for cyclohexane is close to the tetrahedral angle.
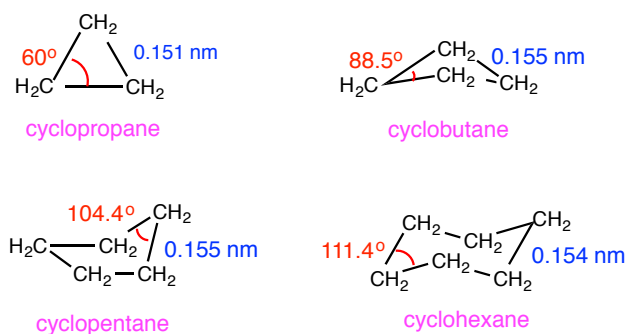

Figure 5.7 The structure of cycloalkanes

(b) Conformational analysis of cyclohexane
(1) Inversion of cyclohexane

The C-C bond rotation associated with ethane and butane takes place also in cycloalkanes. In the case of cyclohexane, a chair form (A) is converted to another chair form (B). This phenomenon is named **inversion** or **ring reversal**. The relation between conformations A and B is similar with that between B and F of ethane (Figure 5.6). Two conformers in each compound are enantiomers (Ch. 8.1).

In the inversion of cyclohexane, a high energy structure should be surmounted during the interconversion between A and B. This high-energy structure corresponds to the *eclipsed* form of ethane or *cis* form for butane. The progress of inversion is as follows: starting from chair form, it converted to a half-chair form which is highest in energy, through pseudo-stable twist form, boat form which is next to the highest in energy, twist, half-chair, and finally to another chair form (B). The process is depicted in Figure 5.8.
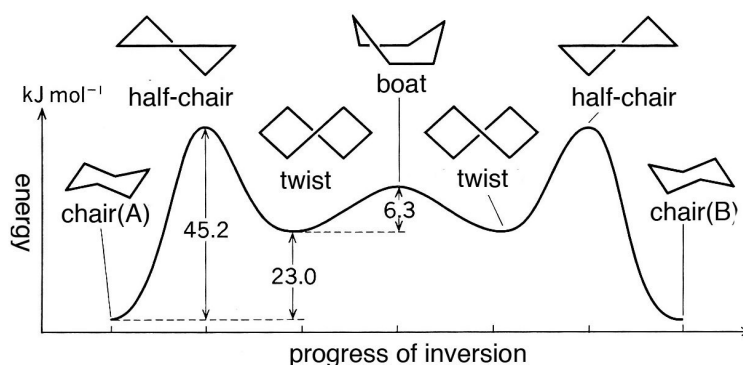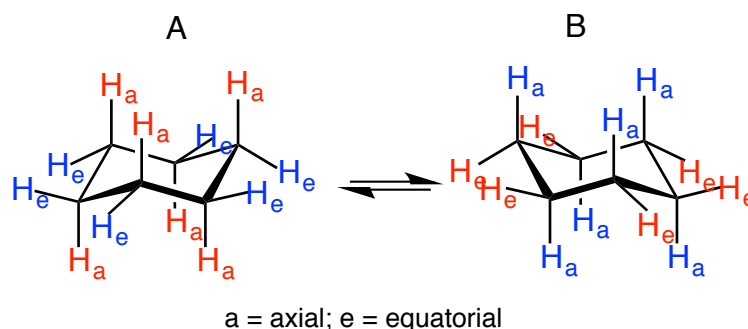

Figure 5.8 Inversion of cyclohexane ring

(2) Axial and equatorial bonds

In Figure 5.8, all hydrogen atoms are not shown for simplicity's sake. However, the change of stereochemical environment of each hydrogen atoms during the inversion is very interesting. Let us

examine Figure 5.9 where all hydrogen atoms are shown. In the chair form A, six out of twelve hydrogen atoms in red colored letters are perpendicular to the molecular plane, while the other six in blue colored letters are included in the plane. A bond perpendicular to the plane is named an **axial** bond, and a bond included in the molecular plane is named an **equatorial** bonds.

When conformer A turns into conformer B by inversion, all axial hydrogen atoms of A (red) are now equatorial hydrogen atoms. Similarly, all equatorial hydrogen atoms of A turn into axial hydrogen atoms (Figure 5.9).

a = axial; e = equatorial

Figure 5.9 Inversion of cyclohexane ring and axial/equatorial bonds

Point: Inversion of cyclohexane

chair form $\rightleftharpoons$ half-chair $\rightleftharpoons$ twist $\rightleftharpoons$ boat $\rightleftharpoons$ twist $\rightleftharpoons$ half-chair $\rightleftharpoons$ chair

axial hydrogen atoms (chair) $\rightleftharpoons$ equatorial hydrogen atoms (chair)

(3) Newman projection of cyclohexane

Newman projection is very useful for the conformational analysis of ethane and butane. In Figure 5.10, Newman projection of chair and boat cyclohexane**s** is shown.

In chair form, the difference between axial and equatorial hydrogen atoms is very clearly demonstrated. In the boat form, **t**wo overlapping like *cis* conformation of butane are observed. Hence the boat form is by 29 kJ mol^{-1} higher in energy than the chair form.
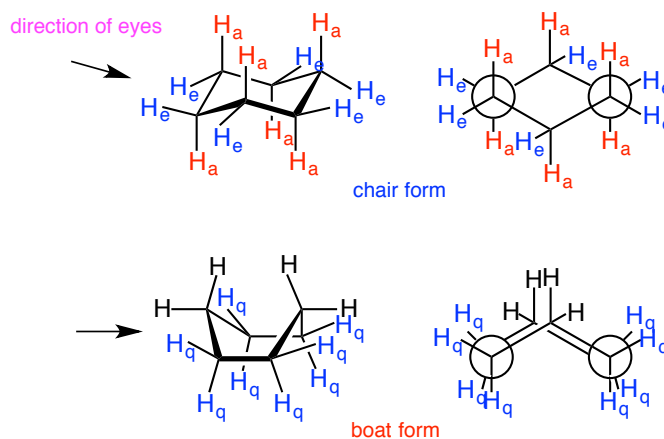

Figure 5.10 The Newman projection of cyclohexane. In the boat form, overlapping of some bonds is inevitable. a: axial, e: equatorial, q: eclipsed

(c) Conformational analysis of methylcyclohexane
(1) 1,3-diaxial interaction

In the case of cyclohexane, the chair conformers A and B are identical because of symmetry and hence have the same amount of energy. This is not applicable to such compounds as methylcyclohexane, a substituted species of cyclohexane that will have conformers with different energy (Figure 5.11).

In conformation A the methyl group is equatorial but it turns into axial by inversion. If the carbon atom to which the methyl group is bonded is named C^1, axial hydrogen atoms bonded to C^3 and C^5 are now close to the methyl group bonded to C^1 to cause steric repulsion. This steric repulsion is named **1,3-diaxial interaction**.

In principle, 1,3-diaxial interaction does exist in cyclohexane itself. However, the interaction between hydrogen atoms is not so significant. The repulsion between a methyl group and a hydrogen atom is large, and the difference in the energy of conformations A and B is considerably large. Hence the equilibrium between two conformers is largely shifted to A where the methyl is equatorial.
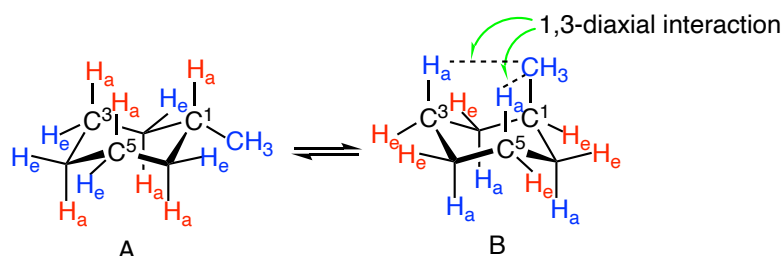
Figure 5.11 Inversion of methylcyclohexane: A; equatorial CH_3, B; axial CH_3

(2) Butane-*gauche* interaction

The 1,3-diaxial interaction is explained by the fact that the *anti* form of *twist* butane is more stable than the *gauche* form. Hence, such interactions as 1,3-diaxial interaction in methylcyclohexane and related compounds is sometimes named **butane-*gauche* interaction**.

Point: 1,3-Diaxial interaction

For all butane units in the molecule, a decision will be made whether the butane unit is *anti* or *gauche*. The one with larger number of *anti* form is more stable.

Butane in *gauche* form is less stable than the *trans* (*anti*) form and the former has larger energy.

**Exercise 5.5** Butane-*gauche* interaction

How many butane units suffer from butane-*gauche* interaction in *equatorial*- and *axial*-methylcyclohexane, respectively?

Answer

Pick up all butane units, which contain the methyl group. In *axial* isomer, there are two *gauche* butane units while in the *equatorial* isomer there is none. All are *anti* form.
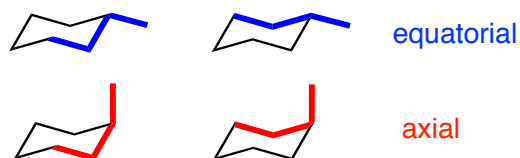
5.6 Reactions of cycloalkanes

The C-C-C angle of cyclopropane deviates from the tetrahedral angle to a considerable extent. Hence the ring suffers from large strain and the ring tends to open at the reaction. The reaction with chlorine gives chlorocyclopropane while the reaction with bromine gives 1,3-dibromopropane. In this reaction, cyclopropane behaves in a manner similar to ethylene.
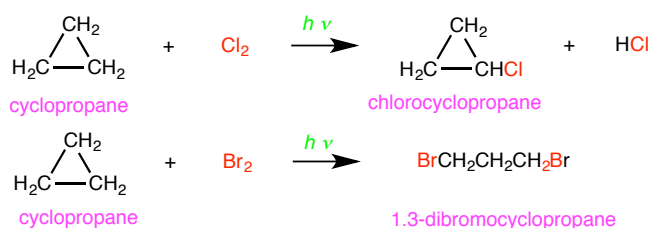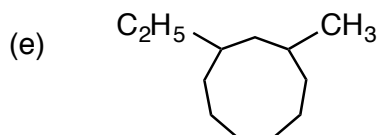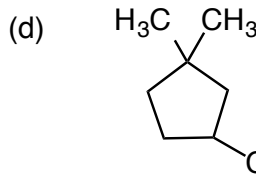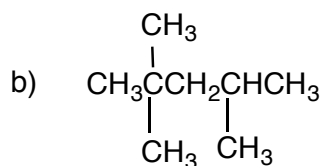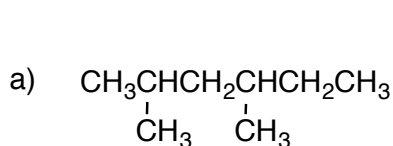

The reaction of cyclopentane and larger rings is similar to those of corresponding alkanes.
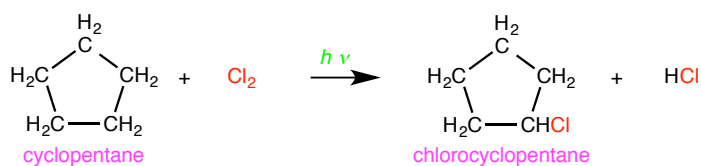
Problems

5.1

Name the following alkanes and cycloalkanes.

a) $CH_3CHCH_2CHCH_2CH_3$
           | |
          CH_3 CH_3

b) CH_3
            |
    $CH_3CCH_2CHCH_3$
            | |
          CH_3 CH_3

c) $(CH_3CH_2CH_2)_3CH$

(d) H_3C CH_3 (cyclopentane ring with CH_3)

(e) C_2H_5 (cyclooctane ring with CH_3)

5.2

Draw the structural formulas of the following alkanes and cycloalkanes.

(a) 5-ethyl-4,4-dimethyloctane

(b) 2,4,6-trimethylheptane

(c) 1,1,4-trimethylcyclohexane

(d) cyclononane

5.3

The names of the following compounds are not correct. Point out the errors and correct these.

(a) 2,2-dimethyl-6-ethylheptane

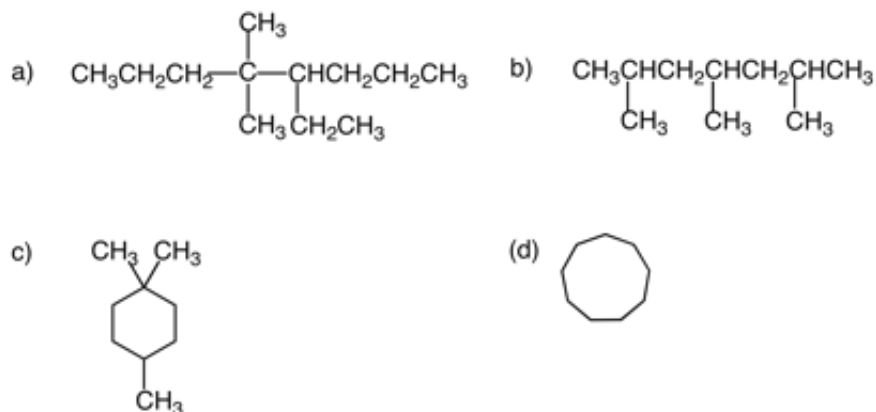(b) 4-ethyl-5,5-dimethylhexane

(c) 5,5,6-trimethyloctane

5.4

Attempt the conformational analysis of bromoethane CH_3CH_2Br.

(a) Sketch the twist angle-energy diagram.

(b) Estimate the approximate value of the energy of H-H interaction in eclipsed form based on the difference of energy between the eclipsed and staggered forms of ethane, 12.1 kJ mol^{-1}.

(c) The barrier for the rotation of C-C bond in bromoethane is 15.0 kJ mol^{-1}. Estimate the energy of interaction between bromine and hydrogen in eclipsed bromoethane.

Answers

5.1

(a) 2,4-dimethylhexane

(b) 2,2,4-trimethylpentane (its common name is isooctane)

(c) 4-propylheptane

(d) 1,1,3-trimethylcyclopentane

(e) 1-ethyl-3-methylcycloheptane.

5.2

5.3

(a) 2,2-dimethyl-6-ethylheptane → 2,2-dimethyl-6-methyloctane (the longest chain should be chosen).

(b) 4-ethyl-5,5-dimethylhexane → 3-ethyl-2,2-dimethylhexane (locants should be as small as possible).

(c) 5,5,6-trimethyloctane → 3,4,4-trimethyloctane (locants should be as small as possible).

5.4

(a) A figure similar to Figure 5.5 should be drawn although the barrier is higher.
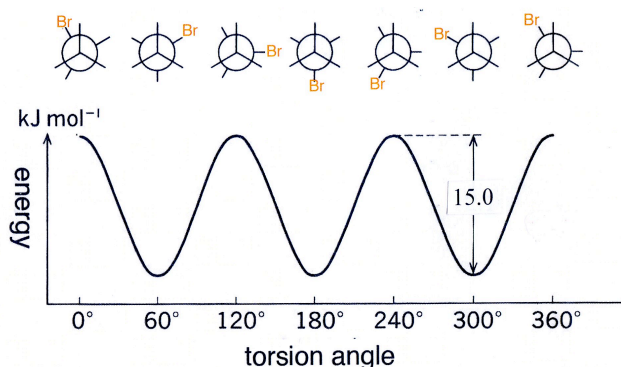
(b) 4.03 kJ mol^{-1} (=12.1/3)

(c) 6.94 kJ mol^{-1} (=15.0 - (4.03 x 2)).