Chapter 2
Alkanes and Cycloalkanes

from

Organic Chemistry

by

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Chapter Outline of the Book

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**Note: Chapters marked with an (*) are not yet posted.*

2: Alkanes and Cycloalkanes

(continued next page)

2: Alkanes and Cycloalkanes

•*Alkanes*
•*Alkane Systematic Nomenclature*
•*Cycloalkanes*
•*Conformations of Alkanes*
•*Conformations of Cycloalkanes*
•*Conformations of Alkylcyclohexanes*

Preview

You learned in the Chapter 1 that all organic molecules have carbon skeletons. These carbon skeletons show great diversity in the ways that C atoms bond to each other, and in their three-dimensional shapes. **Alkanes** and **cycloalkanes** consist entirely of carbon skeletons bonded to H atoms since they have no *functional groups*. As a result, they serve as a basis for understanding the structures of all other organic molecules. This chapter describes the skeleltal **isomerism** of *alkanes* and *cycloalkanes*, their three-dimensional **conformations**, and their **systematic nomenclature** that is the basis for the names of all other organic compounds.

2.1 Alkanes

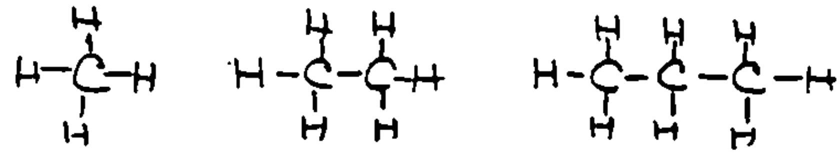
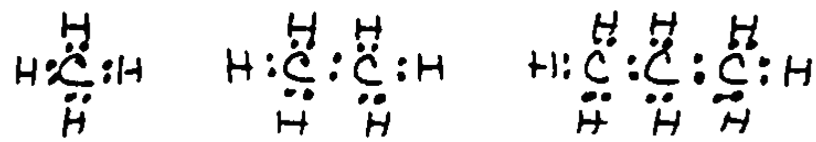
We refer to **alkanes** as **hydrocarbons** because they contain only C (carbon) and H (hydrogen) atoms. Since alkanes are the major components of petroleum and natural gas, they often serve as a commercial starting point for the preparation of many other classes of organic molecules.

Structures of Alkanes (2.1A)

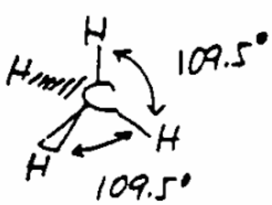
Organic chemists use a variety of different types of structures to represent alkanes such as these shown for *methane* (one C), *ethane* (two C's), and *propane* (three C's). [graphic 2.1]

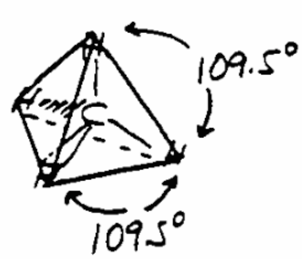
Kekulé, Electron-Dot and Three-Dimensional Structures. The structures showing C and H atoms connected by lines are **Kekulé structures**. Remember from Chapter 1 that these lines represent chemical bonds that are pairs of electrons located in molecular orbitals encompassing the two bonded atoms. Chemists sometimes emphasize the presence of electrons in the bonds using **electron dot formulas**. The C atoms in alkanes are *tetrahedral* so their H-C-H, C-C-H, and C-C-C bond angles are all close to 109.5°. **Solid** and **dashed**

2.1. Different Types of Structures

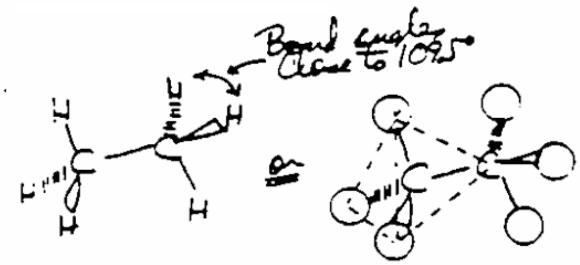
Name	Methane	Ethane	Propane
Kekulé Structure			
Electron Dot Formula			
Three-Dimensional Structure			
Condensed Structural Formula	CH_4	CH_3CH_3	$CH_3CH_2CH_3$
Molecular Formula	CH_4	C_2H_6	C_3H_8

2.2. C-H Bond Angles in Methane





Ethane (CH_3-CH_3)



3-D Structures

wedge bonds shown in Figure [graphic 2.1] help us to visualize alkane **three-dimensional structures**.

> **Tetrahedral Bond Angles**. We learned in Chapter 1 that organic molecules generally adopt three dimensional structures in which the electron pairs in the chemical bonds are as far away from each other as possible according to the **Valence Shell Electron Pair Repulsion Model (VSEPR)**. For C's with four attached atoms (terahedral C's), the VSEPR Model predicts that the angles between chemical bonds should be 109.5°. [graphic 2.2] While angles between bonds at tetrahedral C are usually close to 109.5°, this specific value occurs only when the four other atoms (or groups of atoms) attached to the carbon atom are identical to each other. When they are not all identical, the bond angles adjust to accommodate the different size groups. [graphic 2.3]

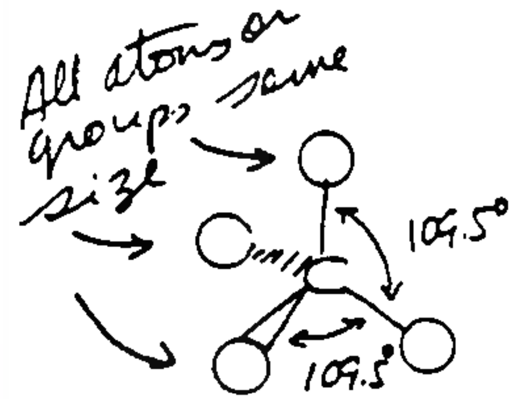
Condensed Structural Formulas. We will frequently represent alkanes using **condensed structural formulas** such as CH_4 (methane), CH_3CH_3 (ethane) and $CH_3CH_2CH_3$ (propane). With practice, you will see that these condensed formulas show how the atoms bond together. [graphic 2.4] They give more structural information than **molecular formulas** such as C_2H_6 (ethane), or C_3H_8 (propane) since *molecular formulas* show only the types and numbers of atoms in a molecule, but not the arrangements of the atoms.

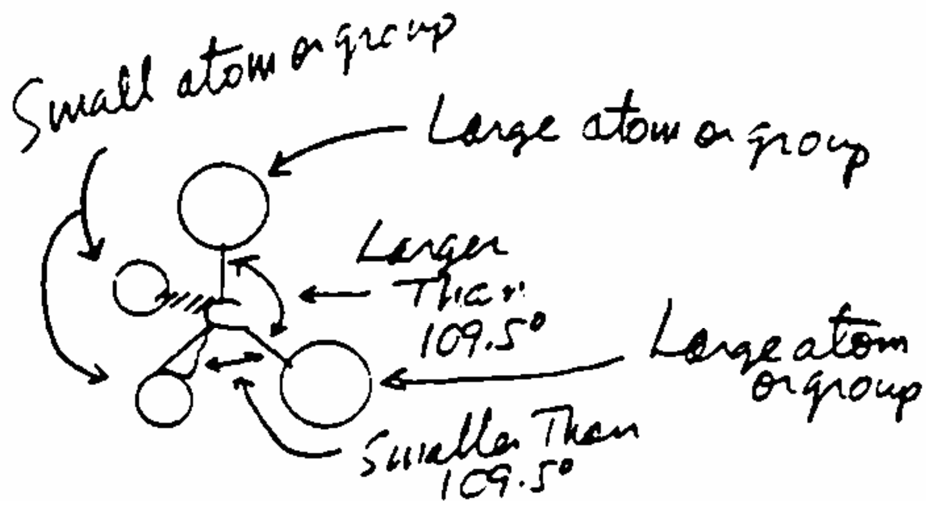
Molecular Formulas. You can see from the molecular formulas CH_4, C_2H_6, and C_3H_8, that the general molecular formula for alkanes is C_nH_{2n+2} where n is the number of C atoms. While it does not show how C's are attached to each other, it does allow you to predict the number of H's required for a specific number of C's. For example a C_4 alkane must have 10 H's (2n+2 = 2(4) +2 = 10), but the resulting molecular formula C_4H_{10} does not tell you the specific structures for its two possible Kekulé structures. [graphic 2.5]

Structural Isomers. All alkanes with four or more C's have both **unbranched** and **branched** carbon skeletons such as those shown for C_4H_{10}. Since these two C_4H_{10} alkanes have the same molecular formula, but differ in the way that their C atoms bond to each other, they are called **structural isomers**.

Organic chemists refer to *unbranched* alkanes as **linear** or **straight-chain** alkanes even though they are not *straight* or *linear*. The C-C-C angles are tetrahedral (approximately 109.5°), so the carbon chains adopt a zig-zag pattern. [graphic 2.6] The terms *linear* and *straight-chain* mean that all of the C's bond to each other in a *continuous chain*. It is possible to touch all of the C atoms in an *unbranched* alkane by tracing a pencil along the carbon chain

2.3

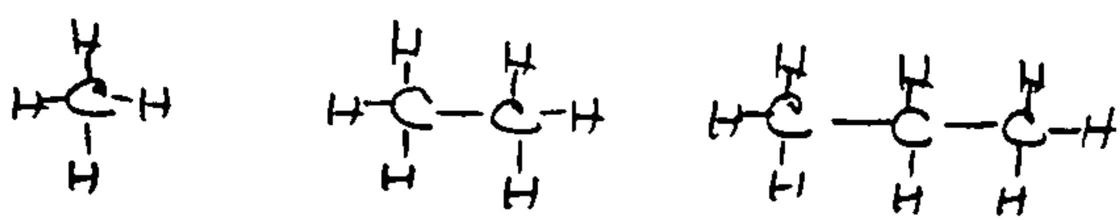




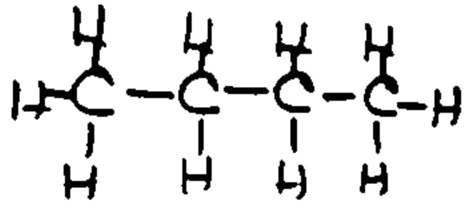
2.4. Condensed Structural Formulas

	CH_4	CH_3CH_3	$CH_3CH_2CH_3$
means	CH_4	CH_3-CH_3	$CH_3-CH_2-CH_3$

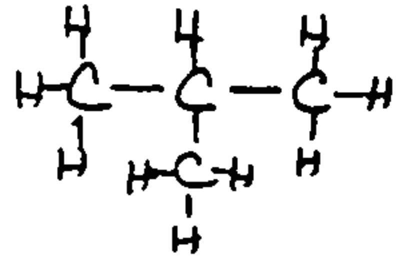
means



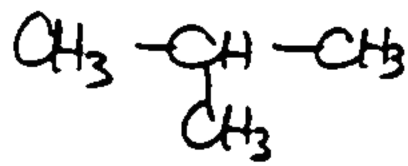
2.5. Structures Corresponding to C_4H_{10}



and



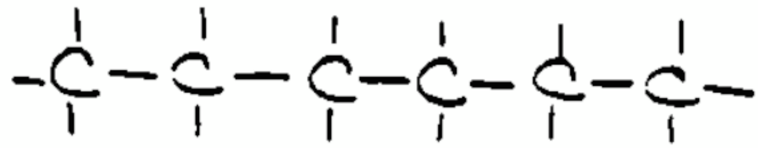
or $CH_3-CH_2-CH_2-CH_3$



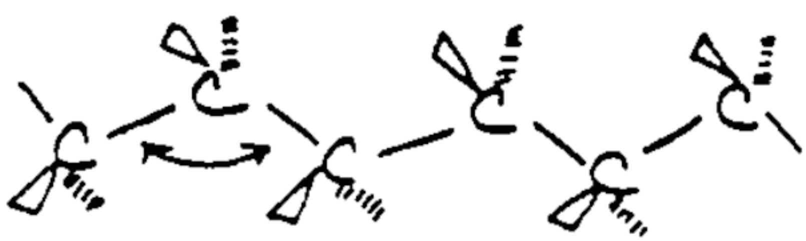
or $CH_3CH_2CH_2CH_3$ $(CH_3)_2CHCH_3$

(Unbranched) isomer (branched) isomer

2.6



Actually looks like



~109.5°

without lifting it or backtracking along one of the chemical bonds. This is not possible with *branched* alkanes such as that shown for C_4H_{10}.

Line-Bond Structures. Organic chemists also draw alkane structures using **line-bond structures** or **line drawings** that do not show C's and H's. [graphic 2.7] *Line-bond structures* save time in writing chemical structures because they are simpler than Kekulé structures. They also clearly show the basic skeletal features of the molecule. A disadvantage is that the absence of C's and H's makes it initially harder for you to visualize complete structures. You must remember that there is a C at the end of each line segment, and at each corner where two lines meet. You must also remember that there are H's attached to each C in the correct number to satisfy each C's desire for four bonds.

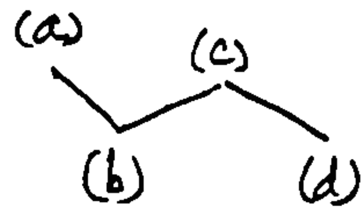
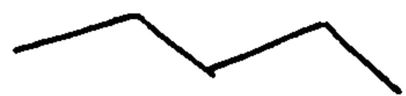
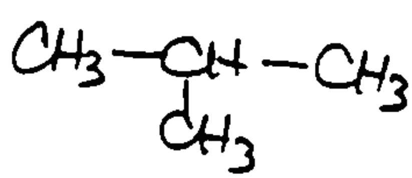
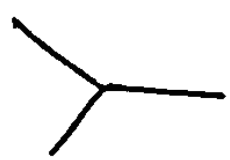
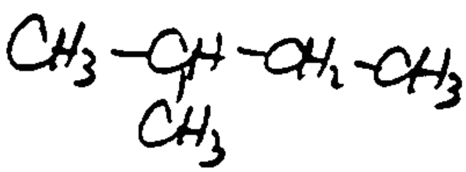
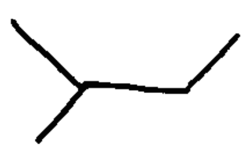
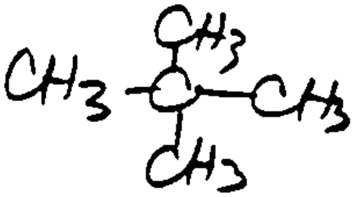
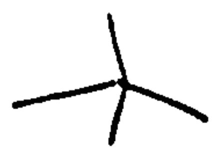
Alkane Names and Physical Properties (2.1B)

Table 2.1 shows the names, *condensed formulas*, and some physical properties, for the C_1 through C_{12} *unbranched* alkanes. This table does not include three-dimensional structures, but you can draw them in the same way that we did earlier for *methane*, *ethane*, and *propane*.

Table 2.1. Names, Formulas, Boiling Points, and Melting Points of C_1 through C_{12} Unbranched Alkanes.

Carbon Number	Name	Formula	Boiling Point (°C)	Melting Point (°C)
C_1	Methane	CH_4	-164	-182
C_2	Ethane	CH_3-CH_3	-89	-183
C_3	Propane	CH_3-CH_2-CH_3	-42	-190
C_4	Butane	CH_3-CH_2-CH_2-CH_3	-1	-138
C_5	Pentane	CH_3-CH_2-CH_2-CH_2-CH_3 or CH_3-$(CH_2)_3$-CH_3	36	-130
C_6	Hexane	CH_3-$(CH_2)_4$-CH_3	69	-95
C_7	Heptane	CH_3-$(CH_2)_5$-CH_3	98	-91
C_8	Octane	CH_3-$(CH_2)_6$-CH_3	126	-57
C_9	Nonane	CH_3-$(CH_2)_7$-CH_3	151	-51
C_{10}	Decane	CH_3-$(CH_2)_8$-CH_3	174	-30
C_{11}	Undecane	CH_3-$(CH_2)_9$-CH_3	196	-26
C_{12}	Dodecane	CH_3-$(CH_2)_{10}$-CH_3	216	-10

2.7. Line-Bond Drawings

Condensed Structural Formula	Line-Bond Structure
(a) (b) (c) $CH_3-CH_2-CH_3$	
(a) (b) (c) (d) $CH_3-CH_2-CH_2-CH_3$	
$CH_3-CH_2-CH_2-CH_2CH_3$	
	
	
	

Each C is tetrahedral and each bond is as far away from other chemical bonds as possible as we show here for *butane* and *pentane*. [graphic 2.8]

Physical Properties. You can see from the boiling points in Table 2.1 that *methane*, *ethane*, *propane*, and *butane* are gases at room temperature. The other alkanes shown are liquids because their boiling points are above room temperature while their melting points are below room temperature. The lowest molecular mass *unbranched* alkane that can be a solid at room temperature is *octadecane* ($C_{18}H_{38}$ or CH_3-$(CH_2)_{16}$-CH_3) (m.p. 28°C) and those with more than 18 C's are also solids. You can see that alkane *boiling points* increase with increasing molecular mass. For example, the boiling point of butane (C_4H_{10}) is about 0° C and each higher molecular mass alkane formed by adding a CH_2 group to butane boils at a temperature ranging from 20° to 30° higher than the previous alkane. We will see later that this b.p. increase of 20-30° per CH_2 group also applies to other types of organic compounds.

Names. You can also see in Table 2.1 that all alkane names end in *-ane* just like their general name *alkane.* The prefix of each name (*meth-, eth-, prop-, but-, pent-*, etc.) indicates the number of carbon atoms in its carbon chain. All of the prefixes except those for the C_1-C_4 alkanes come from the Greek names for the numbers of C's in the alkane. *Memorize all of these prefixes in Table 2.1, and the number of carbons that correspond to them. They are the basis for all organic nomenclature.*

2.2 Alkane Systematic Nomenclature

The unbranched and branched C_4H_{10} structural isomers have different names because they have different structures. [graphic 2.9] To provide a unique name for each organic molecule, organic chemists use a method of systematic nomenclature that we describe in this section for alkanes. We will name *unbranched alkanes* as shown in Table 2.1, while we will name *branched alkanes* as "*alkyl-substituted*" unbranched alkanes.

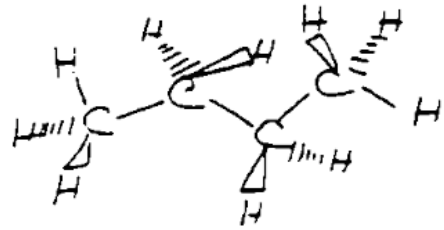
Alkane Nomenclature Rules (2.2A)

The following rules illustrate the basic principles for naming simple *branched* alkanes. The names *3-methylhexane* and *4-ethyl-3-methyloctane* for the alkanes shown here are based on these rules. [graphic 2.10]

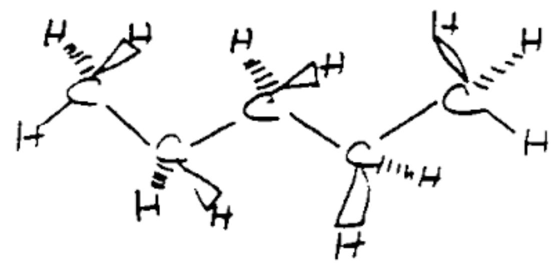
Rule1. *The longest continuous chain of C atoms in the branched alkane is the "parent alkane" and we use this parent alkane as the basis for the name of the compound.* [graphic 2.11]

2.8. 3-D Structures of Butane and Pentane

<u>butane</u>



<u>pentane</u>



2.9. Names of C_4H_{10} Isomers

$CH_3-CH_2-CH_2-CH_3$ $\qquad$ $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$

<u>butane</u> $\qquad$ <u>2-methylpropane</u>

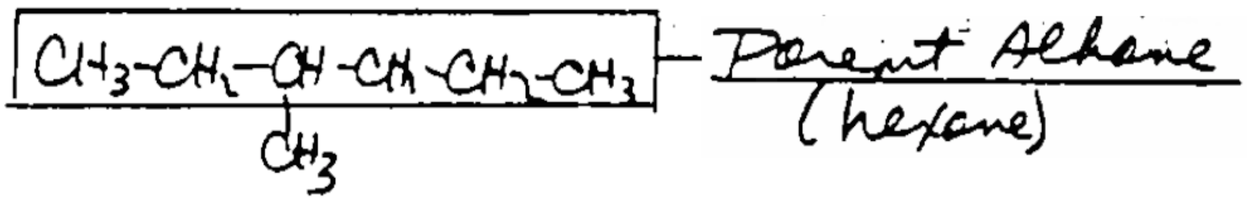
2.10 $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2CH_2CH_3$

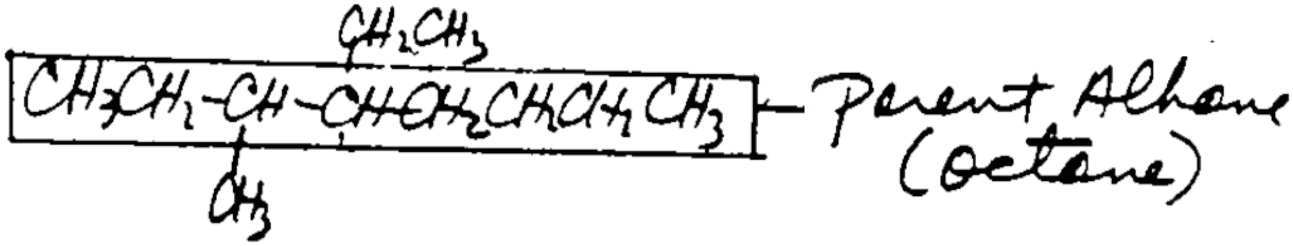
<u>3-methylhexane</u>

$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-\overset{\displaystyle CH_2CH_3}{\overset{|}{C}H}-CH_2CH_2CH_2CH_3$

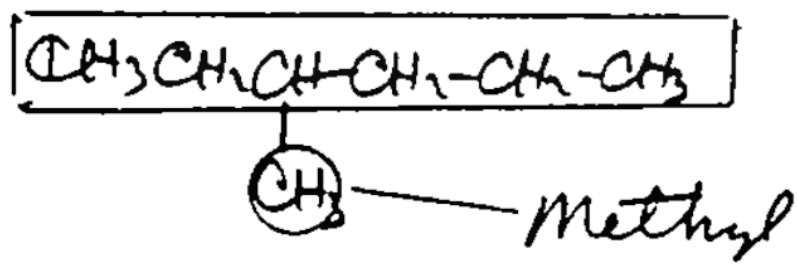
<u>4-ethyl-3-methyloctane</u>

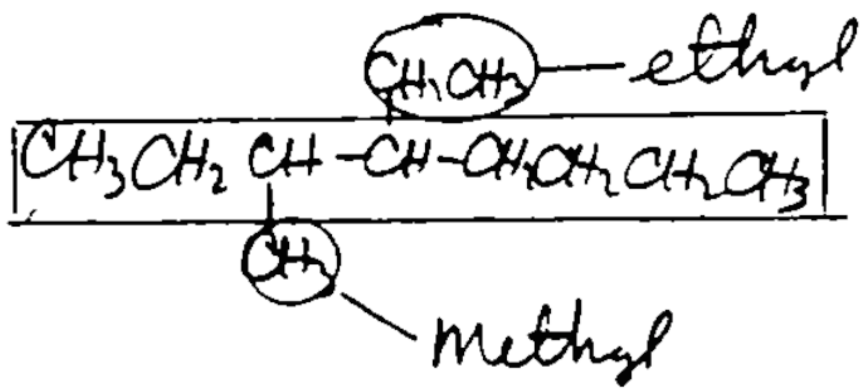
2.11


Parent Alkane
(hexane)


Parent Alkane
(octane)

2.12


Methyl


ethyl
Methyl

Rule 2. *The individual hydrocarbon fragments or groups attached to the parent alkane are "alkyl" groups.* The names of *alkyl* groups come from the names of their "corresponding alkanes" by dropping the ending *"ane"* and adding *"yl"*. [graphic 2.12] We form the "corresponding alkane" to an alkyl group by adding the missing H to the alkyl group. [graphic 2.13]

Rule 3. *We number the parent alkane by assigning C1 to its end carbon closest to a C substituted with an alkyl group.* [graphic 2.14]

Rule 4. *We place the name of each alkyl group, with the number of the C in the parent alkane to which it is bonded , in* <u>*alphabetical*</u> *order in front of the name of the parent alkane.* This final step leads to the complete names of these branched alkanes as shown here. [graphic 2.15]

In more complex molecules, you may need to use one or more of the following additions to these rules.

Addition to Rule 1: *When two or more chains of C atoms in a branched alkane correspond to the same parent alkane, we choose the chain with the most attached alkyl groups as the parent alkane.* [graphic 2.16]

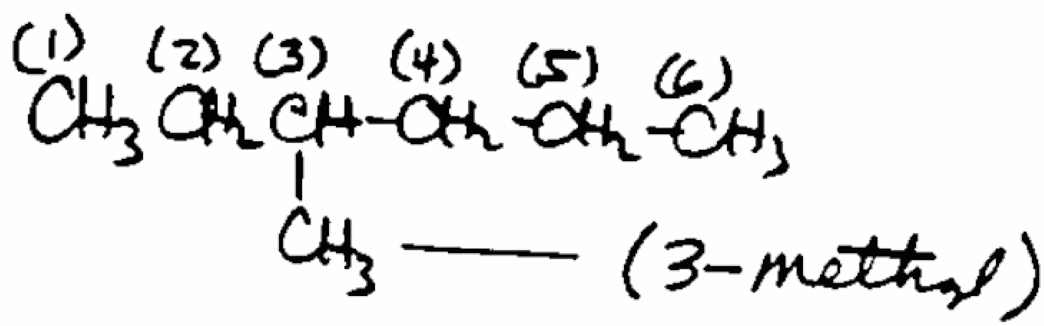
Addition to Rule 3: *If the first alkyl group on the parent alkane is on a C with the same number counting from either end of the chain, we assign C1 to the end C that places the* <u>*next*</u> *attached alkyl group at the lowest number C.* Repeat this rule as necessary until you reach a point of difference. If you find none, assign C1 to the end of the parent alkane so that the alkyl group that appears first in the name, due to its alphabetical ordering, has the lowest number. [graphic 2.17]

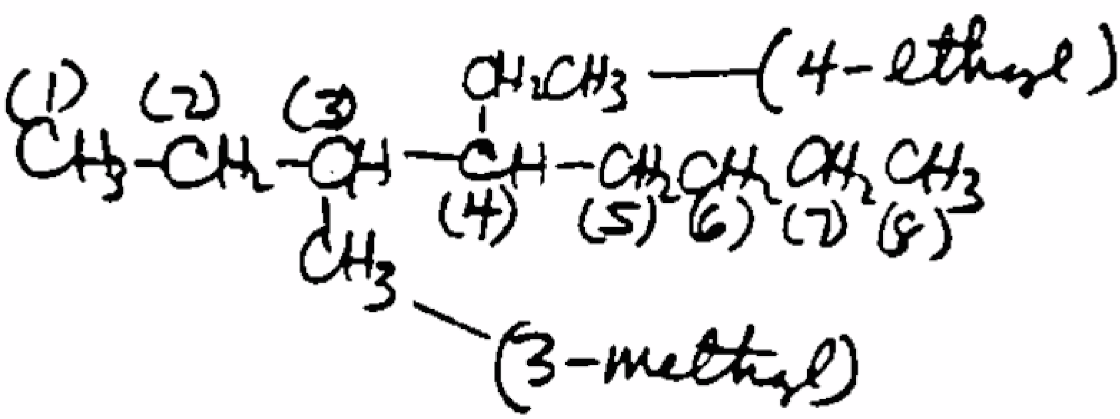
The Prefixes Di, Tri, and Tetra. When two methyl groups are on the parent alkane, we combine their names together using the term *dimethyl* and place the numbers of their parent alkane C's in front of this term. [graphic 2.18] Three methyl groups are *tri*methyl, four are *tetra*methyl, while we use the prefixes in Table 2.1 (5 = *penta*, 6 = *hexa*, etc.) for 5 or more methyl groups. We will use the prefixes *di*, *tri*, etc., for two or more identical alkyl groups of any type. These prefixes do not determine the alphabetical order of the names of attached groups. For alphabetical ordering purposes, we consider di<u>m</u>ethyl to begin with the letter <u>m</u> as in <u>m</u>ethyl.

2.13

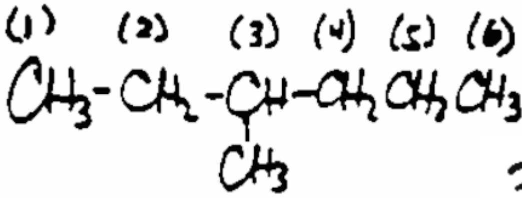
Alkyl Group	Corresponding Alkane
CH_3- methyl	CH_4 methane
CH_3CH_2- ethyl	CH_3CH_3 ethane

2.14

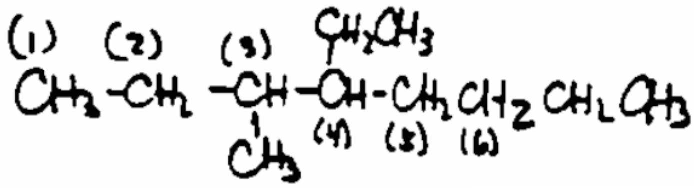




2.15

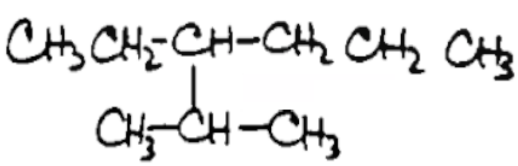


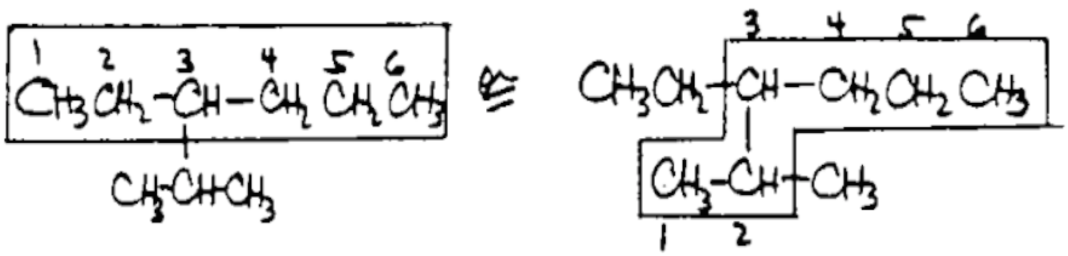
3-methylhexane



4-ethyl-3-methyloctane

2.16





- hexane parent alkane
- ~~one~~ alkyl group

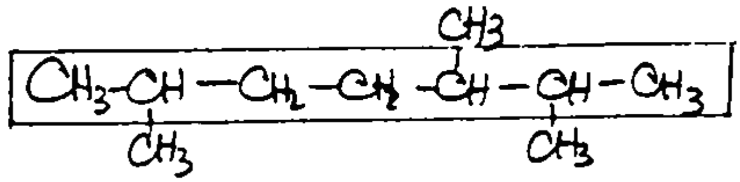
No!!

- hexane parent alkane
- two alkyl groups

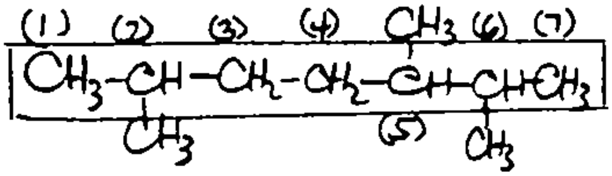
yes!!

$\boxed{\text{3-ethyl-2-methylhexane}}$

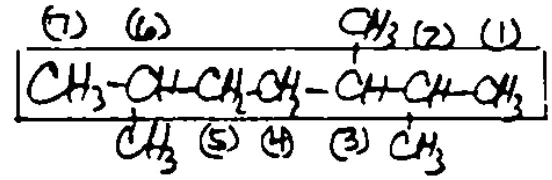
2.17



Parent alkane (heptane)



or



2-methyl
$\boxed{5}$-methyl
6-methyl

NO!!

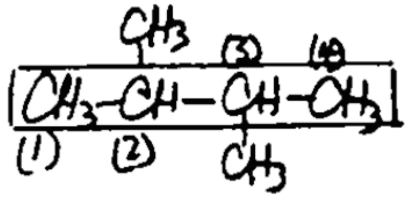
or

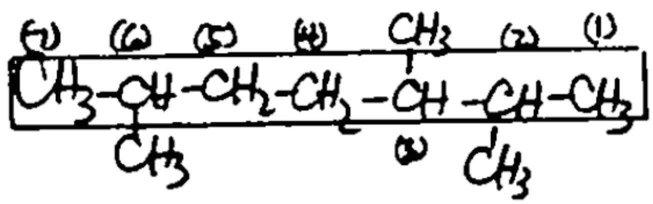
2-methyl
$\boxed{3}$-methyl
6-methyl

Yes!!

3-methyl has lower C number than 5-methyl

2.18





2,3-dimethylbutane

2,3,6-trimethylheptane

Many Ways to Draw the Same Molecule. You can usually draw a specific molecule in many different ways as we show here for 2-methylbutane. [graphic 2.19] In each case, the parent alkane is butane (C4) with a single attached methyl group (CH_3) at C2 so all of these structures are the same molecule (2-methylbutane).

Alkyl Groups Besides Methyl (2.2B)

You can create an alkyl group by removing one H from any linear or branched alkane. This means that there are many alkyl groups other than *methyl* (CH_3) and *ethyl* (CH_3CH_2) such as the two shown here that we can create from propane. [graphic 2.21]

Names of Alkyl Groups. The two alkyl groups that we have created from propane have different structures so they must have different names. Their names **1-methylethyl** and **propyl** are based on the following rule:

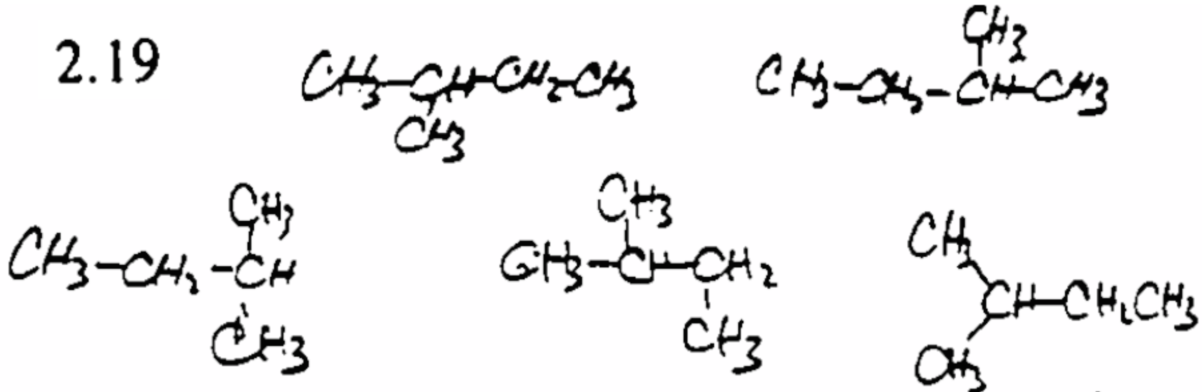
The C of the alkyl group that is attached to the parent alkane is C1 of the alkyl group.

After we have identified C1 of the alkyl group using this rule, we assign a root name to the alkyl group based on its longest continuous chain of C atoms that begins with C1. In the case of the *propyl* group, C1 is the end carbon of a three carbon "propane" chain so its root name *propyl* is derived from *propane* by replacing *ane* with *yl*. [graphic 2.22] Since this alky group has no other C atoms besides those in this three carbon chain, its full name is also *propyl*.

In contrast to the *propyl* group, the point of attachment of the *1-methylethyl* group (its C1) is the <u>middle</u> C of a three-carbon chain. [graphic 2.23] As C1 of this group, this middle C becomes the end of a "longest continuous chain" made up of only <u>two</u> C's (an "ethane" chain) so we give the root name *ethyl* to this group. This *ethyl* group defined by our assignment of C1 also has a *methyl* group bonded to its C1. We indicate the presence of this *methyl* group on C1 by naming the whole group *1-methylethyl*. The point of attachment on the alkyl group to the parent alkane is always defined as C1 of the alkyl group so we do <u>not</u> indicate that with a number in the alkyl group name. The "1" in *1-methylethyl* indicates the location of the *methyl* on the *ethyl* group.

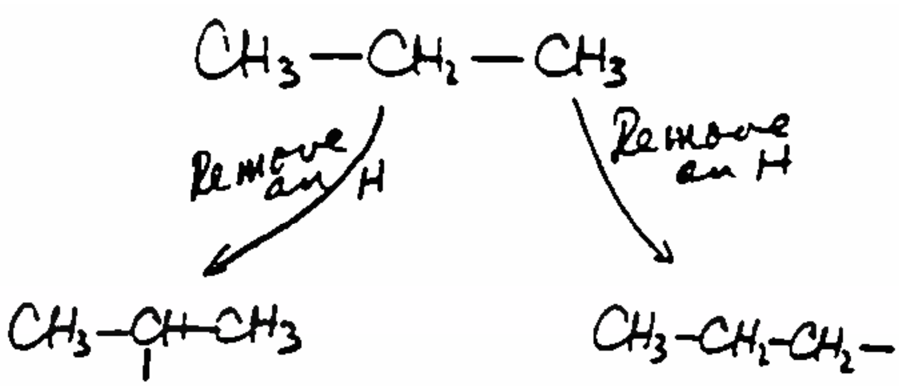
We use these rules to name alkyl groups derived from branched or linear alkanes. Examples are the *2-methylpropyl* and *1,1-dimethylethyl* groups derived from the branched alkane *2-methylpropane*. [graphic 2.24] While you can create very complex alkyl groups by removing different H's from highly branched alkanes, such complex alkyl group names do not often

2.19



All of These are 2-methyl butane

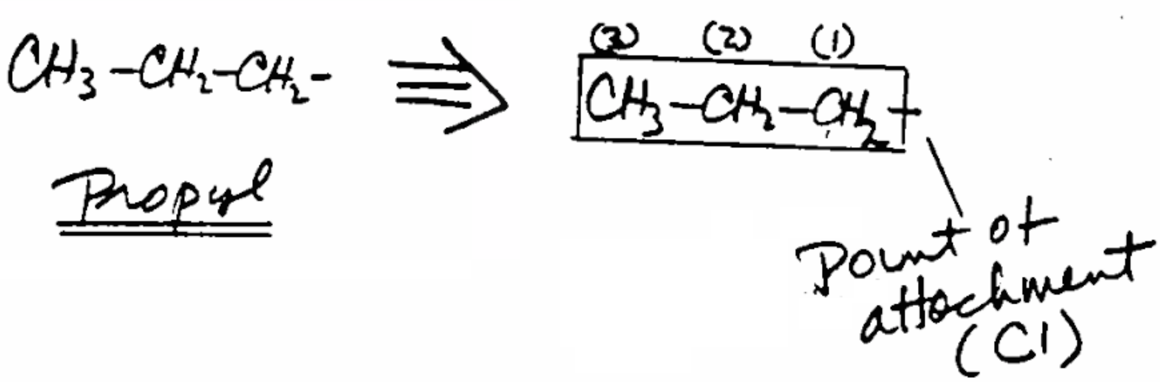
2.21. Formation of Alkyl Groups from Propane



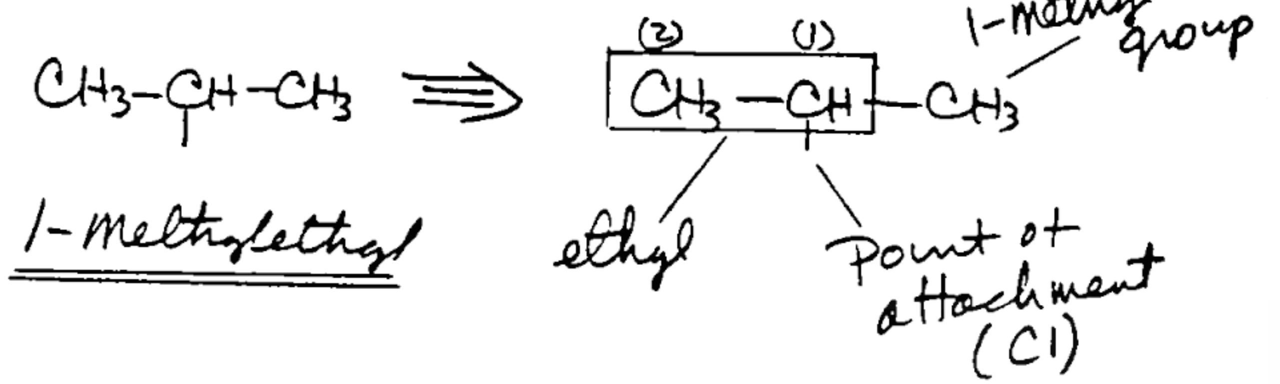
1-methylethyl group

Propyl group

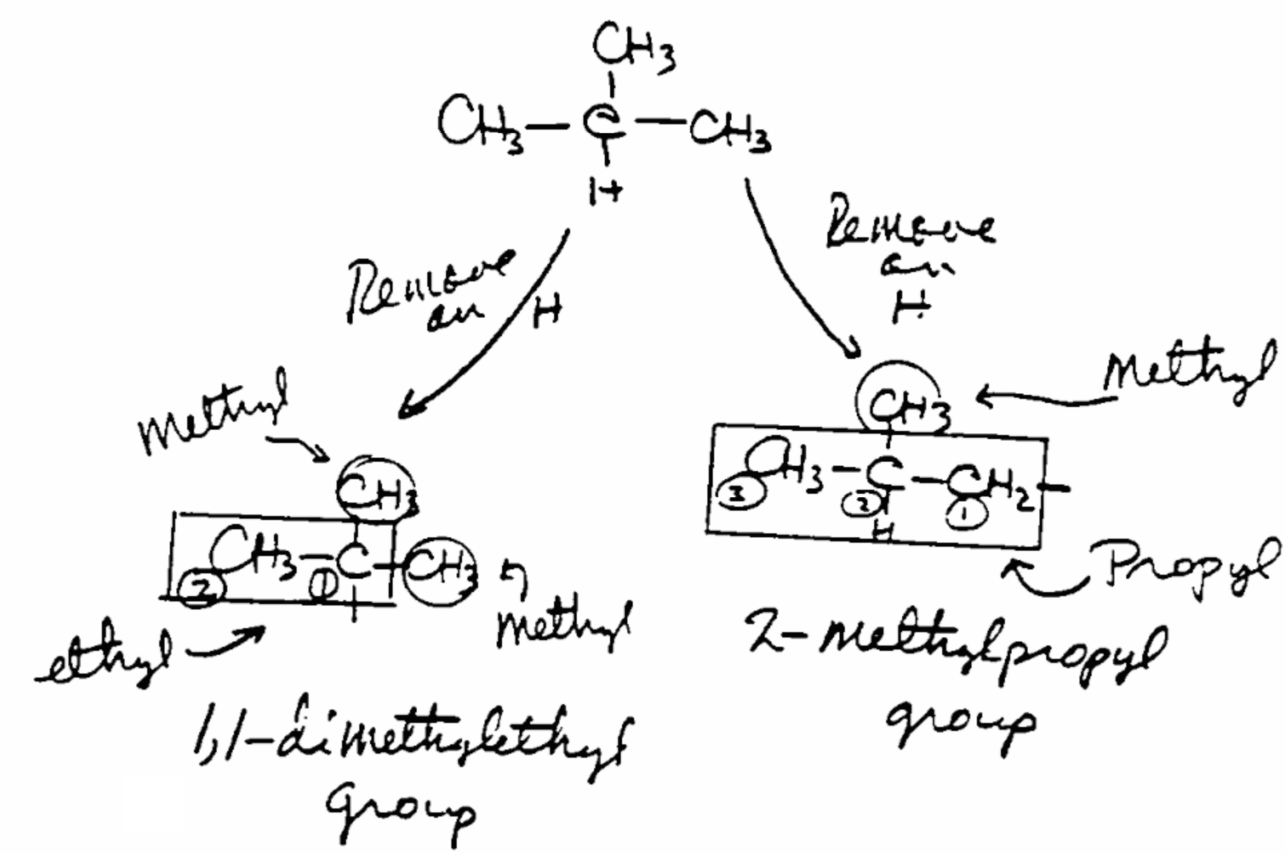
2.22



2.23



2.24. Formation of Alkyl Groups from 2-Methylpropane



appear in names of organic molecules. They usually become part of a parent alkane that is substituted with a number of small alkyl groups.

Isopropyl and t-Butyl. In addition to methyl, ethyl and propyl groups, we frequently encounter both *1-methylethyl*, and *1,1-dimethylethyl* groups . However they almost always appear as **isopropyl** and ***tert*-butyl** in names of organic compounds. These **common names** are not based on modern systematic nomenclature rules, but they have been used for so long and so widely that they are now incorporated into systematic nomenclature. [graphic 2.25] For correct alphabetical ordering, we use the "i" of isopropyl. However, you may be surprised to learn that we use the "b" of *tert*-butyl since hyphenated prefixes are not used for alphabetical ordering! The prefix "*tert*" is an abbreviation for "tertiary" and is often abbreviated "*t*" as in *t*-butyl. It is used in the name of this group because a C with three attached alkyl groups, such as the C in C$(CH_3)_3$, is called a *tertiary* carbon as we will see later in the text.

Common Nomenclature. A number of alkyl groups, and even certain branched alkanes, have common names that you may encounter such as those in Table 2.2.

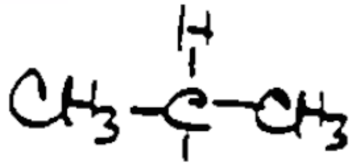
Table 2.2. Common Names of Some Alkyl Groups and Alkanes

Alkyl Group	Common Name	Systematic Name
$CH_3CH_2\underline{C}H_2$	n-propyl	propyl
$CH_3\underline{C}HCH_3$	isopropyl*	1-methylethyl
$CH_3CH_2CH_2\underline{C}H_2$	n-butyl	butyl
$CH_3CH_2\underline{C}HCH_3$	sec-butyl	1-methylpropyl
$(CH_3)_2CH\underline{C}H_2$	isobutyl	2-methylpropyl
$(CH_3)_3\underline{C}$	tert-butyl*	1,1-dimethylethyl
$CH_3(CH_2)_3\underline{C}H_2$	n-pentyl or n-amyl	pentyl
$(CH_3)_2CHCH_2\underline{C}H_2$	isopentyl or isoamyl	3-methylbutyl
$(CH_3)_3C\underline{C}H_2$	neopentyl	2,2-dimethylpropyl

*Accepted as systematic name
C is the point of attachment of the alkyl group

Alkane	Common Name	Systematic Name
$CH_3CH_2CH_2CH_3$	n-butane	butane
$(CH_3)_3CH$	isobutane	2-methylpropane
$(CH_3)_4C$	neopentane	2,2-dimethylpropane
$(CH_3)_3CCH_2CH(CH_3)_2$	isooctane	2,2,4-trimethylpentane

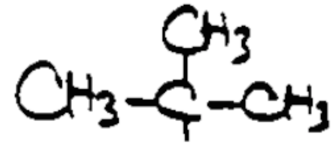
2.25



1-Methylethyl

or

isopropyl

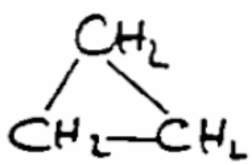


1,1-dimethylethyl

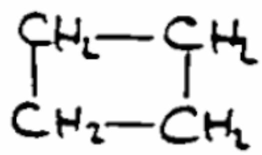
or

<u>tert</u>-butyl

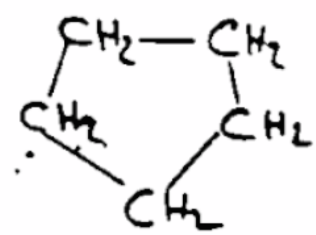
2.26. Some Cycloalkanes



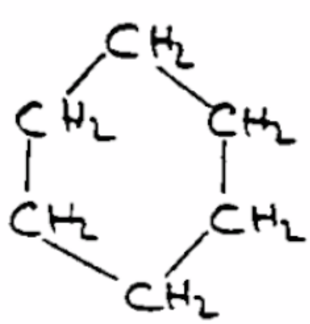
Cyclopropane
C_3



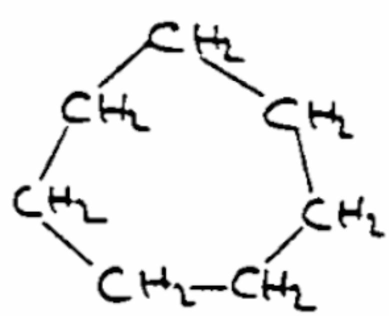
Cyclobutane
C_4



Cyclopentane
C_5



Cyclohexane
C_6



Cycloheptane
C_7

Except for *isopropyl* and *tert-butyl*, the use of common names is decreasing in organic chemistry journals and textbooks. However, you may see these common names in older organic chemistry literature, as well as in the literature of allied chemical disciplines such as biochemistry, chemical engineering, environmental chemistry, and agricultural chemistry.

2.3 Cycloalkanes

Cycloalkanes are hydrocarbons with three or more C atoms in a *ring*. [graphic 2.26] While linear or branched alkanes have distinct carbon atoms at the ends of their longest straight chains, this is not the case with cycloalkanes. The general molecular formula for a *cycloalkane* is C_nH_{2n} in contrast to C_nH_{2n+2} for an *alkane*.

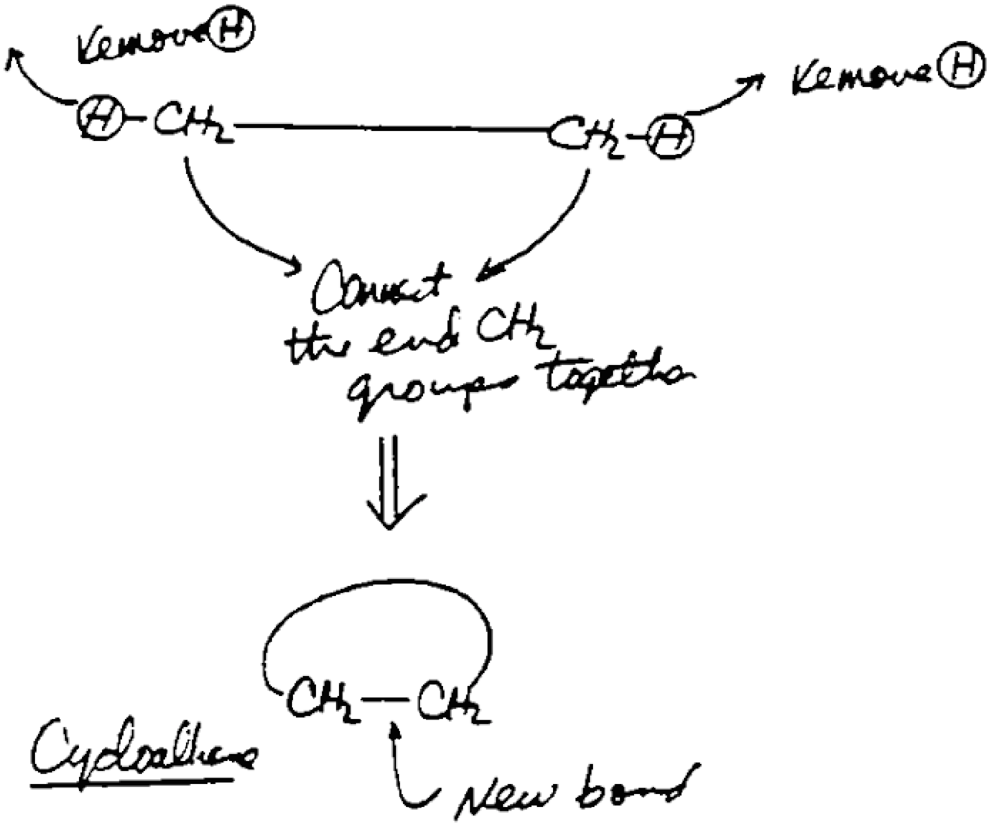
Structural Information from Molecular Formulas. While molecular formulas do not provide detailed structural information, they give important basic information about structures. For example, if the molecular formula of a hydrocarbon fits the formula C_nH_{2n}, you can conclude that it is not an alkane since alkanes must have the molecular formula C_nH_{2n+2}. Organic chemists state that a hydrocarbon with fewer than 2n+2 H's is **"hydrogen deficient"** or has one or more "**sites of unsaturation"**. The formula C_nH_{2n} for a cycloalkane indicates that it has 1 *site of unsaturation*, or a *hydrogen deficiency index of 1*, because it is missing 2 H atoms (missing an H_2) compared to an alkane. You can imagine the hypothetical formation of a cycloalkane by removing two H atoms from the end C's of an alkane and then forming a C-C bond. [graphic 2.27]

The general formula for *alkenes* (see Chapter 1), such as *ethene* (CH_2=CH_2), is also C_nH_{2n} (*1 site of unsaturation* or *hydrogen deficiency index of 1*). In contrast, the molecular formula for *alkynes*, such as *ethyne* (CH≡CH), is C_nH_{2n-2} (it is missing 2 H_2 units) so it has *2 sites of unsaturation* or a *hydrogen deficiency index of 2*. As a result, a hydrocarbon with molecular formula C_nH_{2n+2} must be an *alkane*, one with the formula C_nH_{2n} may be a *cycloalkane* or *alkene*, while one with the formula C_nH_{2n-2} could be an *alkyne*, a *diene* (2 C=C), a hydrocarbon with a C=C and a ring, or a hydrocarbon with two rings.

Structural Drawings (2.3A)

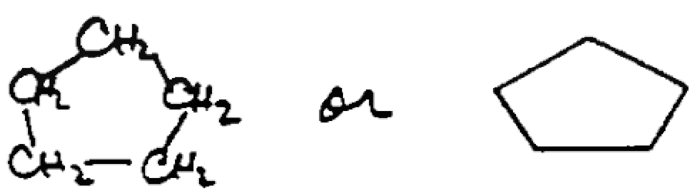
Organic chemists usually draw cycloalkanes as *line-bond* structures that do not show ring C's and H's. [graphic 2.28] Cyclopentane is an *unsubstituted* cycloalkane, while methyl-cyclohexane is an example of a *branched* or *substituted* cycloalkane. When a ring C of a cycloalkane has only one bonded alkyl group, it is important to remember that these line-bond structures usually do not show the H atom also bonded to that C.

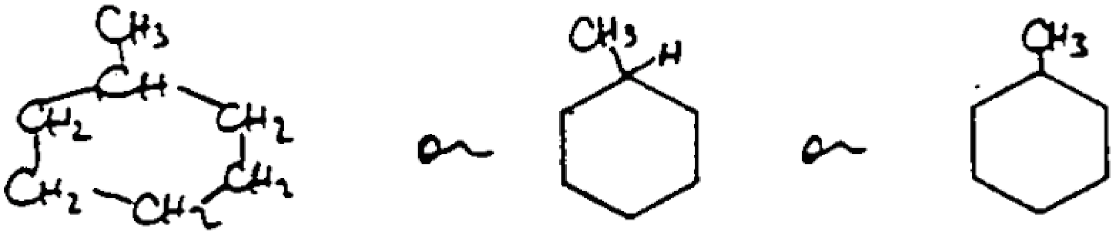
2.27. Formation of a Cycloalkane



2.28

Cyclopentane





Methylcyclohexane

Nomenclature (2.3B)

We name unsubstituted cycloalkanes by placing the prefix *cyclo* in front of the name of the linear alkane (Table 2.1) with the same number of C's as in the ring. We name branched cycloalkanes as "*alkylcycloalkanes*" if the alkyl group has the same or a smaller number of C's than the cycloalkane. [graphic 2.30] If the alkyl group contains more C's than the ring, we name the compound as a "*cycloalkylalkane*" as shown by this example of a cyclobutyl ring attached to a C_6 alkyl group. [graphic 2.31] This latter method may also be the best way of naming a branched cycloalkane if an alkyl group on a ring has a complex name.

Numbering a Cycloalkane. A cycloalkane has no "end carbon" so it is unnecessary to use a number to indicate the position of the alkyl group on an alkylcycloalkane with one alkyl group (a *monoalkylcycloalkane*) (see Figure [graphic 2.30]). However, you must use numbers to indicate the relative positions of two or more ring alkyl groups as we show above. We assign C1 to a ring carbon <u>with an alkyl group</u> so that each successive alkyl group in the name has the lowest possible number.

Sometimes application of this rule gives two equivalent choices such as for cyclohexane substituted with an *ethyl* and *methyl* group on adjacent C's. [graphic 2.32] In each case, the two alkyl groups are on C1 and C2, so we assign C1 to the C with the group that is alphabetically first in the name.

Physical Properties (2.3C)

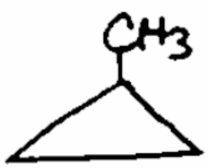
Cycloalkanes have boiling points (Table 2.3) approximately 10° to 20° higher than those of their corresponding alkanes (Table 2.1).

Table 2.3. Boiling Points of Cycloalkanes and Alkanes

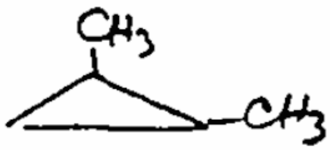
Carbon Number	**Cycloalkane**	**Alkane**
C_3	-33°	-42°
C_4	12°	-1°
C_5	49°	36°
C_6	81°	69°
C_7	119°	98°
C_8	149°	126°

Boiling points increase as attractive forces increase between molecules in the liquid state. The more rigid (less flexible) structures of cycloalkanes compared to alkanes permit greater attractive interactions between cycloalkane molecules. As a result, cycloalkane boiling points are higher than those of alkanes with approximately the same molecular mass. In contrast,

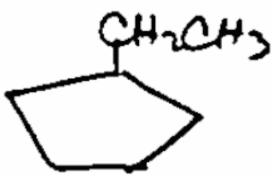
2.30



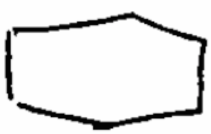
methylcyclopropane



1,2-dimethylcyclopropane

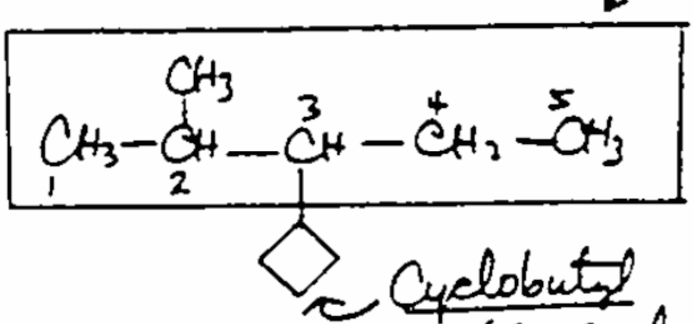


ethylcyclopentane



1-ethyl-2-methylcyclohexane

2.31

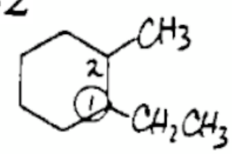


C6 alkyl group

Cyclobutyl
(C4 cycloalkyl group)

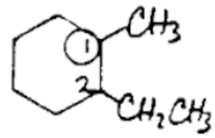
3-cyclobutyl-2-methylpentane

2.32



$\boxed{\text{1-ethyl-2-methylcyclohexane}}$

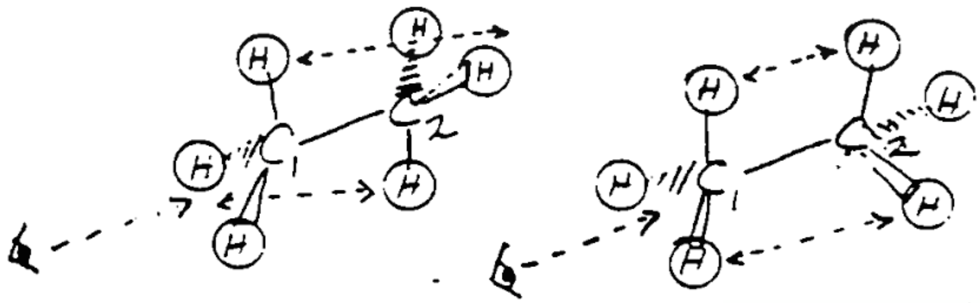
Correct!



2-ethyl-1-methylcyclohexane

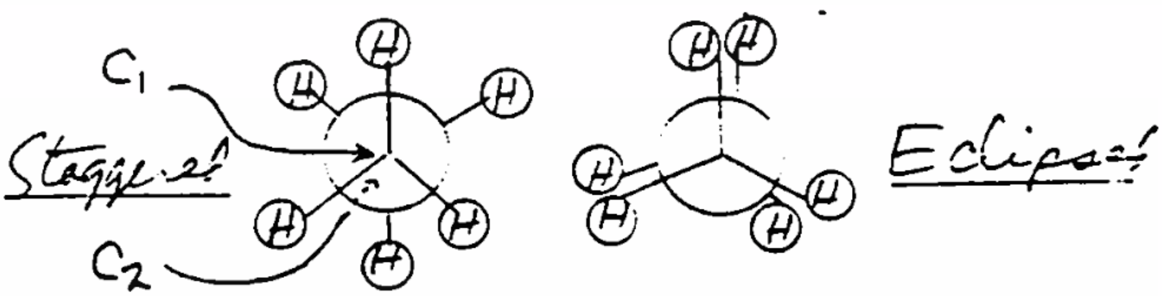
InCorrect!

2.34 Staggered and eclipsed conformations of ethane showing "eyeballs" looking along the C1-C2 bonds.



Staggered Eclipsed

2.35 Newman projections of ethane. The viewer is looking along the C1-C2 bond of ethane shown in Figure 1.22. C1 is in front and C2 is behind C1.



branched alkanes have lower boiling points (Table 2.4) than either their unbranched or cyclic analogs because they are more compact and have less surface area to interact with neighboring molecules.

Table 2.4. Boiling Points for C_5 Alkanes and Cyclopentane.

Compound	Boiling Point
cyclopentane	49°
pentane	36°
2-methylbutane	28°
2,2-dimethylpropane	10°

2.4 Conformations of Alkanes

Now that you have studied the structural formulas and nomenclature for alkanes and cycloalkanes, we can examine their *three-dimensional structures* (**conformations**) in more detail. This section focuses on the *conformations* of alkanes, while the two that follow it explore those of cycloalkanes.

Staggered and Eclipsed Conformations of Ethane (2.4A)

Methane has just one three-dimensional structure, but this is not the case for *ethane*. Because its two CH_3 groups rotate with respect two each other about the C-C bond, it can have many *conformations* including the **staggered** and **eclipsed** *conformations* that we show here. [graphic 2.34]

A Comparison of Staggered and Eclipsed Conformations. The *staggered* and the *eclipsed* conformations of ethane are conformational extremes for this molecule. In the *staggered conformation*, the C-H bonds on one C are as far away from those on the other C as possible. In contrast, they are as close to each other as possible in the *eclipsed* conformation. In order to keep the electron pairs in its bonds as far apart as possible, we will see that ethane preferentially exists in a *staggered conformation*.

Newman Projections. You can see the origin of the terms *staggered* and *eclipsed* by viewing these two conformations along (down) their carbon-carbon bonds from C1 to C2. The resulting views (Figure [graphic 2.35]) are those that the "eyeball sees" as it looks at C1 from the end of the molecule (Figure [graphic 2.34]). [graphic 2.35] The C-H bonds on the back carbon (C2) of the *staggered* conformation appear to be "staggered" between the C-H bonds on the front carbon (C1). In the *eclipsed* conformation, the C-H bonds on the front carbon (C1) block (*eclipse*) the view of those on the back carbon (C2).

If you view the eclipsed conformation at a slight angle rather than directly down the C1-C2 bond, the H's on the back carbon are partially visible (Figure [graphic 2.35]) and this is how we will usually draw projection views of eclipsed conformations. These "end-on" projection views along (down) C-C bonds are called **Newman Projections** and are named after Professor Melvin Newman* (1908-1993), of Ohio State University (*see page 2-58).

Rotation about the C-C Bond (2.4B)

The staggered conformation of ethane is its most favorable conformation, but ethane does not exist exclusively in this conformation.

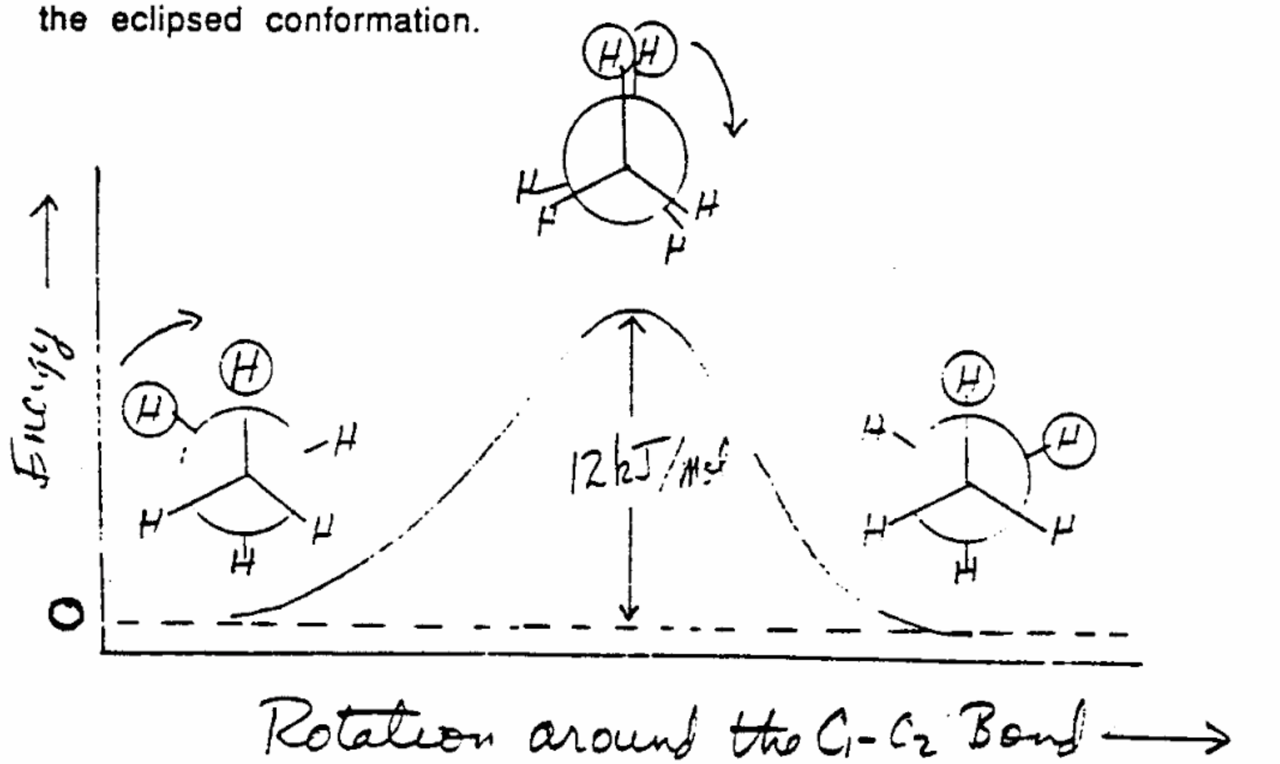
Rapid Rotation about C-C Bonds. There is extremely rapid **internal rotation** about the C-C bond. Ethane passes from a *staggered* through an *eclipsed* to a *staggered* conformation at a rate of about 10^{11} times per second (100,000,000,000 times per second) at room temperature. The **energy diagram** in Figure [graphic 2.36] shows how the energy of an ethane molecule changes as one CH_3 rotates about the C1-C2 bond with respect to the other CH_3. [graphic 2.36] You can see that the total energy of the ethane molecule is lowest in the staggered conformation and increases to a maximum value in the eclipsed conformation. The difference in energy between these two conformations is about 12 kJ/mol.

Energy Values. We use the SI energy units of **J** (**joules**) and **kJ** (**kilojoules**) in this text that you are familiar with from general chemistry. However, organic chemists often refer to energies in **cal** (**calories**) and **kcal** (**kilocalories**). A calorie is approximately four times larger than a joule (1 cal = 4.184 joules) so multiplying any energy value in *cal* (or *kcal*) by 4 gives the approximate energy value in *J* (or *kJ*). Similarly, dividing any energy value in *J* (or *kJ*) by 4 gives the approximate energy in *cal* (or *kcal*). In most situations where you need to interconvert between J and cal, the approximate conversion factor of 4 will prove to be satisfactory.

Energy and Stability. The low energy *staggered* conformation of ethane is more **stable** than its high energy *eclipsed* conformation. It is important for you to understand the relationship between *stability* and *energy* because we use these terms interchangeably throughout this text. You see in Figure [graphic 2.36] that the *more stable* (or *more favorable*) *staggered* conformation is *lower* in energy than the *less stable* (or *less favorable*) *eclipsed* conformation. When comparing two or more molecules, or conformations of molecules, that with *lowest energy* is *most stable* while that with *highest energy* is *least stable*.

least stable = least favorable = highest energy
most stable = most favorable = lowest energy

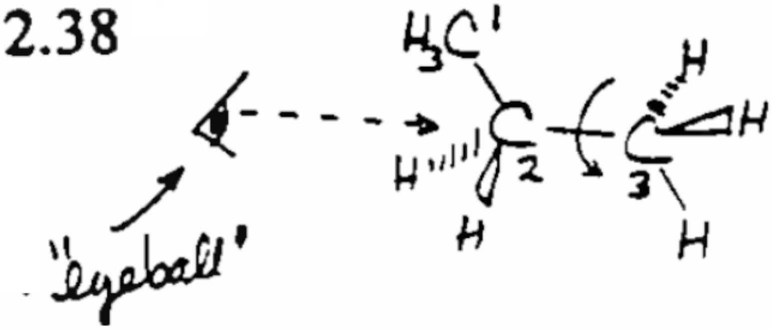
2.36 Energy diagram for rotation about the C1-C2 bond in ethane. The staggered conformation has an energy 12 kJ/mol lower than that of the eclipsed conformation.



2.37 $\overset{1}{C}H_3 - \overset{2}{C}H_2 - \overset{3}{C}H_3$

Rotation Occurs about both C–C bonds

2.38



Relative Energies *versus* Absolute Energies. We can assign an arbitrary value of 0 kJ/mol as the energy of the staggered conformation of ethane in Figure [graphic 2.36], but that is not its **absolute** energy. Its absolute energy is its **heat of formation** from its elements. However in order to compare different conformations of the same molecule, it is more convenient to talk about **relative** energies (the difference between absolute energies of the conformations). Since *eclipsed* ethane has an absolute energy 12 kJ/mol *higher* than that of *staggered* ethane, we can assign an energy value of 12 kJ/mol to the eclipsed conformation and a value of 0 kJ/mol to the staggered conformation. We will do this in all of the other energy diagrams shown below. However, it is important to remember that the assignment of an energy of 0 kJ/mol to a specific conformation simply reflects that this conformation has the lowest absolute energy of those conformations being compared with each other.

Conformations of Other Alkanes (2.4C)

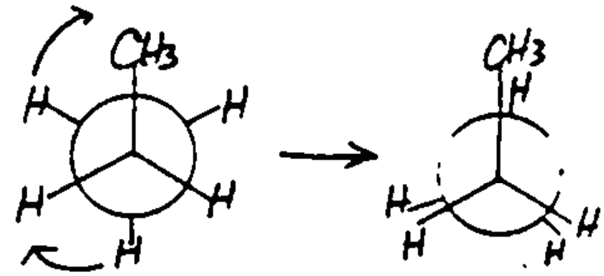
Staggered and eclipsed conformations due to C-C bond rotation occur in almost all alkanes. Just as we saw for ethane, the "most stable" or "lowest energy" conformations of these alkanes are those where atoms attached to bonded carbons are *staggered* with respect to each other as we illustrate below for *propane* and *butane*.

Propane. Propane has two C-C bonds and rotation occurs around each of them. [graphic 2.37] Let's look at rotation about the bond we label C2-C3 using a three-dimensional structure. [graphic 2.38] When we analyze rotation about C2-C3, we can show the C1 methyl group simply as CH_3. A view along (down) the C2-C3 bond of a staggered conformation shows C2 in front and C3 behind it, while all of the groups on C2 and C3 are staggered with respect to each other. [graphic 2.39] Rotation of the back methyl group (C3) with respect to C2 gives an eclipsed conformation. As we continue rotation about C2-C3, the groups on C2 and C3 once again become staggered and this staggered conformation is identical to the original staggered conformation.

The energy diagram showing these staggered and eclipsed propane conformations looks identical to the one we showed for ethane in Figure [graphic 2.36] except that the eclipsed conformation of propane has an energy 14 kJ/mol higher than its staggered conformation. This is 2 kJ/mol greater than the energy difference for eclipsed and staggered ethane (12 kJ/mol). It is possible to completely rotate (360° rotation) about <u>either</u> of the C-C bonds in propane alternately forming eclipsed and staggered forms. Because the two C-C bonds are completely equivalent, all the staggered conformations of propane are identical to each other, as are all its eclipsed conformations.

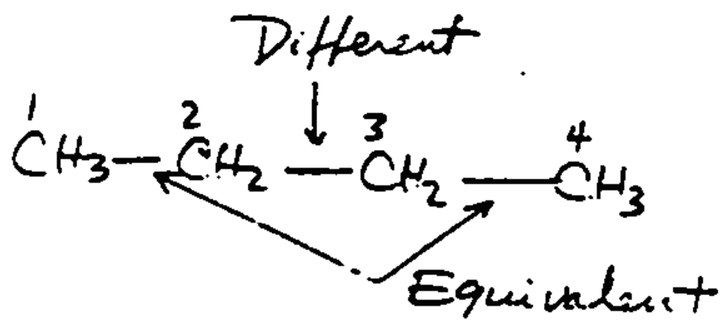
2.39 Newman projections for the staggered and eclipsed conformations resulting from rotation about the C2-C3 bond in propane.

Staggered

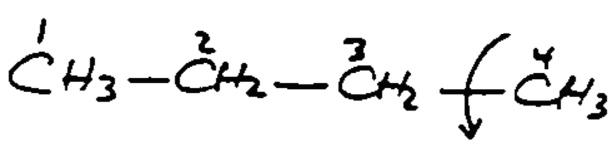


Eclipsed

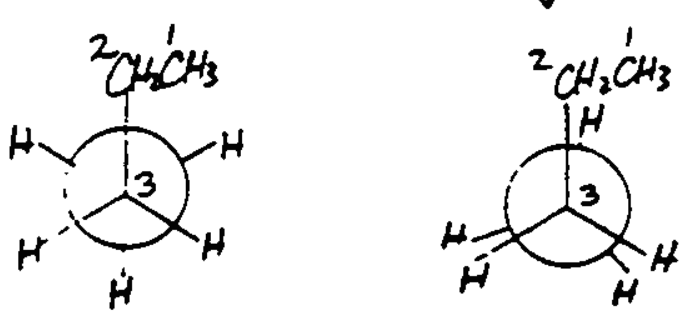
2.40



2.41 Newman projections for the staggered and eclipsed conformations resulting from rotation about the C3-C4 bond in butane.



Staggered



Eclipsed

Butane. In contrast to propane, the C-C bonds in *butane* are not all equivalent to each other. While C1-C2 is equivalent to C3-C4, these two bonds differ from the C2-C3 bond. [graphic 2.40] The conformations arising from rotation about C3-C4 (or C1-C2) of butane are similar to those that we showed for propane in Figure [graphic 2.39] except that a CH_3CH_2 group replaces CH_3 on the front carbon. [graphic 2.41]

As a result, the energy diagram for rotation about C3-C4 (or C1-C2) of *butane* has the same appearance as that of propane (or ethane), and the relative energies of these eclipsed forms of butane and of propane (Figures [graphic 2.39} and [graphic 2.41]) are both 14 kJ/mol. Although the CH_3CH_2 group is larger than CH_3, CH_3CH_2 can rotate so that it appears, to the C-H bonds on the other carbon, to be almost the same size as CH_3 . [graphic 2.41a]

In contrast, rotation about C2-C3 in butane has a more complex energy diagram. [graphic 2.42] While the eclipsed forms all have higher energies than the staggered forms, there are two different *staggered* and two different *eclipsed* forms. We will explain this in the next section after we first consider all of the factors that determine the relative energies of conformations.

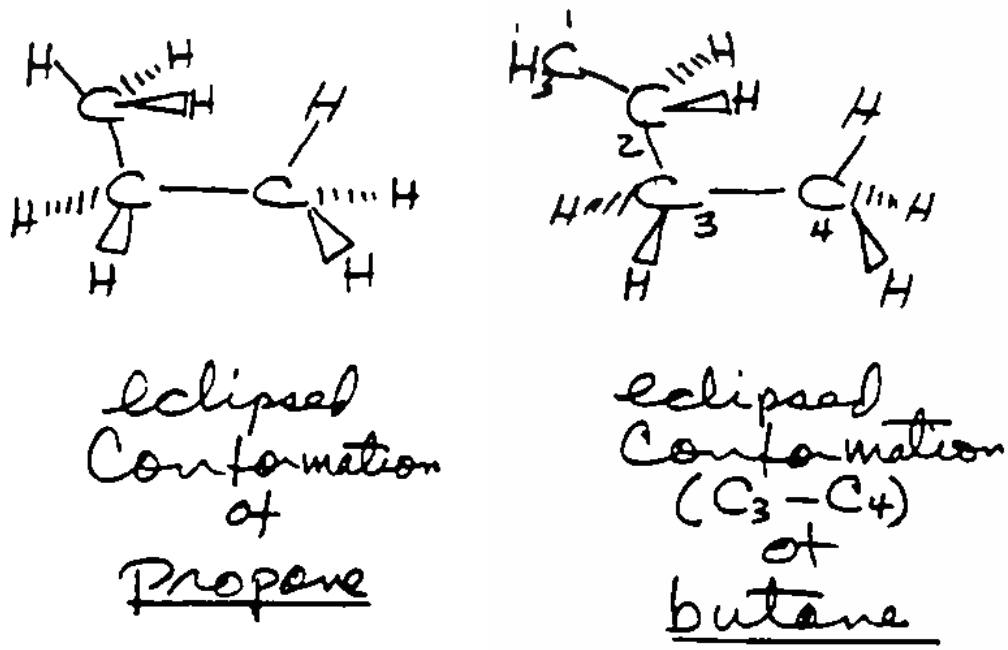
Torsional Strain and Steric Strain (2.4D)

The relative energy of any conformation is the sum of its **torsional strain** and **steric strain**. Eclipsed conformations of a molecule always have higher energies than its staggered conformations because of *torsional strain*. In contrast, energy differences among a group of eclipsed conformations, or among a group of staggered conformations for a molecule, are due to differences in *steric strain*.

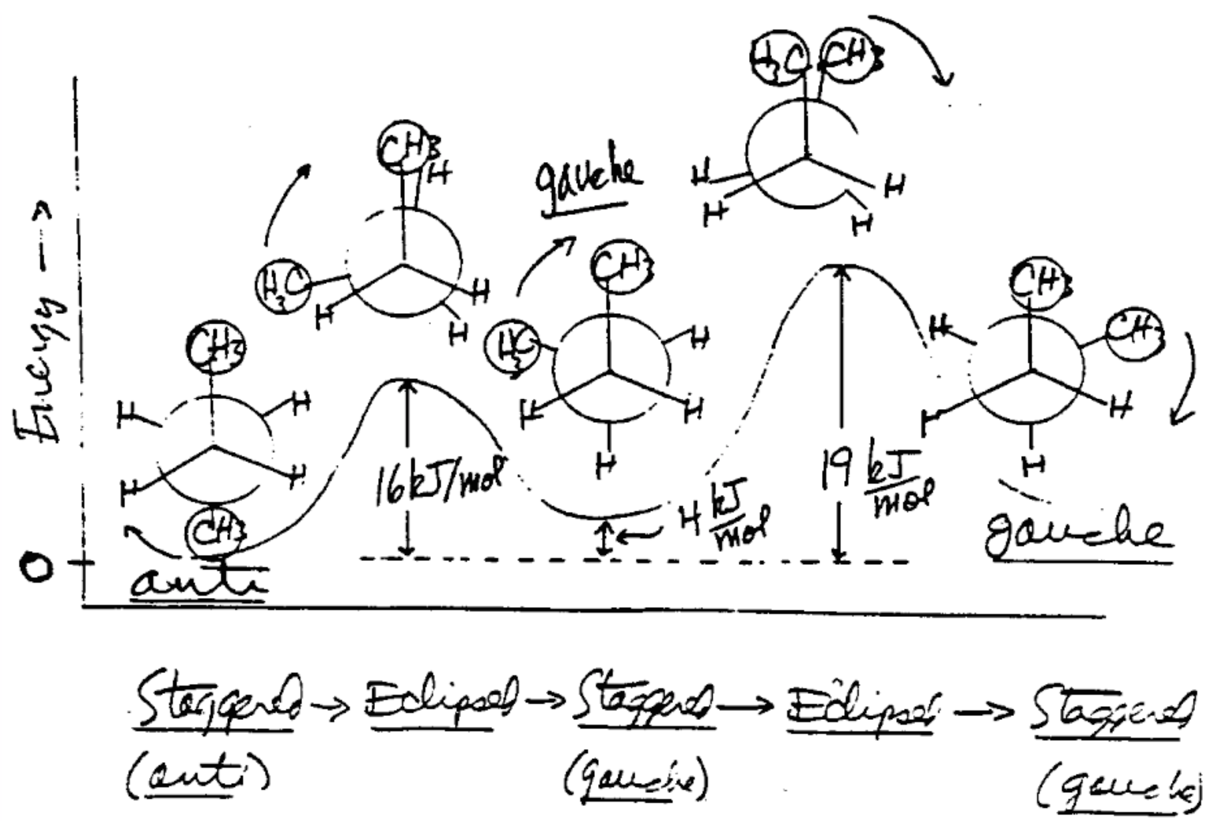
Torsional Strain. *Torsional strain* arises from the close approach of *electron pairs* in eclipsed chemical bonds on adjacent atoms and is present in any eclipsed conformation. Molecules prefer to be in staggered conformations where there is no torsional strain. We assign the 12 kJ/mol energy difference between eclipsed and staggered ethane (Figure [graphic 2.36]) as the *torsional strain* in any eclipsed conformation of an alkane.

Steric Strain. The higher energies of eclipsed conformations of *propane* (14 kJ/mol) or *butane* (14 or 16 or 19 kJ/mol), compared to those of eclipsed *ethane* (12 kJ/mol), are the result of *steric strain* in addition to the 12 kJ/mol of *torsional strain*. The C2-C3 eclipsed conformation of butane with two eclipsed methyl groups (Figure [graphic 2.42]) has a relative energy of 19 kJ/mol compared to the lowest energy staggered conformation of butane.

2.41a



2.42 An energy diagram for the conformations resulting from rotation about the C2-C3 bond in butane. The Newman projections of these conformations are also shown.



Since 12 kJ/mol of this 19 kJ/mol of relative energy is *torsional strain*, this eclised conformation has 7 kJ/mol of *steric stain* (7 kJ/mol$_{\text{(steric strain)}}$ = 19 kJ/mol$_{\text{(total strain energy)}}$ - 12 kJ/mol$_{\text{(torsional strain)}}$). This 7 kJ/mol of *steric strain* energy arises from the CH_3---CH_3 eclipsing interaction that places the H atoms on one CH_3 group in the space required by the H atoms on the other CH_3. [graphic 2.43]

The other type of C2-C3 eclipsed conformation of butane (Figure [graphic 2.42]) has a relative energy of 16 kJ/mol. Since 12 kJ/mol of this energy is *torsional strain*, there is 4 kJ/mol of *steric strain* (4 kJ/mol$_{\text{(steric strain)}}$ = 16 kJ/mol$_{\text{(total strain energy)}}$ - 12 kJ/mol$_{\text{(torsional strain)}}$). This steric strain arises from interference between the H's on the CH_3 groups with the H's on the eclipsed C-H bonds in the two CH_3---H eclipsing interactions. [graphic 2.44]

These steric strain energies show that one CH_3---CH_3 eclipsing interaction (7 kJ/mol) is much worse energetically than one CH_3---H eclipsing interaction (2 kJ/mol = 4 kJ/mol/2). Additional evidence that a CH_3---H eclipsing interaction leads to 2 kJ/mol of steric strain is provided by a comparison of the data for proane and ethane. The eclipsed conformation of propane (14 kJ/mol) with one CH_3---H eclipsing interaction is 2 kJ/mol higher in energy than the the eclipsed conformation of ethane (12 kJ/mol) which has only H---H eclipsing interactions (only *torsional strain*).

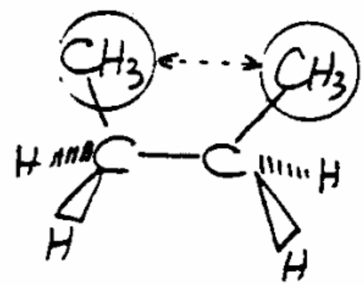
Anti and Gauche Staggered Conformations (2.4E)

Since *staggered* conformations have no eclipsed bonds, they have no *torsional* strain. However staggered conformations may have *steric* strain. For example, steric strain causes the energy of the ***gauche*** staggered conformation of *butane* (Figure [graphic 2.42]) to be 4 kJ/mol higher than that of its ***anti*** staggered conformation.

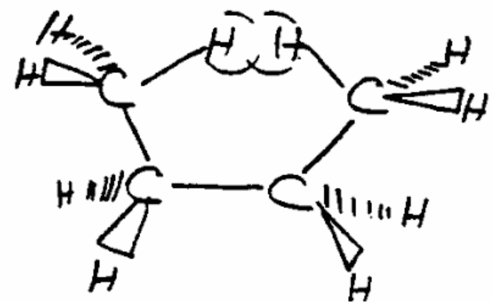
Anti Conformation. Organic chemists use the term *anti* to refer to the *staggered* butane conformation with the CH_3 groups on C2 and C3 as far from each other as possible (Figure [graphic 2.42]). This is because the CH_3's are "opposite" (*anti*) or "opposed" to each other. There is no *steric* strain between CH_3's in this conformation because they are so far apart.

Gauche Conformation. In contrast, the two methyl groups attached to the C2-C3 bond are closer together in the *gauche* (or **skew)** *staggered* conformation (Figure [graphic 2.42]) so named because *gauche* is a French word that means "not plane", "twisted", or "skew". *Steric* strain arising from interaction between "gauche" methyl groups causes the *gauche* staggered conformation to have an energy that is 4 kJ/mol higher than that of the *anti*

2.43

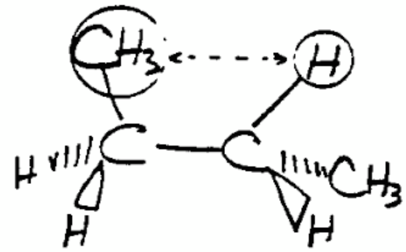


or

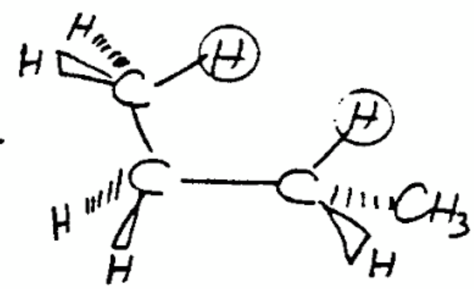


Eclipsed CH_3 Groups
Very Unfavorable
(+19 kJ/mol)

2.44

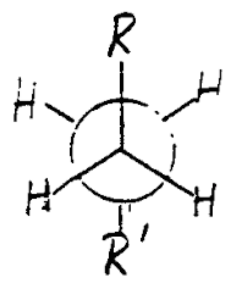


or

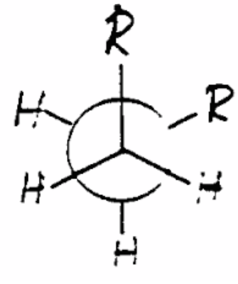


CH_3 and H Eclipsed
Less Unfavorable
(+16 kJ/mol)

2.45 Staggered conformations resulting from rotation about the indicated C-C bond of the general structure of an alkane (RCH_2-CH_2R').



RCH_2–CH_2R'



anti
R and R'

gauche
R and R'

staggered conformation. We will use the terms *gauche* and *anti* to describe the relationship, in *staggered* conformations, between any two groups attached to opposite ends of a C-C bond. [graphic 2.45]

Why Do "Unstable" Conformations Exist? Why don't molecules exist exclusively in their lowest energy (most stable) conformations? Why do molecules rotate about their C-C bonds and pass through unfavorable eclipsed conformations? Why do molecules exist in both higher energy *gauche* and lower energy *anti* conformations? The answer is that there is sufficient **thermal energy**, at any temperature above absolute zero (0 Kelvin), to cause rotation to occur about single chemical bonds. That *thermal energy* causes molecules to pass through eclipsed forms as they oscillate between staggered forms. It also allows molecules to exist in all possible staggered conformations although more stable staggered forms are always present in greater amounts than less stable staggered forms.

2.5 Conformations of Cycloalkanes

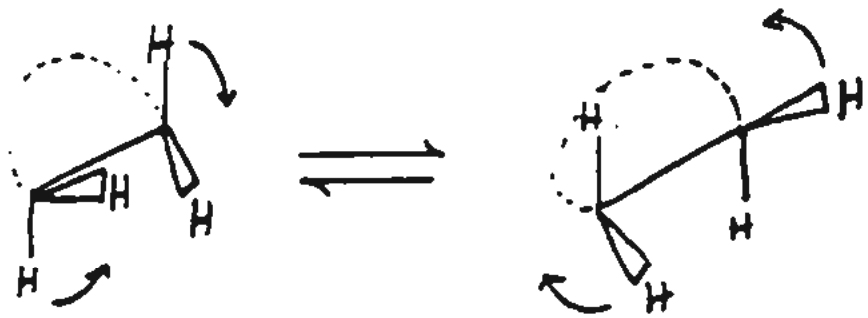
Cycloalkanes also have staggered and eclipsed conformations, but they have fewer conformational possibilities than alkanes because their rings prevent full 360° rotation about ring C-C bonds. Rotational motions about C-C bonds in rings are primarily back and forth **rocking** motions shown in Figure [graphic 2.46]. [graphic 2.46] The geometric constraints of a ring also produce **angle strain**. *Angle strain* results when C-C-C bond angles are significantly different from 109.5°. The most favorable conformations of cycloalkanes reflect a balance between their *torsional* strain, *steric* strain, and *angle* strain .

Cyclopropane, Cyclobutane and Cyclopentane (2.5A)

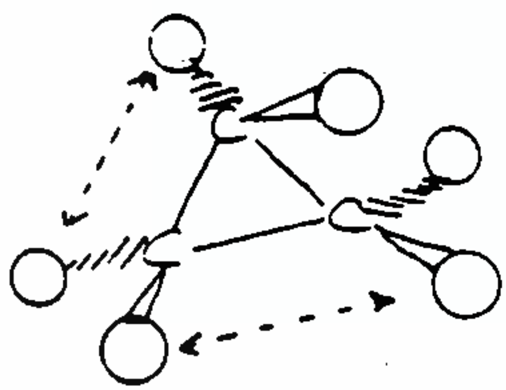
Cyclopropane has very high *angle strain* because its three C atoms are in the same plane and must have 60° bond angles. *Torsional strain* is also at a maximum because each C-H bond is fully eclipsed. [graphic 2.47] In spite of all this strain, *cyclopropane* exists as a stable molecule. However, we will see in later chapters that cyclopropane rings are more chemically reactive than those of larger cycloalkanes.

Cyclobutane and **cyclopentane** have less *angle* strain and less *torsional* strain than *cyclopropane*. They are not planar and their so-called **ring puckering** decreases their torsional strain because it partially staggers adjacent C-H bonds. [graphic 2.48] Unlike cyclopropane, *cyclobutane* and *cyclopentane* continually flex between different conformations. [graphic 2.49] In *cyclopentane*, the pucker in its ring (often compared to the flap of an envelope) moves around the ring allowing eclipsed C-H bonds on the C-C bond opposite the "flap" to periodically become partially staggered.

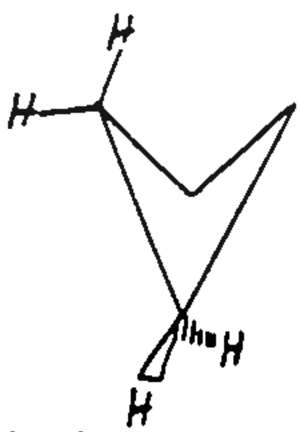
2.46 Rotation about the C-C bond in a ring causes the attached C- H bonds to rock back and forth between different conformations.



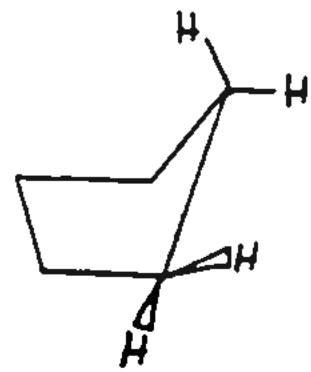
2.47 3-D structure of cyclopropane showing that all attached groups are eclipsed.



2.48

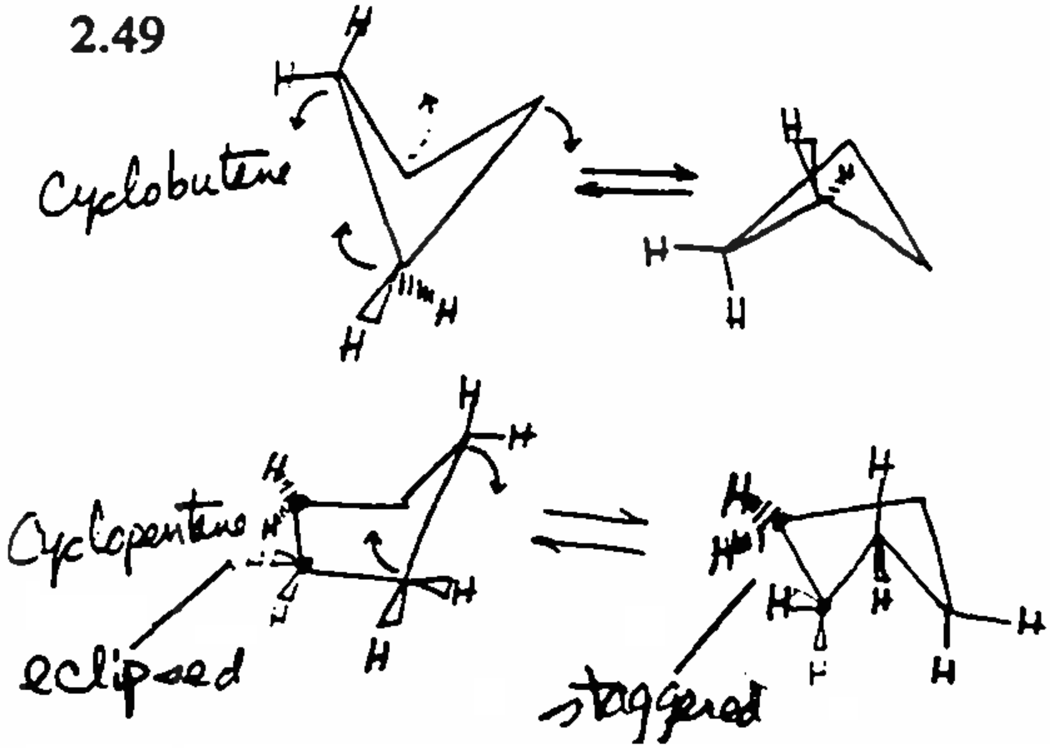


Cyclobutane

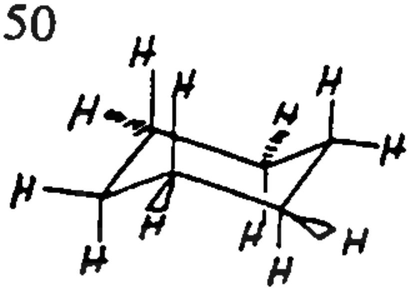


Cyclopentane

2.49

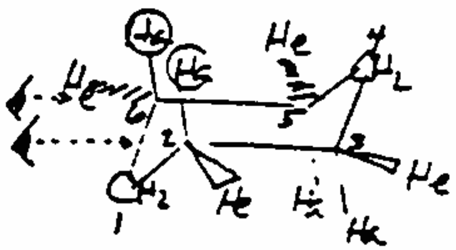


2.50

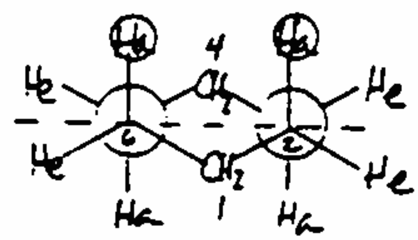


Chair Conformation of Cyclohexane

2.51 Cyclohexane chair conformations and "Newman-type" projection resulting from simultaneously looking down the C2-C3 and C6-C5 bonds.



Chair form



Newman-type Projection

Cyclohexane (2.5B)

Among all of the cycloalkanes, *cyclohexane* best achieves tetrahedral bond angles and staggered bonds by adopting **chair conformations**. [graphic 2.50] If you look along (down) any of the six C-C bonds in one of these *chair conformations* (such as the C2-C3 or C6-C5 bonds shown in Figure [graphic 2.51]), you see that all of the bonds on each C-C are fully staggered. [graphic 2.51]

The *Newman projection* represents the view that you see when looking at both the C2 and C6 carbons (looking down the C2-C3 and C6-C5 bonds) at the same time. Since all C-H and C-C bonds in the chair conformation of cyclohexane are staggered, it has no torsional strain. In addition, because the C-C-C angles are almost tetrahedral, it has virtually no angle strain.

Strain in Different Cycloalkanes. The energy released **(-Δ_cH)**, when a cycloalkane (C_nH_{2n}) undergoes complete reaction with oxygen (combustion), to form CO_2 and H_2O, provides information about the amount of strain (strain energy) in the cycloalkane.

$$C_nH_{2n} + 1.5n\ O_2 \rightarrow n\ CO_2 + n\ H_2O + \textit{Energy } (-\Delta_c H)$$

That **Energy of Combustion** (-Δ_cH) for each cycloalkane (Table 2.5) reflects not only the energy change for conversion of the C-H and C-C bonds (and O-O bond in O_2) to C-O and H-O bonds, but also the *torsional*, *steric*, and *angle* strain released when the ring breaks.

Table 2.5. Energies of Combustion (-Δ_cH) and Strain for Cycloalkanes.

Cycloalkane (C_n)	Energy of Combustion (-Δ_cH)(kJ/mol)	-Δ_cH/n (kJ/mol)	"Strain" (kJ/mol)
cyclopropane (C_3)	2091	697	38
cyclobutane (C_4)	2746	687	28
cyclopentane (C_5)	3320	664	5
cyclohexane (C_6)	3953	659*	(0)
cycloheptane (C_7)	4637	663	4
cyclooctane (C_8)	5310	664	5

*Reference value for comparison of relative strain ("Strain" = (-Δ_cH/n) - 659).

In order to directly compare cycloalkanes of different ring size, we must divide the *Energy of Combustion* (-Δ_cH) by *n* (the C_n ring size). This corrects for the different numbers of C-C and C-H bonds in each alkane. The resulting values of -Δ_cH/n are the amount of energy released *per CH_2 group* in each alkane and they each include a component due to strain release. The energy values in the last column are the relative amount of "Strain" *per* CH_2 group in each cycloalkane compared to that in cyclohexane. They correspond to [(-Δ_cH/n) - 659] where 659 kJ/mol is the value of -Δ_cH/n for cyclohexane. This "strain" is greatest for cyclopropane, decreases steadily from cyclopropane to cyclohexane, and then increases slightly for cycloheptane and cyclooctane.

Axial and Equatorial Hydrogens. We have labelled H atoms as H_a or H_b in the chair conformation of cyclohexane and its Newman projection (Figure [graphic 2.51]). You can see that H_a hydrogens (called **axial** H's) point straight *up* or *down* from the dashed line and those on any two adjacent carbon atoms are *anti* to each other. In contrast, H_e hydrogens (called **equatorial** H's) on any two adjacent carbons point out around the edge of the molecule and are *gauche* to each other. All H's in cyclohexane are either *axial* or *equatorial* as shown here. [graphic 2.52]

Axial, Equatorial and Chair. We refer to H_a's as *axial* because their C-H bonds are parallel to an imaginary axis through the center of a cyclohexane ring and perpendicular to the plane of the ring. The H_e's are called *equatorial* because they surround the cyclohexane ring as if they were lying on its imaginary equator. The origin of the term *chair* is self-explanatory.

Drawing Cyclohexane Chair Conformations. You can use the stepwise procedure in Figure [graphic 2.53] to draw chair conformations. [graphic 2.53]

(1) *Draw the ring skeleton of the chair as shown in steps 1a and 1b.*

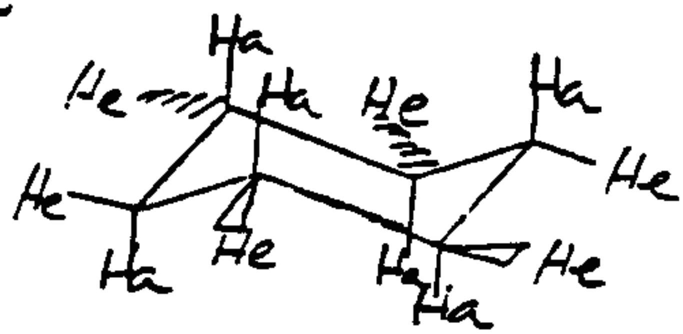
(2) *Add a C-H_a bond pointing straight up on each "up" ring carbon (step 2a), and straight down on each "down" ring carbon (step 2b).*

(3) *Add a C-H_e bond to each ring carbon pointing sideways away from the ring (step 3).*

It is important to draw the carbon skeleton of the chair (steps 1a and 1b), and then add all of the *axial* hydrogens (H_a)(steps 2a and 2b), before placing the *equatorial* H's (H_e) around the ring (step 3). You have some flexibility as to where you draw equatorial H's (H_e), but all of the axial H's (H_a) need to clearly point up and down alternately in the pattern on the ring that we show in step 2b.

C-C Rotation in Cyclohexane (Ring Flipping). Cyclohexane is a flexible molecule in which partial rotations about all of its C-C bonds transform one staggered *chair* conformation into another staggered *chair* conformation by way of higher energy intermediate conformations with eclipsed bonds. Organic chemists refer to these chair-chair interconversions as **ring-flipping** and we illustrate the overall result of this process in Figure [graphic 2.54]. [graphic 2.54] We have removed the designations H_a and H_e and have

2.52

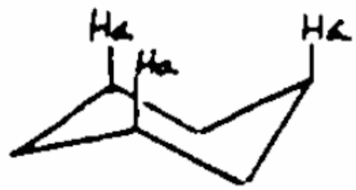


2.53 A stepwise procedure for drawing chair conformations of cyclohexane.

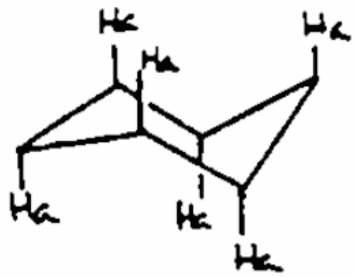
(1a)

(1b)

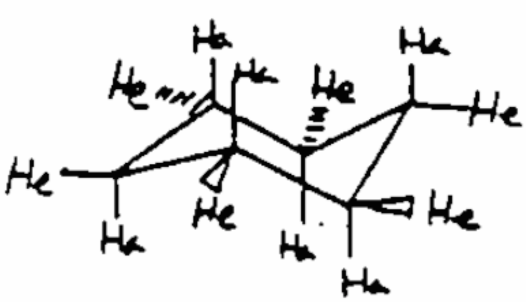
(2a)



(2b)

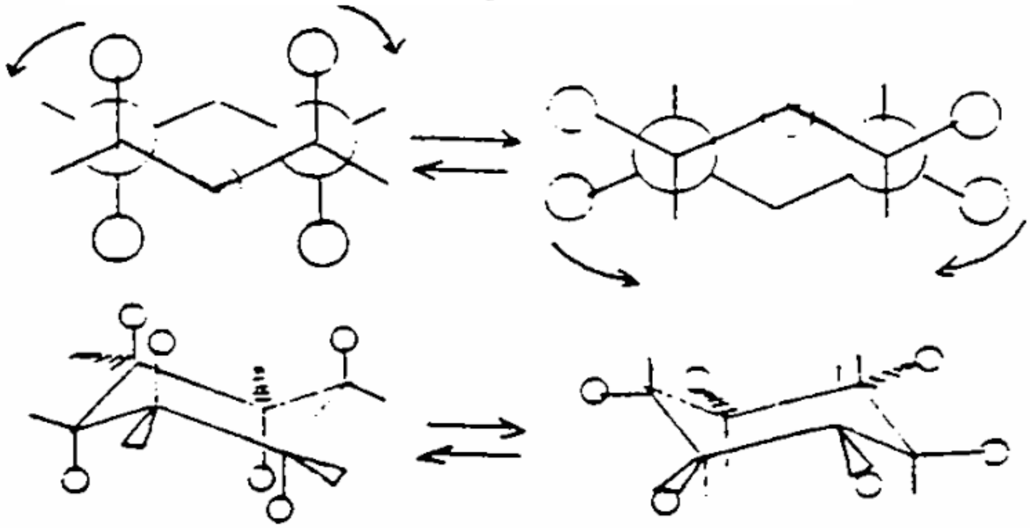


(3)

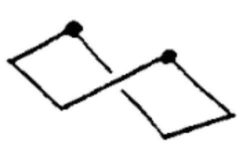


Note- Use Color to distinguish the changes in each step.

2.54 Ring-flipping of cyclohexane chair conformations causes groups attached to the ring to exchange their positions.



2.55

Structure	Conformation Name (Relative energy)
	Chair Conformation (+ 0 kJ/mol)
	Half-Chair Conformation (+45 kJ/mol)
	Boat Conformation (+28 kJ/mol)
	Twist-Boat Conformation (+23 kJ/mol)

replaced the *axial* H's in the left hand drawings with small *spheres*. You can see that these spheres move from *axial* to *equatorial* positions during *ring-flipping*. Ring-flipping occurs about 10^5 times per second (100,000 times per second) at normal temperatures and is equivalent to interconversion of two staggered forms of an alkane.

Other Cyclohexane Conformations. The conversion of one *chair* conformation of cyclohexane into another *chair* conformation by *ring-flipping* is a complex process that involves several higher energy conformations of cyclohexane. [graphic 2.55] The relative energies of these conformations show that they are all greater in energy (less stable) than chair conformations. The interconversion of two *chair* forms occurs as shown here:

chair → [half-chair]* → twist-boat → [half-chair]* → chair

The **twist-boat** is an intermediate conformation that forms during ring-flipping. When one chair ring-flips into another chair, the *twist-boat* conformation must be an intermediate. The transformation of a chair into a twist-boat or *vice-versa* proceeds by way of a high energy conformation called the **half-chair**. The following energy diagram illustrates the energy changes for this series of reactions. [graphic 2.56]

The intermediate *twist-boat* conformation is very flexible and it interconverts with other *twist-boat* conformations by a process called **pseudorotation**.

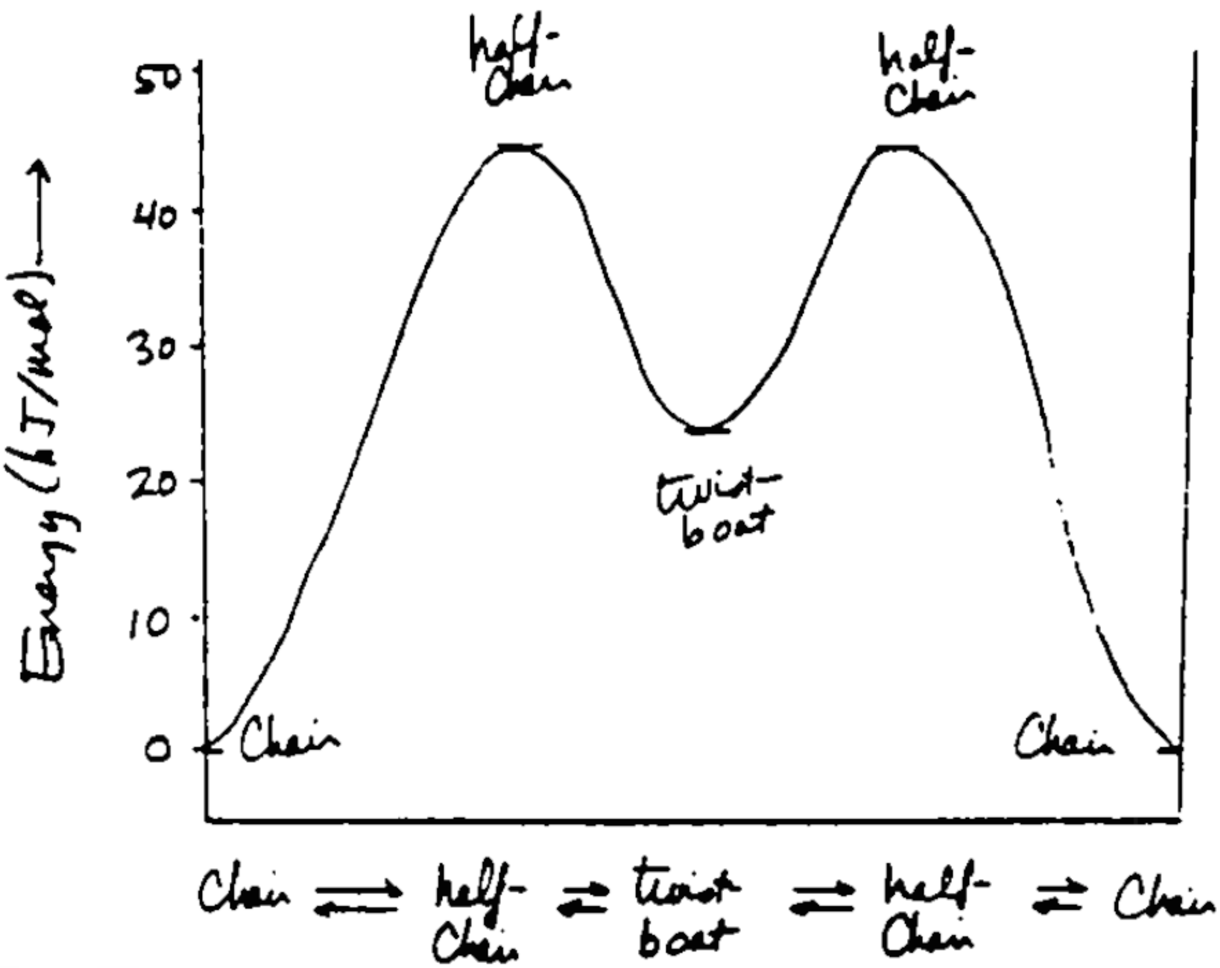
twist-boat → [boat]* → twist-boat → [boat]* → twist-boat

The **boat** conformation is a high energy conformation that the cyclohexane ring must pass through as one *twist-boat* converts to another *twist-boat*. [graphic 2.57] Although the *boat* conformation has unstrained tetrahedral angles, it has very high *torsional* strain due to eclipsing of C-H and C-C bonds, and high *steric* strain due to interactions between the "inside" ("**flagpole**" H's on C1 and C4. As a result, it is about 28 kJ/mol higher in energy (less stable) than a *chair* conformation. The *twist-boat* conformation has a lower energy than the *boat* conformation because its "twist" decreases torsional strain and relieves the sterically unfavorable interactions between the inside H's on C1 and C4 shown in Figure [graphic 2.57]. You can draw a structure of a *half-chair* conformation by flattening one side of a chair conformation of cyclohexane. The best way to picture a *twist-boat* is to make a molecular model of a *boat* conformation and then twist it by pulling the C1 and C4 carbons in opposite directions. [graphic 2.58]

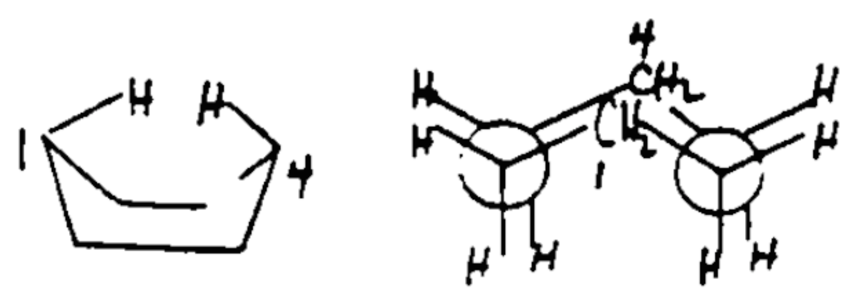
2.6 Conformations of Alkylcyclohexanes

Ring-flipping occurs in cyclohexanes substituted with alkyl groups as well as in unsubstituted cyclohexane. During ring-flipping of alkylcyclohexanes, the alkyl substituents on the ring alternate between equatorial and axial positions.

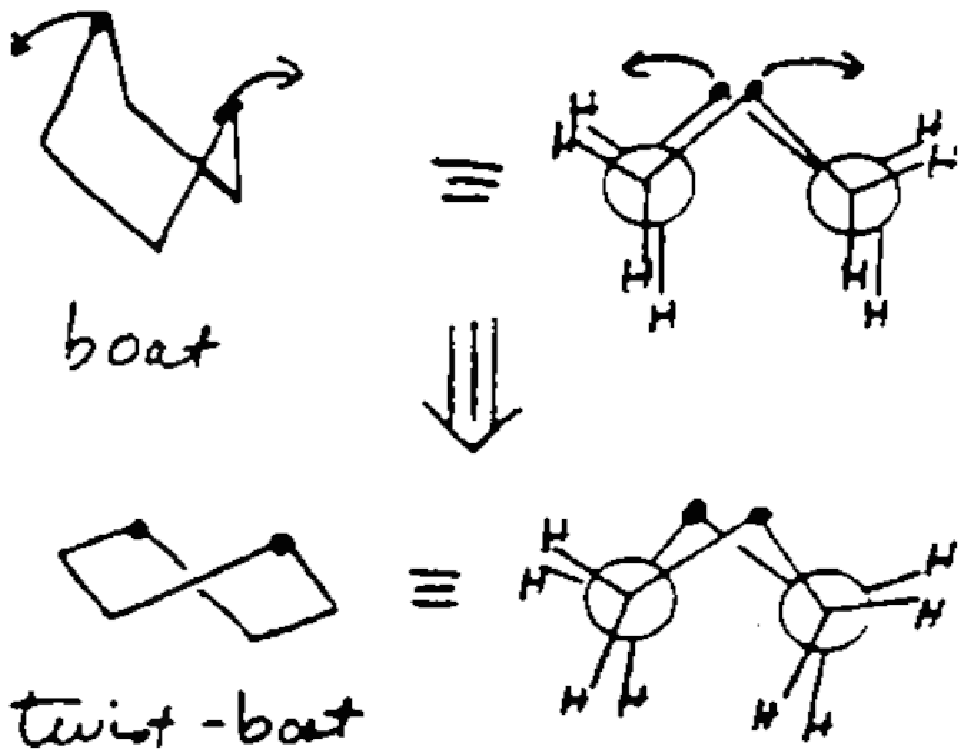
2.56 Energy diagram showing the different conformations of cyclohexane which form during ring-flipping.



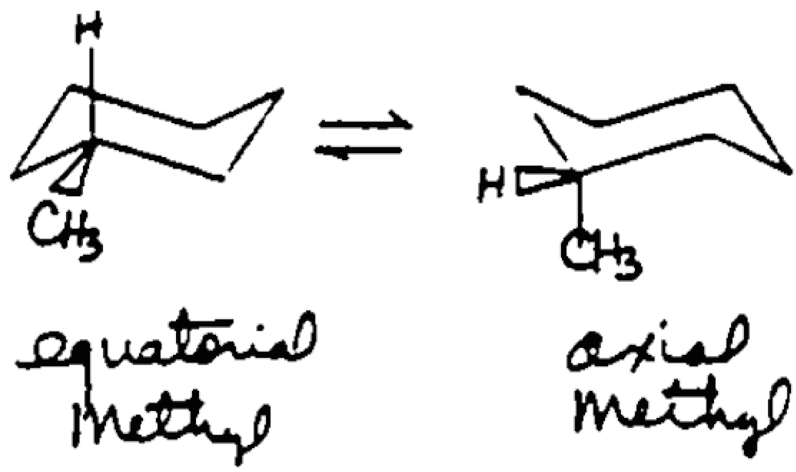
2.57 "boat"



2.58 Formation of twist-boat from boat conformation of cyclohexane.



2.59



Methylcyclohexane (2.6A)

Because of ring-flipping, *methylcyclohexane* is a mixture of a chair conformation with an *equatorial* methyl group and a chair conformation with an *axial* methyl group. [graphic 2.59]

Axial versus Equatorial CH_3. The conformation with *axial* methyl is about 7 kJ/mol higher in energy (less stable) than that with an *equatorial* methyl group. *Newman* projections help explain this energy difference. [graphic 2.60] When the CH_3 shown on the front carbon is equatorial, it is *anti* to the ring CH_2 group on the back carbon. However when the front CH_3 is axial, it is *gauche* to that back CH_2 group. You can also see this in the chair forms of these two conformations. [graphic 2.61] The axial CH_3 is close to the axial H on C3 (and C5), but an equatorial CH_3 is far away from these H's and other atoms on the other side of the ring.

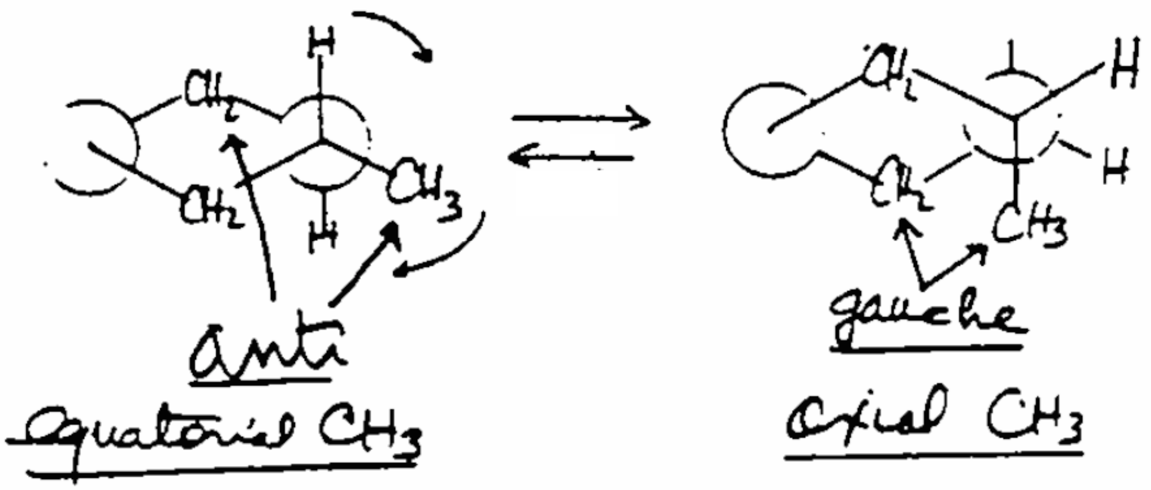
Conformational Mixture. Although methylcyclohexane is a mixture of the *axial* methyl and *equatorial* methyl conformations, we cannot separately isolate these two conformations because they rapidly interconvert by ring-flipping. The mixture of these conformations is the single compound that we call *methylcyclohexane*. This is analogous to *butane* that is a mixture of its *anti* and *gauche* staggered conformations. It is important to understand that the CH_3 group never becomes disconnected from its bonded carbon during interconversions of any of these conformations. No chemical bonds break during ring-flipping since this process involves only partial rotations about C-C bonds.

Other Monoalkylcyclohexanes (2.6B)

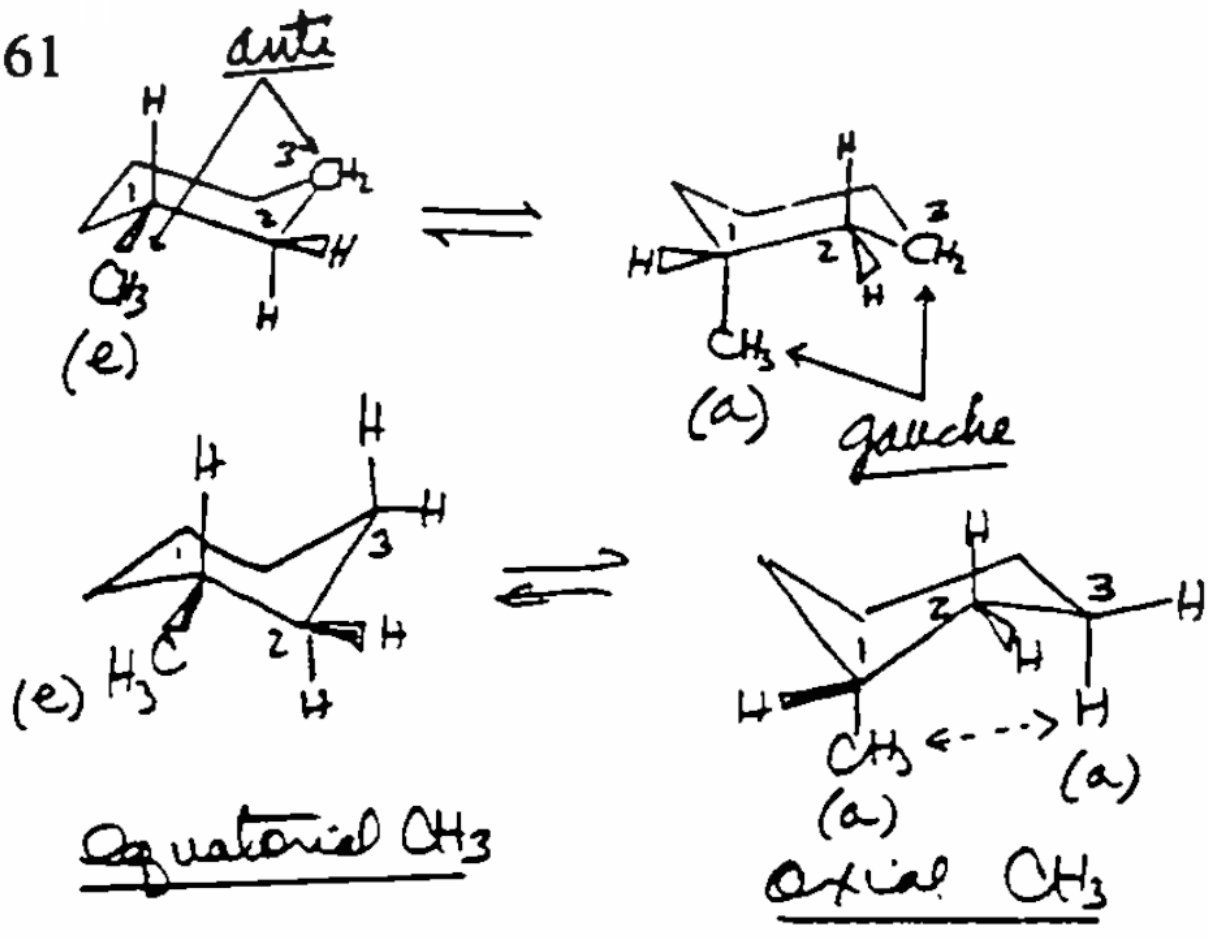
Cyclohexane substituted with an alkyl group other than methyl has an axial and an equatorial conformation analogous to those of *methylcyclohexane*. Any alkyl group (R) on a cyclohexane ring prefers to occupy an equatorial position for the same reasons that cause *equatorial* methylcyclohexane to be more stable than *axial* methylcyclohexane. [graphic 2.62]

Equatorial Preferences. The energy difference between these equatorial and axial conformations of a monoalkylcyclohexane depends on the size of the alkyl group. We refer to the energy differences between cyclohexane conformations with axial *versus* equatorial alkyl groups as **equatorial preferences** (or **A Values**) and show them for different alkyl groups in Table 2.6. The larger the *equatorial preference*, the more the group prefers to be in the equatorial position.

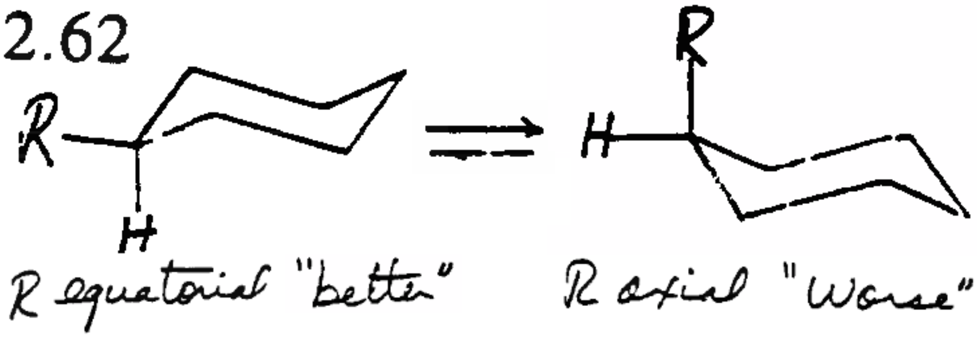
2.60 "Newman-type" projections of methylcyclohexane showing CH3 in equatorial and axial positions.



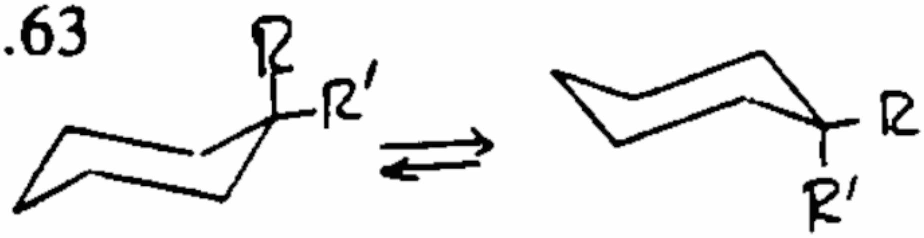
2.61



2.62


R
H
R
H
R equatorial "better"
R axial "worse"

2.63


R
R'
R
R'

2.64

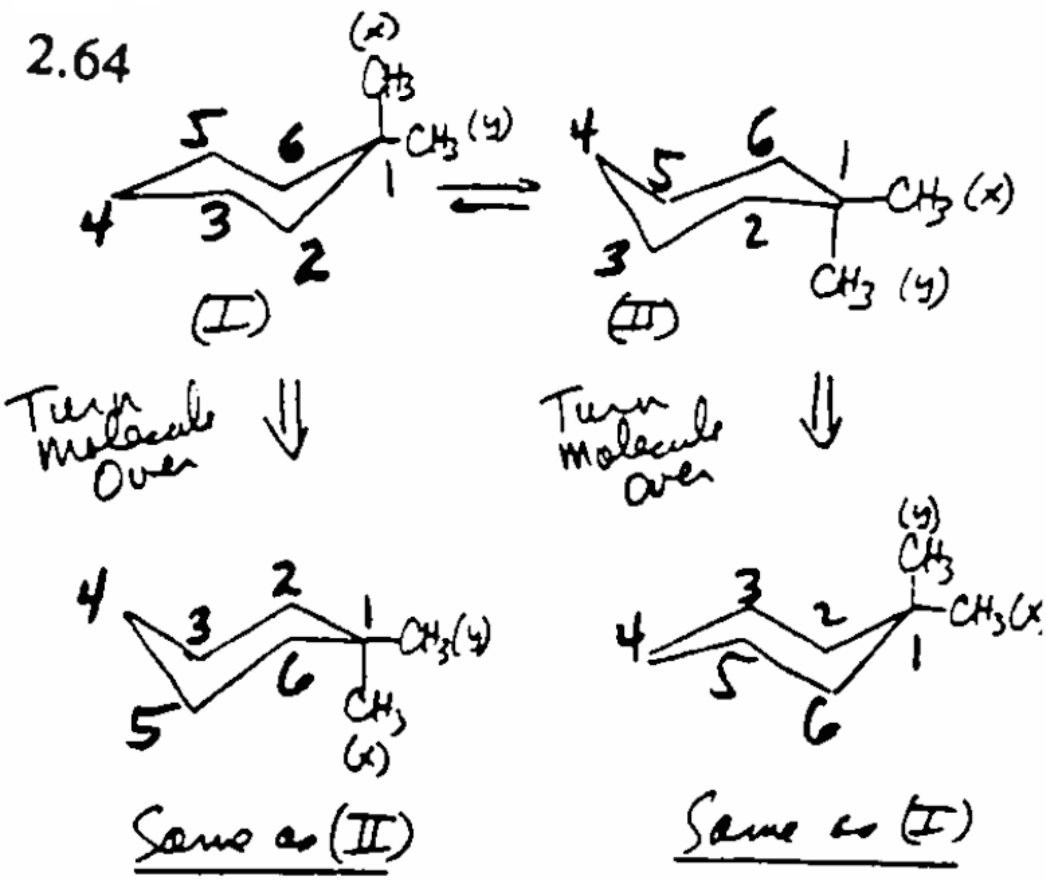

(x)
CH3
CH3 (y)
5
6
1
4
3
2
(I)
4
5
6
1
CH3 (x)
3
2
CH3 (y)
(II)
Turn Molecule Over
Turn Molecule Over
4
2
1
3
CH3(y)
6
5
CH3
(x)
(y)
CH3
3
2
CH3(x
4
1
5
6
Same as (II)
Same as (I)

Table 2.6. Equatorial Preferences (A Values) for Alkyl Groups on Cyclohexane.

Alkyl Group	Equatorial Preference (kJ/mol)*	%Equatorial Conformation (25°)
methyl	7.3	95.0
ethyl	7.5	95.4
i-propyl	9.3	97.7
t-butyl	20	>99.9

*(E_{axial} - $E_{equatorial}$)

Methyl *versus* Ethyl. The equatorial preference for CH_3CH_2 is almost identical to that for CH_3 because the CH_3CH_2 group can rotate (Figure [graphic 2.41a]) away from *gauche* atoms in order to minimize its steric strain. As a result, CH_3 and CH_3CH_2 are comparable in size with respect to these *gauche* interactions such as those shown for CH_3 in Figures [graphic 2.60] and [graphic 2.61]. We saw this same effect earlier with respect to rotation about the C1-C2 bond in butane.

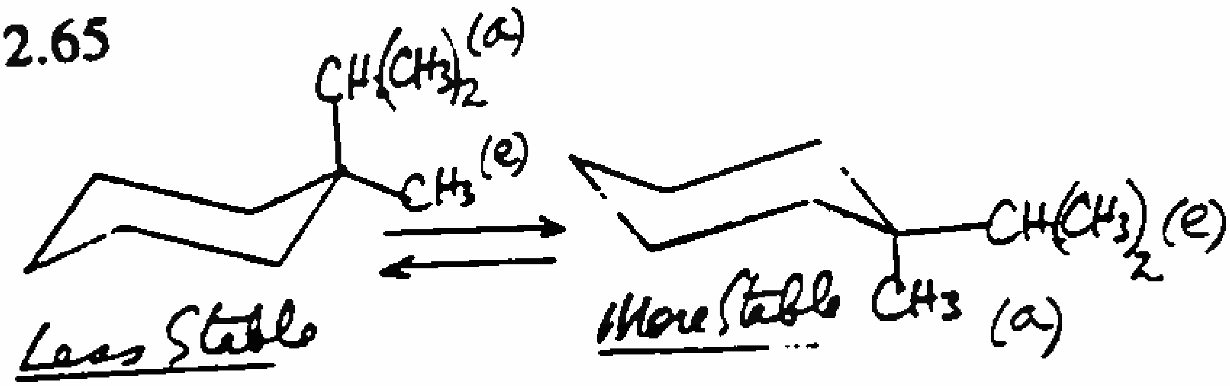
Conformations of Dialkylcyclohexanes (2.6C)

The **conformational analysis** of dialkylcyclohexanes is more complex than that we have just described for monoalkylcyclohexanes. The number of possible conformations for dialkylcyclohexanes depends on the nature of the two alkyl groups and their relative locations on the ring.

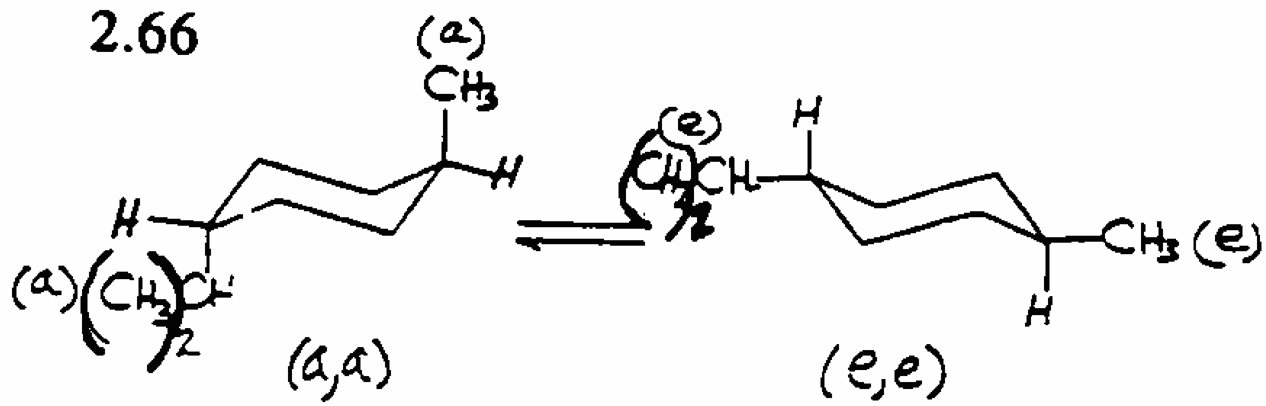
1,1-Dialkylcyclohexanes. When both alkyl groups are on the same carbon, one of them must be *axial* when the other is *equatorial*, and ring-flipping interchanges their positions. [graphic 2.63] When the two R groups are identical as in dimethylcyclohexane (R = R' = CH_3), ring flipping gives chair conformations that are all identical to each other and therefore have the same energy (stability). [graphic 2.64]

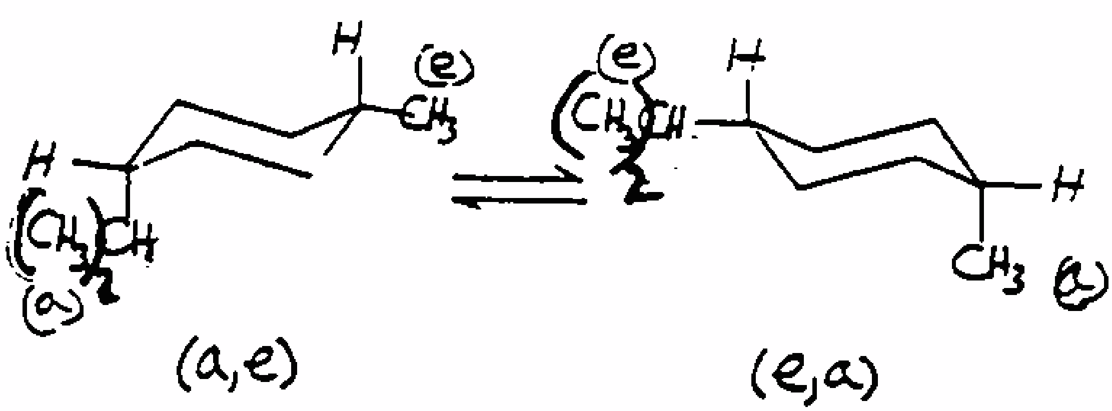
However when the two alkyl groups are not the same, as in *1-isopropyl-1-methylcyclohexane*, ring-flipping gives conformations that have different energies (stabilities). [graphic 2.65] The chair conformation with *axial* $(CH_3)_2CH$ and *equatorial* CH_3 is less stable than that conformation where CH_3 is *axial* and $(CH_3)_2CH$ is *equatorial*. The isopropyl group is larger than the methyl group and has a greater *equatorial preference* (Table 2.6). In spite of their differences in energy, the two chair conformations rapidly interconvert. As a result they are not separable and 1-isopropyl-1-methylcyclohexane is a single chemical compound made up of a mixture of two conformations analogous to the conformational mixture of methylcyclohexane.

2.65


$CH(CH_3)_2$ (a)
CH_3 (e)
Less Stable
$CH(CH_3)_2$ (e)
More Stable
CH_3 (a)

2.66


(a)
CH_3
H
H
(a) $(CH_3)_2CH$
(a,a)
(e)
H
$(CH_3)_2CH$
CH_3 (e)
H
(e,e)


H
(e)
CH_3
H
$(CH_3)_2CH$
(a)
(a,e)
(e)
H
$(CH_3)_2CH$
H
CH_3 (a)
(e,a)

1,4-Dialkylcyclohexanes. In contrast to 1,1-dialkylcyclohexanes, any 1,4-dialkyl-cyclohexane has the potential to exist as two different compounds. As an example, lets consider 1-isopropyl-4-methylcyclohexane. Its isopropyl and methyl groups can each occupy either an axial (*a*) or an equatorial (*e*) position on their ring carbons, so we can draw structures for four possible chair conformations. [graphic 2.66] In the **(*a,a*)-conformation**, $(CH_3)_2CH$ and CH_3 are both *axial*, while both are *equatorial* in the **(*e,e*)-conformation**. Ring-flipping interconverts these *(a,a)* and *(e,e)* conformations so they are in *equilibrium* with each other.

In addition to these *(a,a)* and *(e,e)* conformations, there is an **(*a,e*)-conformation** with *axial* $(CH_3)_2CH$ and *equatorial* CH_3. We can ring-flip this conformation to give the **(*e,a*)-conformation** with *equatorial* $(CH_3)_2CH$ and *axial* CH_3. As a result, the (a,e) and (e,a) conformations are in equilibrium with each other. However, it is not possible by ring-flipping to convert either the (*a,a*) or the (*e,e*) conformation to either the (*a,e*) or the (*e,a*) conformation.

As a result, the equilibrium mixture of (*a,a*) and (*e,e*) conformations is a single compound that we will designate **(*a,a/e,e*)**. The equilibrium mixture of (*a,e*) and (*e,a*) conformations is a different compound that we will designate **(*e,a/a,e*)**. This means that 1-isopropyl-4-methy-lcyclohexane can be the two different compounds (*a,a/e,e*) and (*e,a/a,e*) that do not interconvert with each other by ring-flipping.

Molecular Configurations of 1-Isopropyl-4-methylcyclohexane. Since ring-flipping cannot convert the (*a,a/e,e*) conformational mixture into the (*e,a/a,e*) conformational mixture of 1-isopropyl-4-methylcyclohexane, we say that the (*a,a/e,e*) conformations have a different **molecular configuration** than the (*e,a/a,e*) conformations. Different *molecular configurations* of a compound have identical components bonded to each other at the same atoms, but they differ with respect to the 3-dimensional arrangements of their atoms in space. Different *molecular configurations* can only interconvert by breaking and remaking one or more chemical bonds. As a result, the two different molecular configurations of 1-isopropyl-4-methylcyclohexane are two different compounds and we will see shortly that we must give them different names.

1,2- and 1,3-Dialkylcyclohexanes. The *conformational analysis* of 1,2- or 1,3-dialkylcyclohexanes is analogous to that we just described for the 1,4-dialkylcyclohexane *1-isopropyl-4-methylcyclohexane*. We can bond a methyl and an isopropyl group to C1 and C2, or to C1 and C3, of a cyclohexane ring. Each of these 1,2 or 1,3-dialkylcyclohexanes has an (*e,e*), (*a,a*), (*a,e*), and (*e,a*) conformation similar to those just shown for 1-isopropyl-4-methylcyclohexane. In each of these cases, ring-flipping interconverts only the (*a,a*) and (*e,e*) conformations, and the (*e,a*) and (*a,e*) conformations. [graphics 2.67 and 2.68] As a result, 1-isopropyl-2-methylcyclohexane can be two distinct compounds with different *molecular configurations* that we can designate (*e,e/a,a*) and (*e,a/a,e*), and the same is true for 1-isopropyl-3-methylcyclohexane.

cis and trans Dialkylcycloalkanes (2.6D)

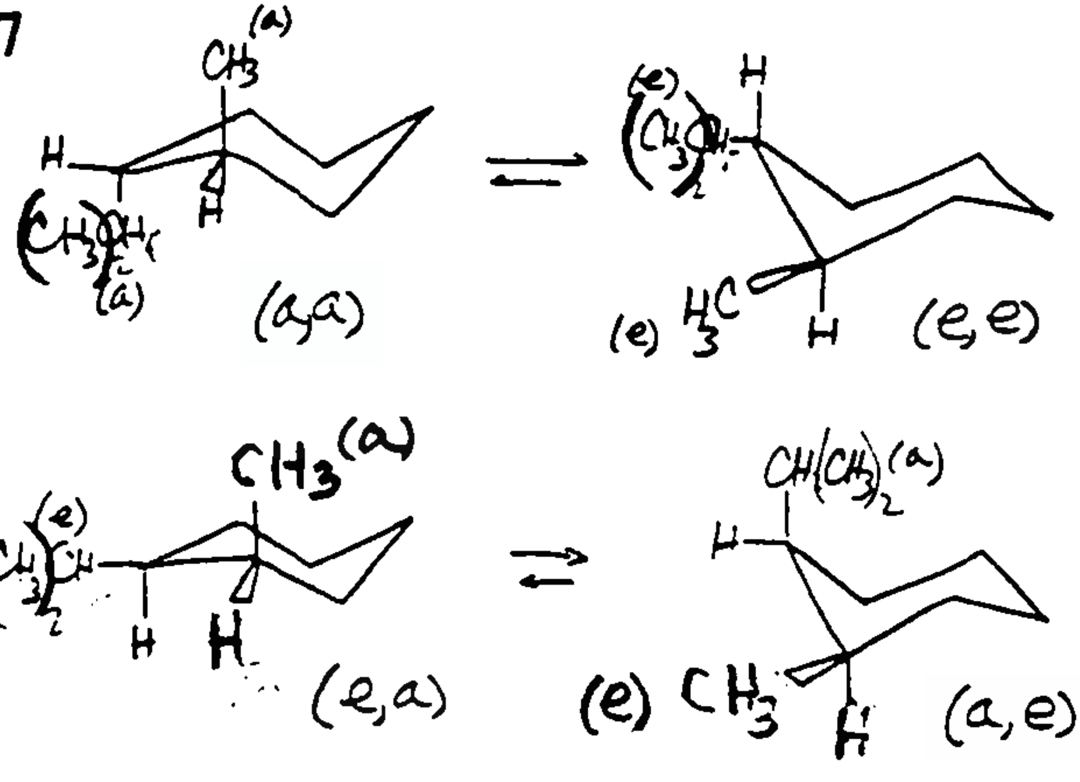
We use the terms ***cis*** and ***trans*** to distinguish these two different molecular configurations for 1,2-, 1,3-, or 1,4-dialkylcyclohexanes. It turns out that all dialkylcycloalkanes <u>with alkyl groups on different C's</u> have *cis* and *trans* configurations. We will first illustrate how these terms are assigned to the two molecular configurations of **1,2-dimethylcyclopropane**, and then assign them to the configurations of the isopropylmethylcyclohexanes.

cis and trans-1,2-Dimethylcyclopropane. *1,2-dimethylcyclopropane* has two different configurations that cannot interconvert. [graphic 2.69] We name the one with the CH_3's on the same side of the ring *cis-1,2-dimethylcyclopropane*, while that with the CH_3's on opposite sides of the ring is *trans-1,2-dimethylcyclopropane*. Organic chemists use these terms because *trans* has a Latin root meaning "across", while *cis* has a Latin root meaning "on this side".

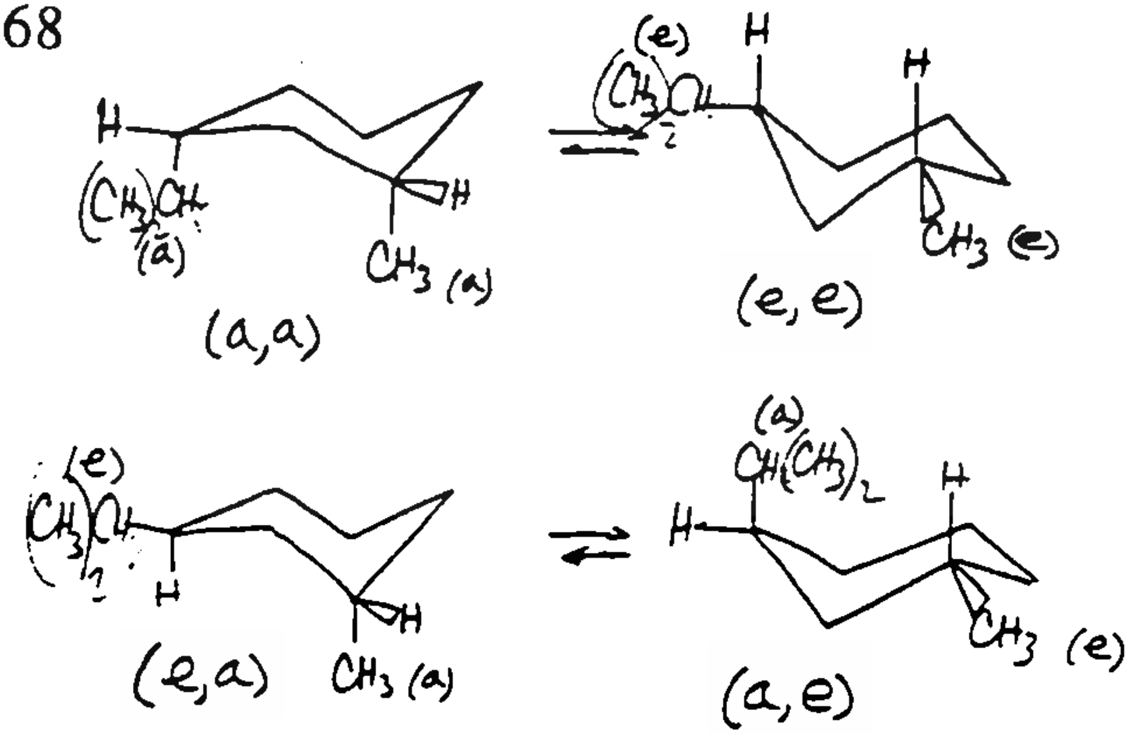
Because a cyclopropane ring is planar and rigid, the *cis* and *trans* configurations of 1,2-dimethylcyclopropane each consist of only one conformation. Although this is not the case for dialkylcyclohexanes, we can still use *cis* and *trans* to distinguish the configurations as we describe below.

cis and trans-1-isopropyl-4-methylcyclohexane. Ring-flipping complicates our assignment of *cis* and *trans* to the two configurations of 1-isopropyl-4-methylcyclohexane. Nonetheless, we assign the term *trans* to the (*e,e/a,a*) mixture because the 1-methyl and 4-isopropyl groups are on <u>opposite</u> sides of the ring (*trans* to each other) in both conformations. You can most easily see the *trans* relationship of these two alkyl groups in the (*a,a*) conformation [graphic 2.70] Since (*a,a*) is in equilibrium with (*e,e*) due to ring-flipping, (*e,e*) is also *trans*. This leaves *cis* for the (*e,a/a,e*) configuration that is an equilibrium mixture of (*e,a*) and (*a,e*) conformations. You can see that the two alkyl groups are on the same side of the ring in each of them. [graphic 2.70a]

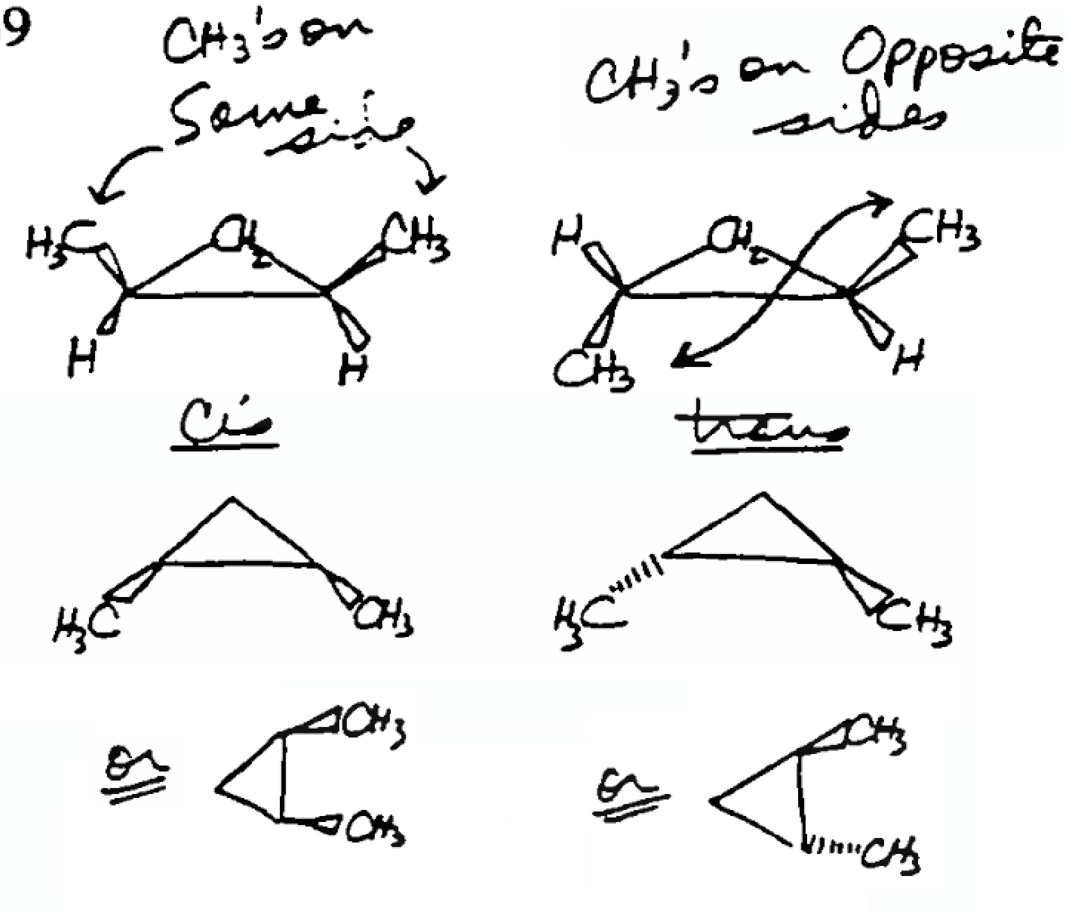
2.67



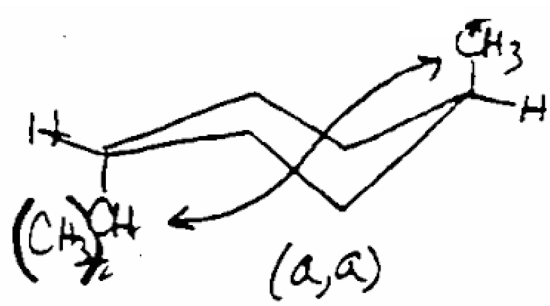
2.68



2.69



2.70. (a,a) Conformation of 1-isopropyl-4-methylcyclohexane

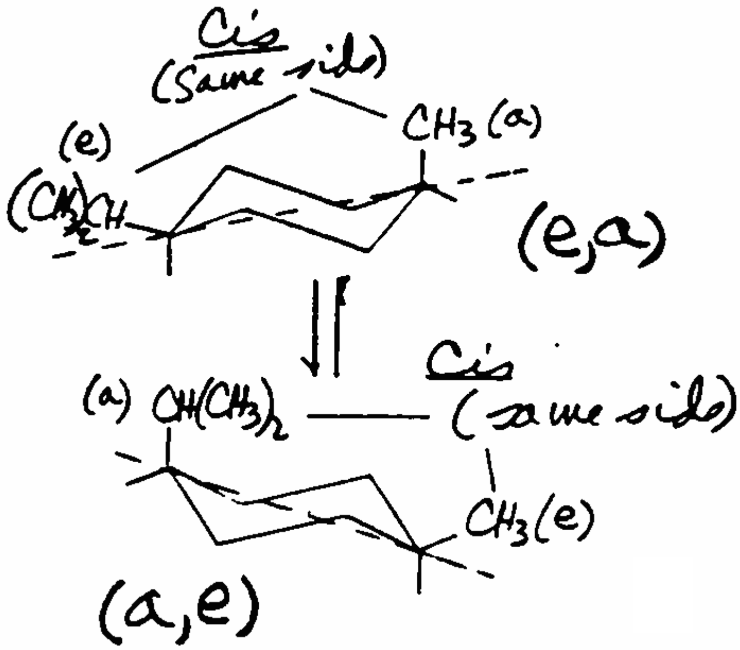


The alkyl groups are trans

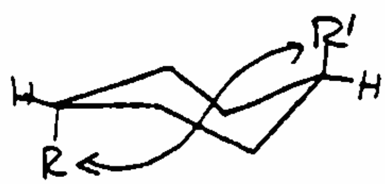
Therefore $(a,a) \rightleftharpoons (e,e)$ } trans

$(a,e) \rightleftharpoons (e,a)$ } cis

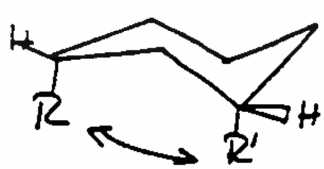
2.70a. (e,a) and (a,e) Conformations of 1-isopropyl-4-methylcyclohexane



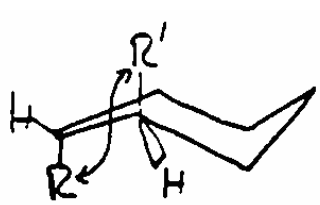
2.71. (a,a) Conformations of Dialkylcyclohexanes

1,4 

R and R' are trans

1,3 

R and R' are Cis

1,2 

R and R' are trans

Use of cis and trans with Other Dialkylcyclohexanes. To assign *cis* and *trans* to the two different configurations of any dialkylcyclohexane with alkyl groups on different C's, first look at the relationship between the two alkyl groups in the (*a,a*) conformation. For any 1,4-dialkylcyclohexane, you can clearly see that the axial alkyl groups are on opposite sides of the ring so (*a,a*) is always *trans*. [graphic 2.71] The same is true for the alkyl groups in the (*a,a*) conformation of 1,2-dialkylcyclohexanes. Since (*a,a*) interconverts with (*e,e*) by ring flipping, (*e,e*) is also *trans* in each of these cases. This leaves the term *cis* for assignment to the (*e,a/a,e*) configuration of both 1,2-dialkylcyclohexanes and 1,4-dialkylcyclohexanes.

In contrast, you can clearly see that the two alkyl groups in the (*a,a*) conformation of 1,3-dialkylcyclohexanes are on the <u>same</u> side of the ring. As a result for 1,3-dialkylcyclohexanes, (*a,a/e,e*) has the *cis* configuration while (*e,a/a,e*) has the *trans* configuration.

Drawings of cis and trans Dialkylcycloalkanes. These detailed conformational analyses allowing *cis* and *trans* assignments to dialkylcyclohexane configurations are complex when we use chair forms. They can also be confusing for cycloalkanes with ring sizes other than C_6. However, we can represent structures of *cis* and *trans* dialkylcyclohexanes as well as those of all other dialkylcycloalkanes in a simple way using *solid* and *dashed wedge* bonds. [graphic 2.72]

Chapter Review

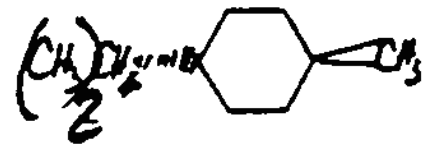
Alkanes

(1) **Alkanes** are **hydrocarbons** in which all C atoms are tetrahedral with bond angles of approximately 109.5°. (2) **Unbranched** alkanes have a continuous chain of C atoms with nothing attached other than H. (3) Unbranched alkanes provide the basic organic nomenclature prefixes *meth* (C_1), *eth* (C_2), *prop* (C_3), *but* (C_4), *pent* (C_5), *hex* (C_6), *hept* (C_7), *oct* (C_8), *non* (C_9), and *dec* (C_{10}). (4) **Branched** alkanes have **alkyl groups** such as *methyl* (CH_3), *ethyl* (CH_3CH_2), isopropyl ($(CH_3)_2CH$) and t-butyl ($(CH_3)_3C$) attached to the **parent alkane** and are named as "**alkylalkanes**". (5) **Kekulé** structures, **condensed** formulas, three dimensional **wedge-bond** drawings, and **line-bond** structures all show structures of alkanes.

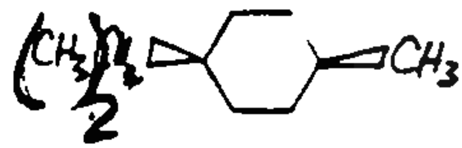
Cycloalkanes

(1) **Cycloalkanes** have rings of tetrahedral C atoms with attached H's. (2) Cycloalkanes with attached alkyl groups are "**alkylcycloalkanes**" or "**cycloalkylalkanes**".

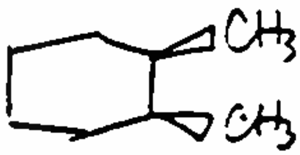
2.72



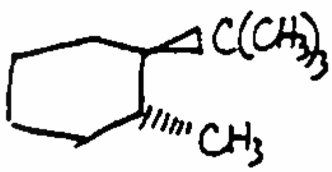
trans



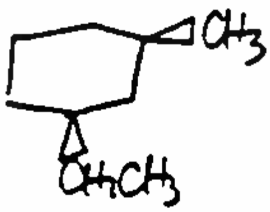
cis



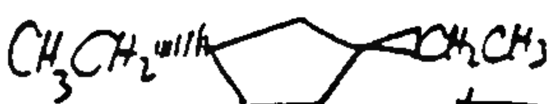
cis-1,2-dimethylcyclohexane



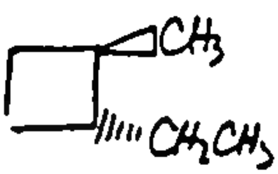
trans-1-t-butyl-2-methylcyclohexane



cis-1-ethyl-3-methylcyclohexane



trans-1,2-diethylcyclopentane



trans-1-ethyl-2-methylcyclobutane

Conformations of Alkanes

(1) Alkanes have **eclipsed** or **staggered** conformations due to rotation about C-C bonds. (2) Eclipsed conformations are highest in energy (least stable), while staggered conformations are lowest in energy (most stable). (3) **Torsional strain** is present in eclipsed conformations, but not in staggered conformations. (4) **Steric strain** can be present in both staggered and eclipsed conformations. (5) Staggered groups on each of two attached C atoms are either ***anti*** or ***gauche*** with respect to each other.

Conformations of Cycloalkanes

(1) Cyclopropane and cyclobutane possess significant **angle strain**, cyclopentane has little angle strain, and cyclohexane has none. (2) Torsional strain is high in cyclopropane and cyclobutane, but less in cyclopentane, and non-existent in cyclohexane. (3) Cyclohexane exists in **chair conformations** with **axial** and **equatorial** C-H bonds. (4) Partial rotation about C-C bonds occurs in all cycloalkanes except cyclopropane. (5) C-C rotation causes rapid interconversion between chair conformations in cyclohexane called **ring flipping**.

Conformations of Alkylcyclohexanes

(1) Alkyl groups of alkylcyclohexanes can be axial or equatorial. (2) Ring flipping switches alkyl groups between axial and equatorial positions. (3) Steric strain is greater for axial than for equatorial alkyl groups. (4) The **equatorial preference** of an alkyl group depends on the size of the group attached to the ring. (5) Dialkylcycloalkanes with alkyl groups on different carbons have ***cis*** or ***trans*** configurations depending on the relative axial or equatorial positions of the two alkyl groups.

A Tribute to Professor Melvin Newman *[see top of page 2-28]*

In August of 2000, I found myself staying at a great B and B (The McMaster House) in Portland, OR. At breakfast there one morning, I met an interesting couple from MA and found myself chatting about our respective lives. When Susan asked what I did when I was not in Portland, I replied that I was a retired professor of chemistry.

She said, how interesting, and asked what kind of chemistry! When I told her that I was an organic chemist, she laughed, and said that perhaps I knew of her father, Melvin Newman! My mouth dropped and I sort of muttered feebly that I had never met him, but that of course every organic chemist, and for that matter every biology major or pre-med in the universe, knew of her dad! I just couldn't believe it! There I was having breakfast with the daughter of one of the true icons of modern organic chemistry.

When breakfast was over and we were preparing to go our separate ways, she asked for my address. She wanted to send me something that she thought I would find interesting. Several weeks later, when I was back in Santa Barbara, I received a note from Susan Newman Katz that included a photograph [next page]!

She said that she had taken the photo when she was in Switzerland on a vacation! She guessed that the Swiss company that made this "tribute" did not realize what they had done. But she couldn't pass up the opportunity to record what she felt was an ironic, if unintentional, tribute to her father. I have scanned that photo and share it with you here! Thanks, Susan!