

Organic Chem #2: Structure of Alkanes, Cycloalkanes, and Alkenes

Bring your model kits to class... we will learn to use them!

Objectives: by the end of this unit, you should be able to...

- Interconvert Fisher, Newman, line-dash-wedge representations of molecules
- Recognize and determine constitutional (structural) isomers of alkanes drawn in any representation
- Determine the relative stability of the staggered, eclipsed and gauche conformers of alkanes given one of the representations of a molecule described above
- Determine the relative stability of the various *conformations* of cycloalkanes (especially cyclohexane) from one of the many representations of the molecule
- Determine the relative stability of the various *stereoisomers* of substituted cycloalkanes (especially cyclohexane)
- Determine the *cis/trans* relationships between any two groups attached to a cyclohexane and identify the most stable conformation of each
- Be able to identify and determine the *E,Z* stereoisomers of any double bond in an alkene by using the priority rules for naming
- Be able to determine the total number of stereoisomers possible in a molecule with more than one double bond

A. Structure and Nomenclature

- Straight- or branched-chain compounds of C and H are termed acyclic hydrocarbons or *alkanes*.

Simple alkanes and their properties

Formula	Name	BP °C
CH ₄	methane	-162
C ₂ H ₆	ethane	-89
C ₃ H ₈	propane	-42
C ₄ H ₁₀	butane	-0.5
C ₅ H ₁₂	pentane	36
C ₆ H ₁₄	hexane	69

- At RT, methane (natural gas) is a gas, while larger alkanes, some of which are in gasoline, exist as liquids.
- All alkanes have the formula **C_nH_{2n+2}**. Note that the molecular formula does not necessarily indicate structure!
- Alkanes comprise a *homologous series*: a group of chemical compounds differing by successive additions of CH₂, with similar chemical structures and physical properties that change gradually, e.g. boiling point. (see previous section)

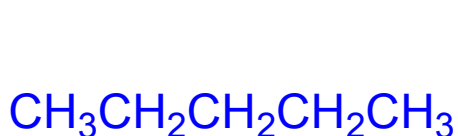
B. Constitutional (Structural) Isomers

- Recall that molecular formula does not indicate structure. This is because covalent bonds permit 3 or more atoms to be bonded in different structural sequences.
- In turn, this generates different **constitutional (structural) isomers: compounds that have the same molecular formula but different bonding sequences (different connectivity of the atoms)**.
- The number of possible isomers rapidly increases with molecular size, since there would be more possible combinations of bonding sequences:

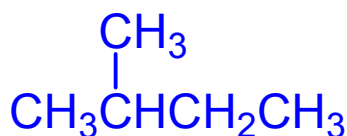
CH ₃	1	C ₈ H ₁₈	18
C ₃ H ₈	1	C ₉ H ₂₀	35
C ₄ H ₁₀	2	C ₁₀ H ₂₂	75
C ₅ H ₁₂	3	C ₂₀ H ₄₂	366,319
C ₆ H ₁₄	5	C ₄₀ H ₈₂	62,481,801,147,341
C ₇ H ₁₆	9		

- This structural diversity is key to the centrality of organic chemistry in biological systems.

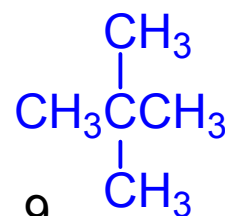
- Structural isomers (with same molecular formula) result in different chemical and physical properties, e.g. the boiling points of various pentanes (C_5H_{12}).



BP (deg C) = 36

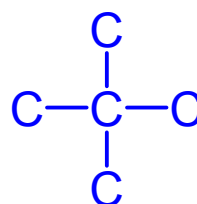
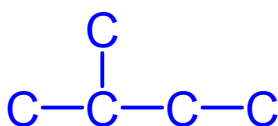
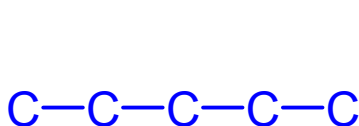


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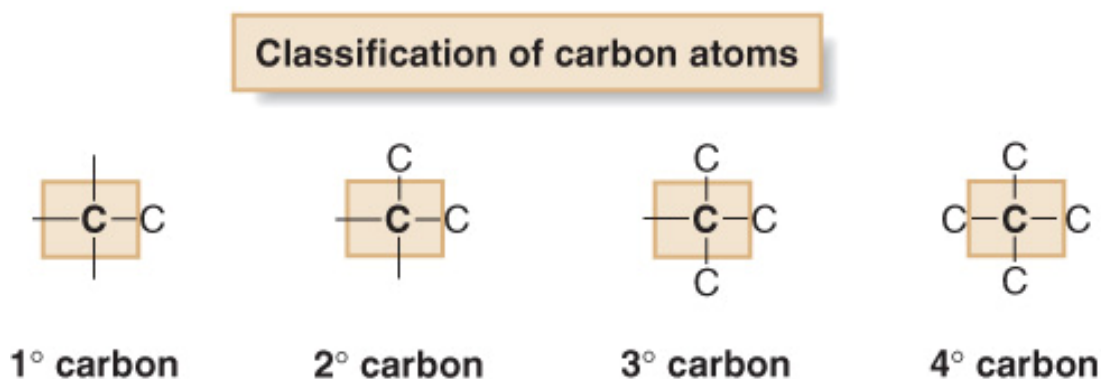
- When drawing possible constitutional isomers, concentrate on the bonding sequence of the carbon atoms.



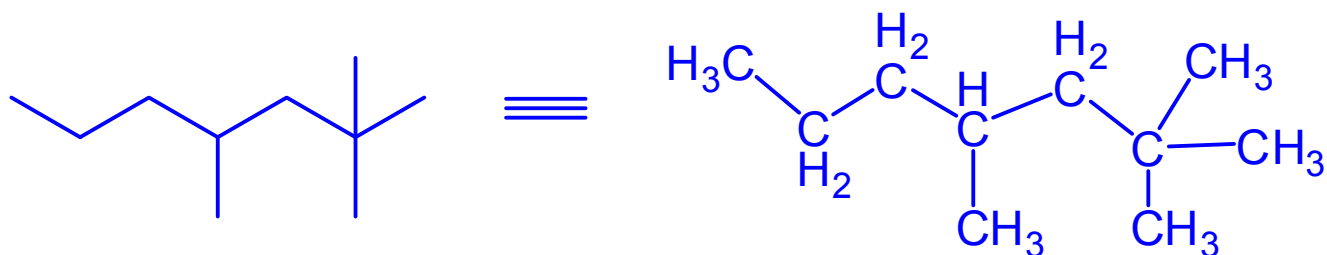
- You must be alert to avoid drawing identical bonding sequences (*i.e.* the same isomer) where the bonds are simply pointing in a different direction. In Lewis structures the bends in a carbon chain do NOT matter.
- $$\begin{array}{c} C-C-C \\ | \quad | \\ C \quad C \end{array}$$
- If you are asked to draw all possible constitutional isomers for a given molecular formula, proceed systematically from the longest possible chain to the shorter ones.
 - Trial and error is the only way! e.g. draw all possible constitutional isomers for C_5H_{12} and C_6H_{14} .

C. Types of Carbon Atoms in a Molecule

- Carbon atoms in molecules are often classified as:
 - Primary (1°) \rightarrow bonded to 1 other C atom
 - Secondary (2°) \rightarrow bonded to 2 other C atoms
 - Tertiary (3°) \rightarrow bonded to 3 other C atoms
 - Quaternary (4°) \rightarrow bonded to 4 other C atoms



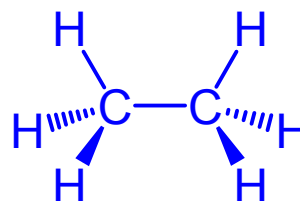
- Example: identify each carbon as 1° , 2° , 3° or 4°



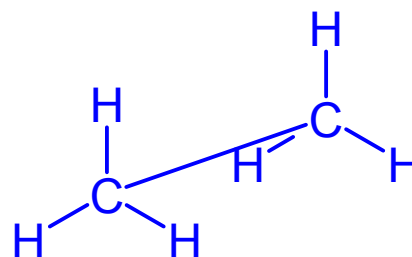
D. 3-D Structure

- There are several conventions for drawing a 3-D molecule on a 2-D surface. For example, ethane CH_3CH_3 .

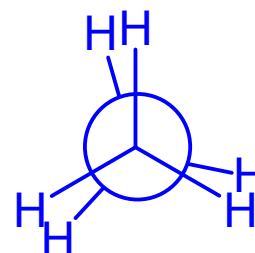
1. **Dot-Line-Wedge** is most versatile and widely used.



2. **Sawhorse projections**: molecule is viewed from the above right. Only useful for small and very simple molecules.



3. **Newman projections**: molecule viewed along one C-C axis. Rear bonds along edge of circle. Very good for showing conformations. Note that the rear circle is the rear atom, and bonds meet at the front atom.

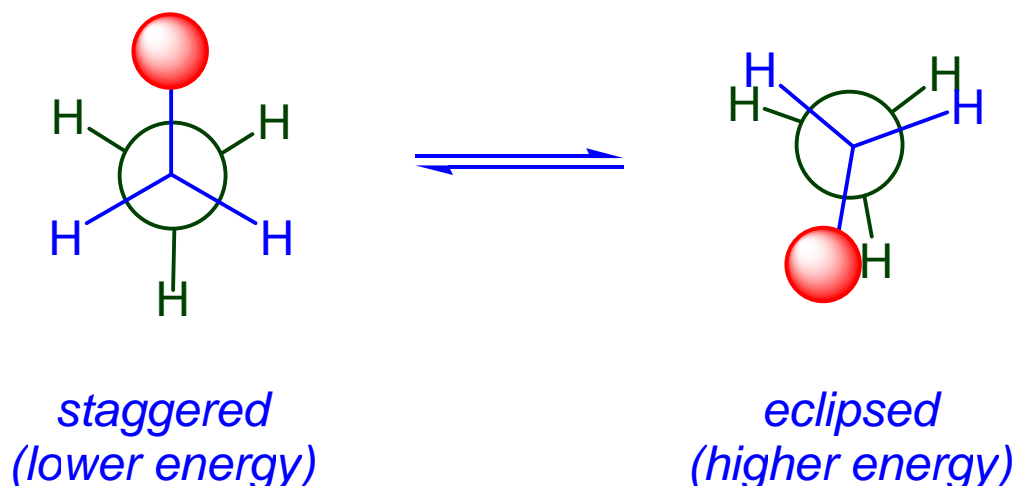
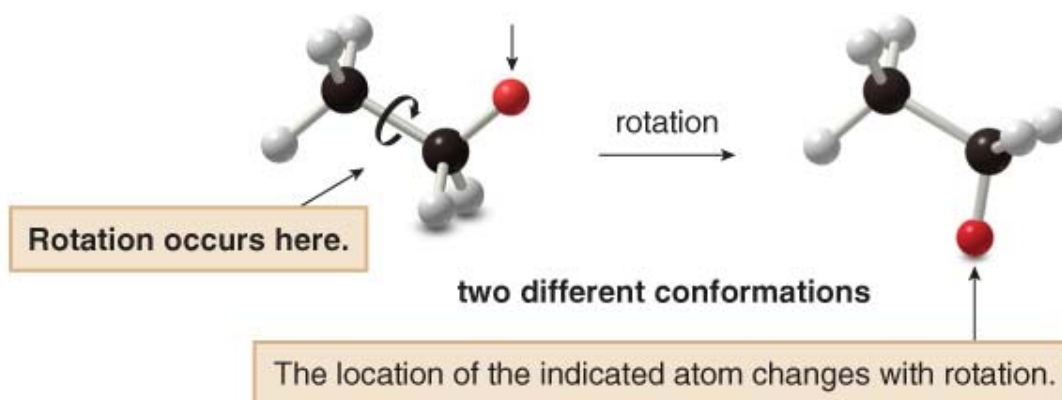


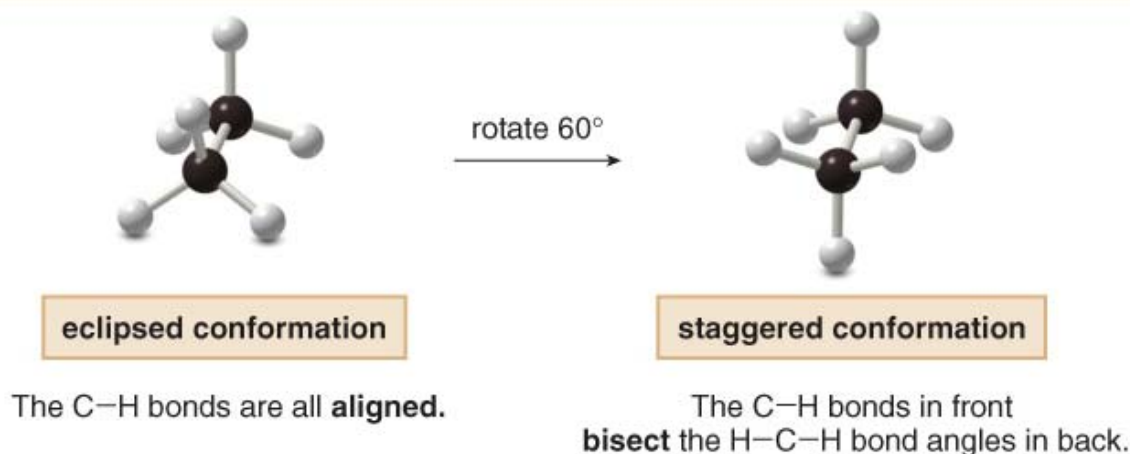
4. **Fischer projections**: useful for molecules with several chiral carbons (more later). C chain written vertically, east-west bonds above plane, north-south below plane. Frequently seen in biology and biochemistry.



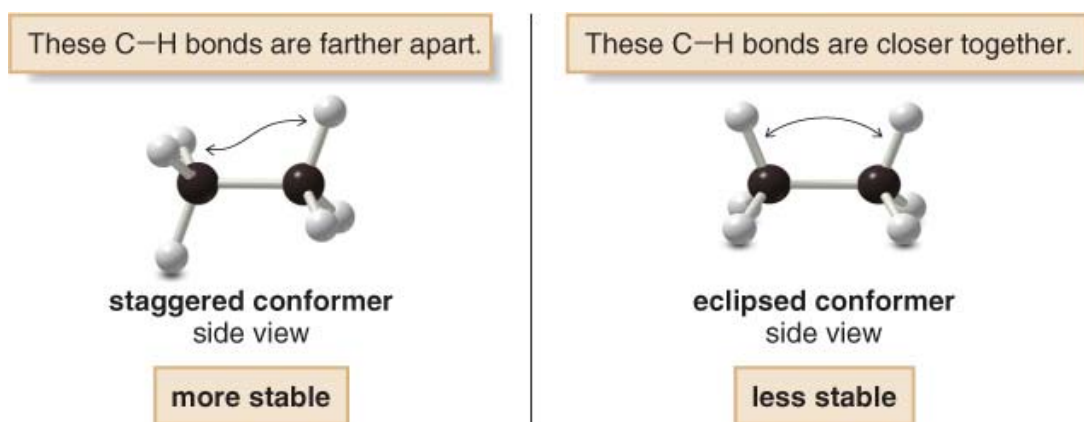
E. Molecular Conformations (not confirmation)

- In each of the different bonding arrangements known as structural isomers, differing short-lived *spatial arrangements* of atoms can result from the rapid rotation of atoms, or groups of atoms, around single bonds. These different arrangements of atoms that are inter-converted by rotation about single bonds are termed **conformations** (different shapes of the same isomer).
- When two atoms or groups are connected by a single bond (σ), they are free to spin about the single bond axis. The strength of σ bonds is unaffected by such rotations.





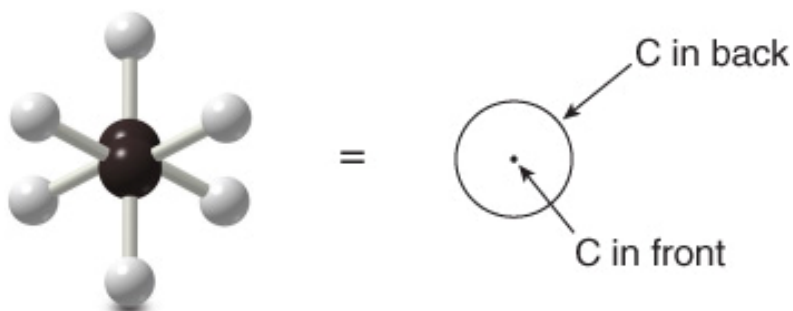
- **Staggered**: each C-X (in this case C-H atom) on the rear carbon is spaced equally between the H atoms on the front carbon. This minimizes repulsion/interaction between front and rear H.
- **Eclipsed**: formed from the 60° rotation of the rear carbon. Each H bonded to the rear carbon (and associated bonding electron pair) is directly aligned (eclipsed) with the front H. Higher energy than staggered conformations.



- Other conformations are intermediate in geometry and energy. For us, we're interested in the above extremes.
- Because these rapidly interconvert (10^6 s^{-1}) at room temperature, they cannot be isolated and are NOT isomers.

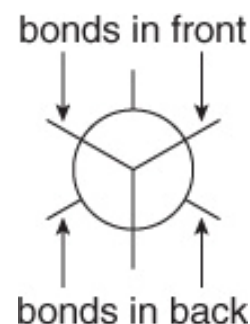
- Aside: How do you draw a Newman projection?

1. Use the correct model of the molecule. Look directly down the C–C bond from the end, and draw a circle with a dot in the center to represent the carbons of the C–C bond.

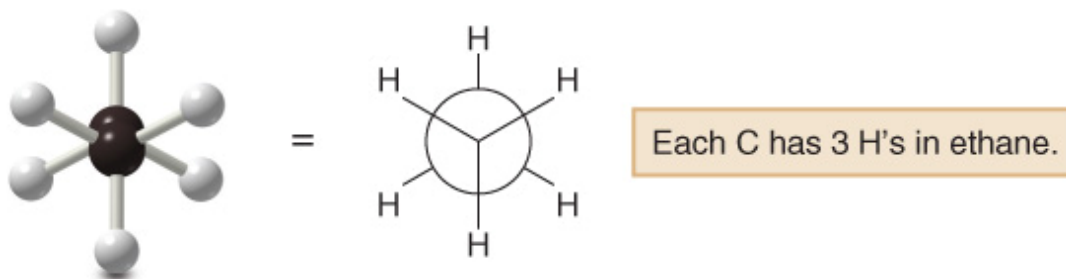


2. Draw in the bonds.

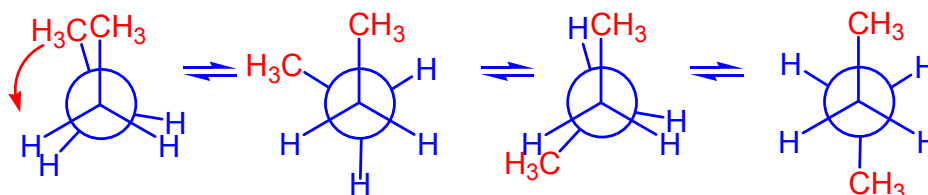
Draw the bonds on the front C as three lines meeting at the center of the circle. Draw the bonds on the back C as three lines coming out of the edge of the circle.



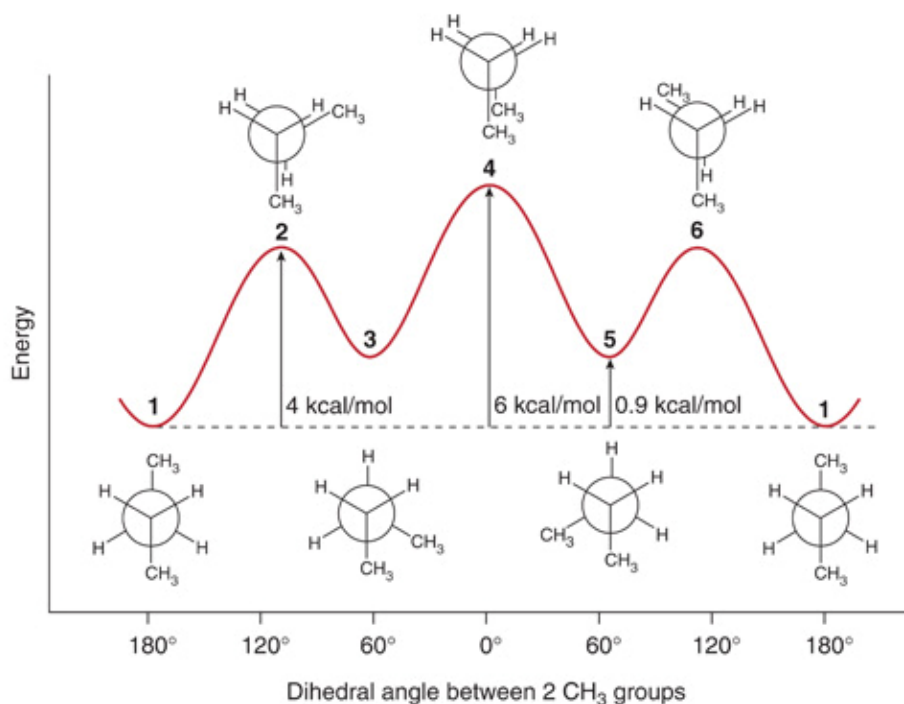
3. Add the atoms on each bond as you see them.



- Consider butane and looking down the C2–C3 bond.



- All representations above are the *same* molecule, but in different conformations. However, they are different in energy. Far left: the least stable (highest energy) conformation has the two large CH_3 groups eclipsed. Far right: the most stable (lowest energy) = staggered.



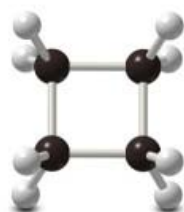
- Staggered conformers 1, 3, and 5 are energy minima. *Anti* conformer 1 is lowest in energy (most stable). *Gauche* conformers 3 and 5 which have some steric strain. Eclipsed conformers 2, 4, and 6 are energy maxima. Eclipsed isomer 4 is highest in energy, because it has the additional steric strain of the two largest CH_3 groups eclipsed.

F. Cycloalkanes

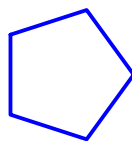
- Hydrocarbons that have closed to form a ring are known as cycloalkanes. All cycloalkanes have the general formula C_nH_{2n} , because two H have to be removed to form the ring.
- There is restricted rotation around the single bonds in cyclic molecules because of the ring structure.
- Cycloalkanes from C_3 to C_5 have nearly (but not quite) all C's in a plane, with the substituents above and below the plane. C_4 and C_5 rings bend (pucker) slightly out of the plane to reduce the eclipsed interactions, even though this increases angle strain (make models of each cycloalkane and look at the strain by looking down each C-C bond.)



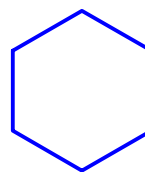
C_3H_6
cyclopropane



C_4H_8
cyclobutane



C_5H_{10}
cyclopentane



C_6H_{12}
cyclohexane

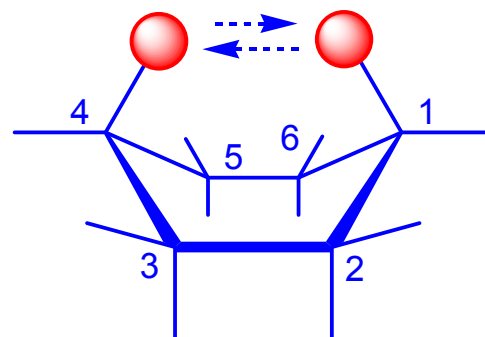
- Cyclopropane: bond angles (60°) are highly strained. All six C-H bonds have an eclipsed conformation (not staggered).
- Cyclobutane (bond angles ca. 90°) and cyclopentane (ca. 109.5°) are puckered rather than flat. This puckering relieves eclipsing interactions of adjacent C-H bonds.
- Cyclohexanes drawn as polygons represent top views. However, side views of the ring reveal conformations!

G. Cyclohexane Conformations

- Make a model of cyclohexane and follow your instructor's advice on how to manipulate them!
- There are two distinct conformations in which all carbons have normal tetrahedral geometry (all bonds 109.5°).

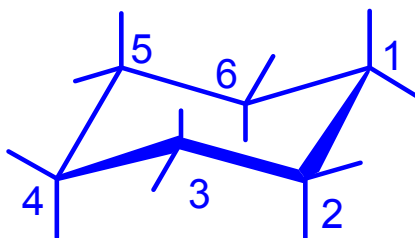
1. Boat Conformation

- The substituents on carbon 2 & 3, and 5 & 6, are eclipsed. Those on 1 & 4 interact through a flagpole interaction (\longleftrightarrow).



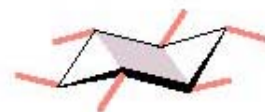
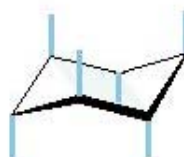
- Such interactions are not favourable, and thus, the boat conformation is present in the conformation equilibrium mixture in very small amounts (typically $< 0.1\%$).

2. Chair Conformation



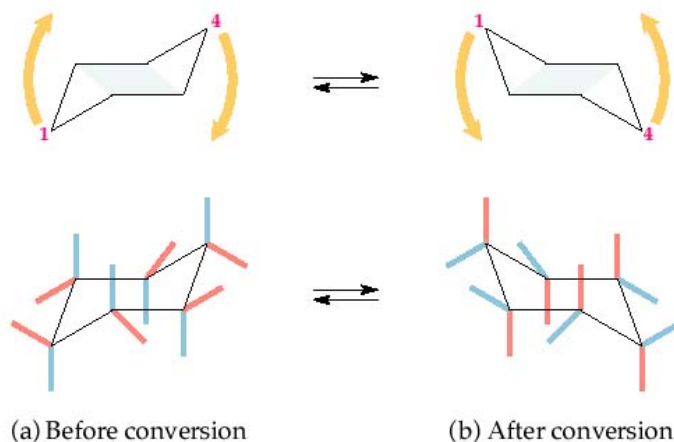
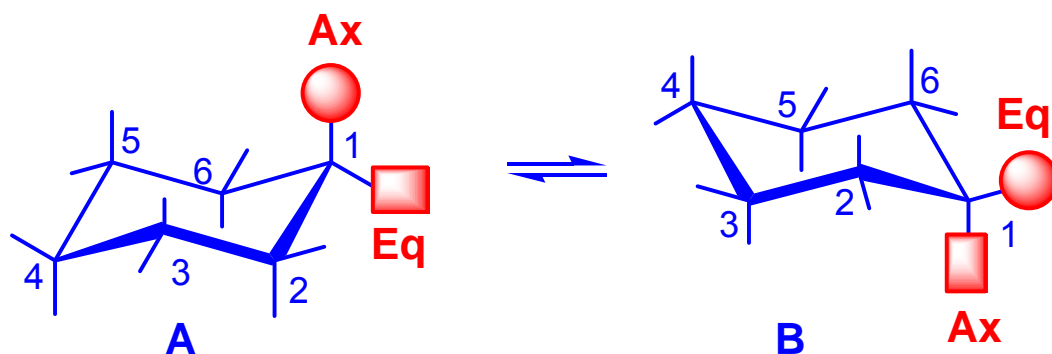
- In this conformation, all C-H bonds on adjacent carbons are staggered (no eclipsing interactions) and there are no flagpole interactions.

- Substituents directed straight up and down are **axial**. There are six of these (blue).



- The other six, directed outward, are termed **equatorial**. These are less crowded, since they are more distant from other substituents on the ring. This means that large groups prefer to be in the equatorial position (red).
- Notice the alternating pattern.** If substituents at one carbon is axial down and equatorial up, the adjacent carbon's substituents are axial up and equatorial down.

- In the diagram below, every chair conformation (A) can change by bond rotation to an equivalent chair (B).
- Using a model of A, grab carbon 4 and twist it up, and grab carbon 1 and twist it down... everything else will fall into place and form B. *i.e.* flip both ends.



- **Aside: How to draw cyclohexane in its chair conformation?**

- 1. Draw the carbon skeleton.**

- a) Start by drawing two parallel lines at an angle, slanted downward from left to right and offset from each other. These are 4 of the C in a plane.
- b) Place the top carbon above and to the right of the plane of the other 4 C and connect the bonds.
- c) Place the bottom carbon below and to the left of the plane of the middle 4 C and connect the bonds.

The bottom middle two C's come out of the page, so bonds to them are often highlighted in bold. The top middle 2 C's are behind the page.

- 2. Label the up C's and the down C's.**

There are three C's above the plane, and three C's below the plane.

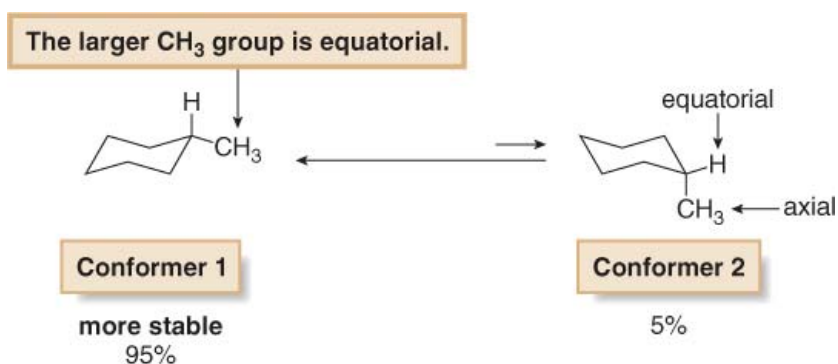
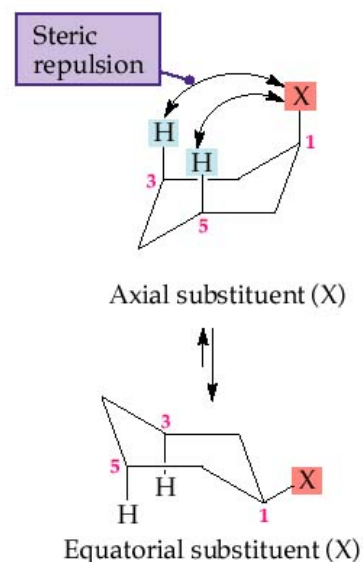
- 3. Draw in the axial H atoms.**

On an *up* carbon the axial H is up.
On a *down* carbon the axial H is down.

- 4. Draw in the equatorial H atoms.**

The axial H is *down* on a down C, so the equatorial H is up. The axial H is up on an up C, so the equatorial H must be down. All C's are tetrahedral.

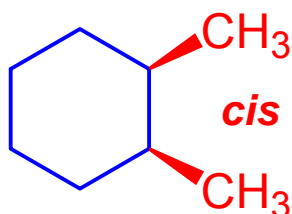
- The two possible chair forms of cyclohexane have some important implications.
- When A changes to B, *all axial substituents become equatorial, and all equatorial ones become axial.*
- Of the two possible chairs, the one favoured (*i.e.* more stable) will be the one where large substituents are placed in the equatorial positions (less crowded). Larger axial substituents create unfavourable 1,3-diaxial interactions, destabilizing a cyclohexane conformer.
- Make a model of methylcyclohexane to verify this.



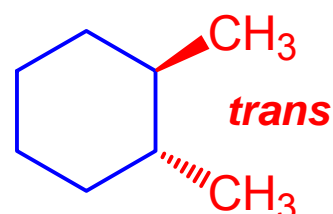
- Thus, for cyclohexane rings with one or more substituent, one chair conformation will be more stable than the other. The more stable one will be the predominant form in the equilibrium mixture. Note that because they rapidly interconvert, they are NOT isomers.

H. Isomerism in Cycloalkanes

- When a cycloalkane bears two or more different substituents, they can occupy two different positions, relative to the approximate ring plane. These two structural possibilities are known as *cis-trans* isomers.



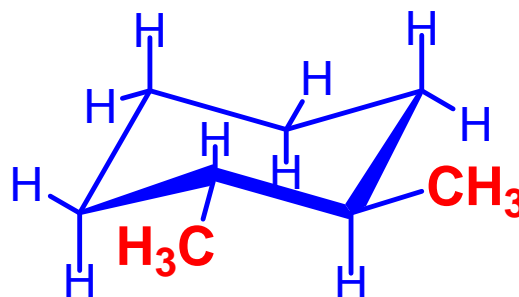
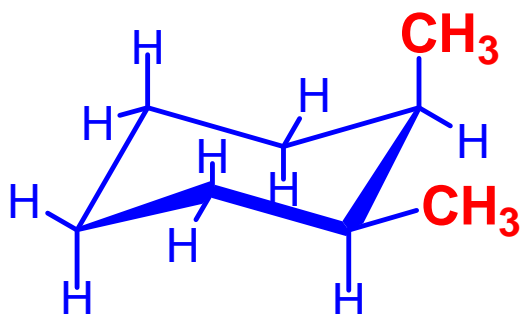
BP = 130 °, MP = -50 °



BP = 124 °, MP = -89 °

- These differ by having substituents on the same (*cis*) or opposite (*trans*) sides. They cannot be interconverted unless covalent bonds are broken.
- This is one type of **stereoisomerism**. Stereoisomers have the **same molecular formula and the same bonding sequence (connectivity)**, but have **different, non-interconverting 3D structures**. That is, the way the groups are oriented in space is different, and they can not be interconverted by rotations around single bonds.
- The more-stable structures are those with the large groups further away from each other, due to reduced steric interactions or hindrance.
- Like all isomers, *cis-trans* isomers do NOT interconvert at room temperature. However, they can each exist in their usual number of conformations.

- When cyclohexane compounds are drawn in their chair conformations, it is important to be able to recognize *cis-trans* relationships.
- Two substituents that both lie above (or both below) the ring plane are *cis*. If one is above the ring plane and one is below, they are *trans*.

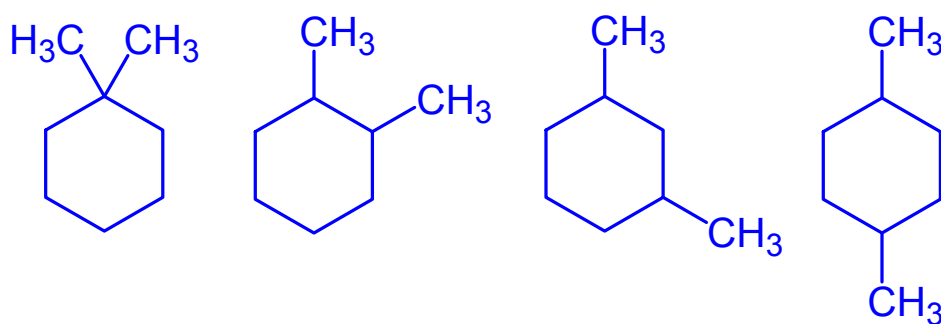


I. Summary (Up To Now)

- So far, we have learned two types of isomerism.

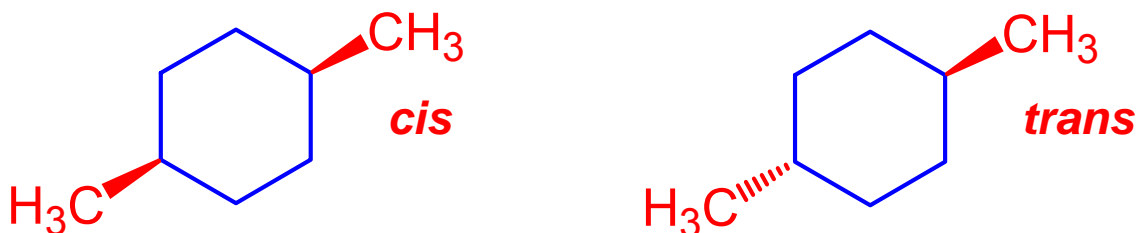
1. Constitutional Isomerism

- For example, cyclohexane with two methyl groups. There are 4, and only 4 constitutional isomers.



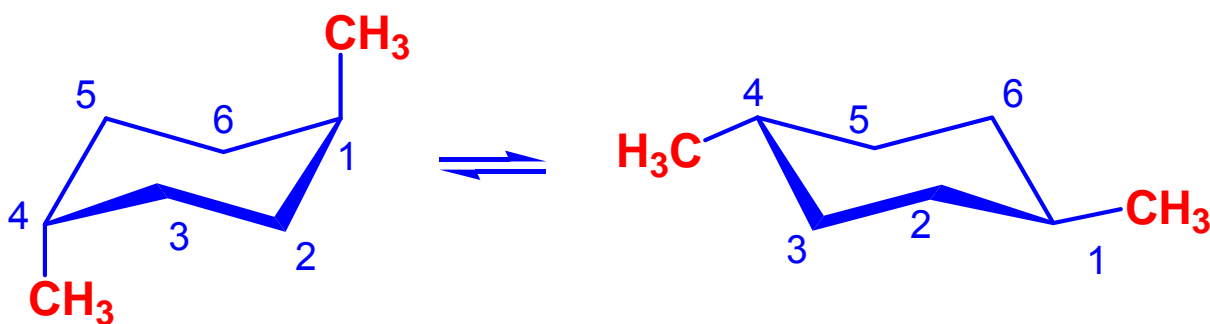
2. *cis-trans* Isomerism

- Different spatial arrangements of groups on rings, e.g. for 1,4-dimethylcyclohexane.



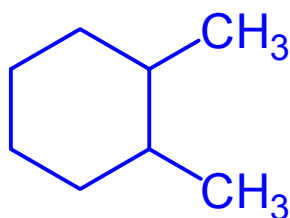
- The polygons above show the top views of the ring. However, these views do not show conformations.

- Whether the views above are called top or bottom views is arbitrary. Simply turning a molecule over does not change the *cis/trans* relationships of the substituents.
- Remember, conformations, which are due to rotation around single bonds, are depicted by side views. Conformations are in equilibrium (cannot be isolated). e.g. for *trans*-1,4-dimethylcyclohexane.



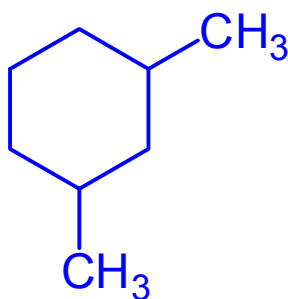
e.g. for *cis*-1,4-dimethylcyclohexane

- Homework: Draw the two chair forms of the following molecule as the *cis* isomer and then as the *trans* isomer. Indicate for each pair, which is the more stable conformer.



1,2-isomer

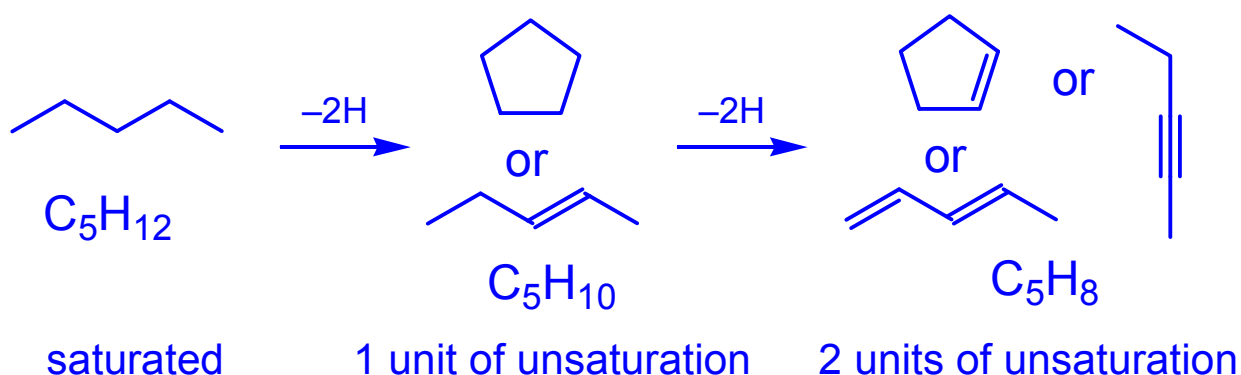
- Now do the same for the 1,3-isomer.



1,3-isomer

J. Structure of Alkenes

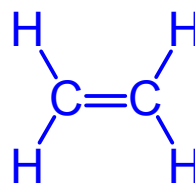
- **Alkenes** are a homologous series of hydrocarbons with the general formula C_nH_{2n} . They have two H less than alkanes because of a C=C double bond.
- **Alkynes** have the formula C_nH_{2n-2} and have a $C\equiv C$ bond.
- Such compounds are said to be **unsaturated** because they have less than the maximum number of hydrogens.
- Each reduction of *two H* from the general alkane formula represents *one unit* of unsaturation.



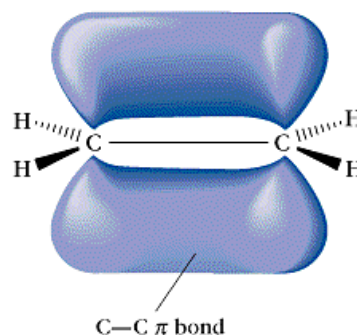
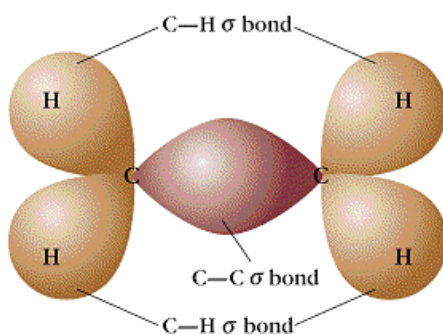
- **Note:** each unit of unsaturation can be a pi-bond (π -bond) or a ring!

K. Shapes of Alkenes and Alkynes

- Alkene: each C is bonded to three groups and is sp^2 (planar) with a bond angle of 120° .
- Alkyne: each C is bonded to two groups and is sp (linear) with a bond angle of 180° .

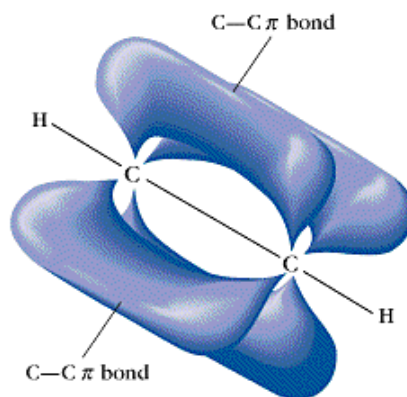
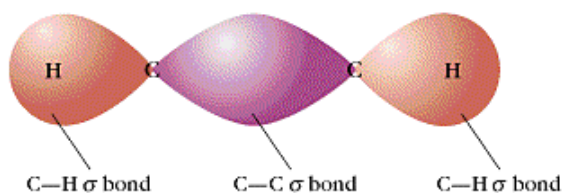


- A double bond (between atoms N, C, O, etc.) consists of two adjacent sp^2 -hybridized atoms.
 - The three sp^2 orbitals are used to form σ bonds to each of the three attached groups.
 - The remaining p orbital overlaps sideways with the p from the adjacent atom to form a π bond (total two p).
 - This results in a planar structure for all atoms involved, for example ethylene:



- Note that π bonds have electron density both above and below the molecular plane.

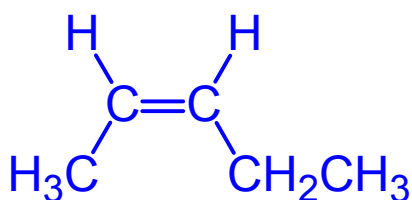
- A triple bond consists of two adjacent sp -hybridized atoms.
 - The sp orbitals are for σ bonds. The two π bonds originate from the sideways overlap of two p orbitals from each of the atoms (total of four p), e.g. ethyne.



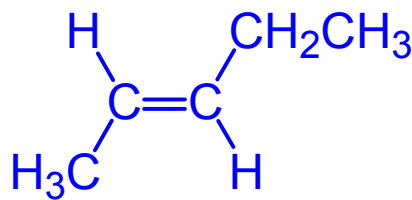
- Linear structure for all atoms involved, and there are two regions of electron density for each of the π bonds.

L. E,Z Isomerism of Alkenes

- A multiple bond prevents free rotation around the atoms of the multiple bond. (Such rotation would require breaking the π bond and is not energetically favourable).
- As a result, *cis-trans* (or geometric) isomers can exist for *non-symmetric* alkenes.

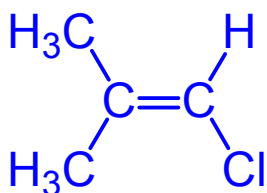


cis-2-pentene
mp = -179° , bp = 38°

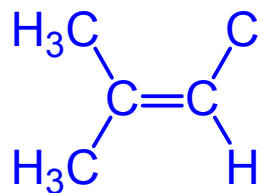


trans-2-pentene
mp = -136° , bp = 36°

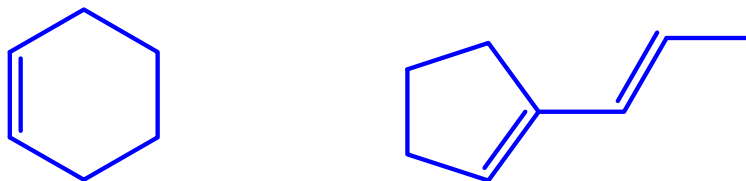
- The terms *cis* and *trans* refer to the relative orientation of designated substituents on the C=C bond, although this nomenclature only really applies to alkenes substituted once on each carbon and is sometimes ambiguous and E/Z nomenclature is preferred (always in Chem 20)
- Recognize that if any of the two substituents on any one of the two carbons is identical, there cannot be *cis/trans* isomers. The molecule shown below has no stereoisomers.



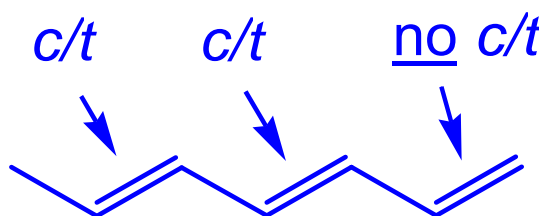
same as



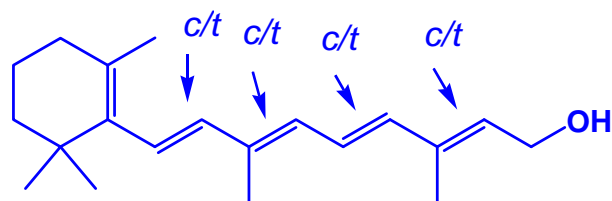
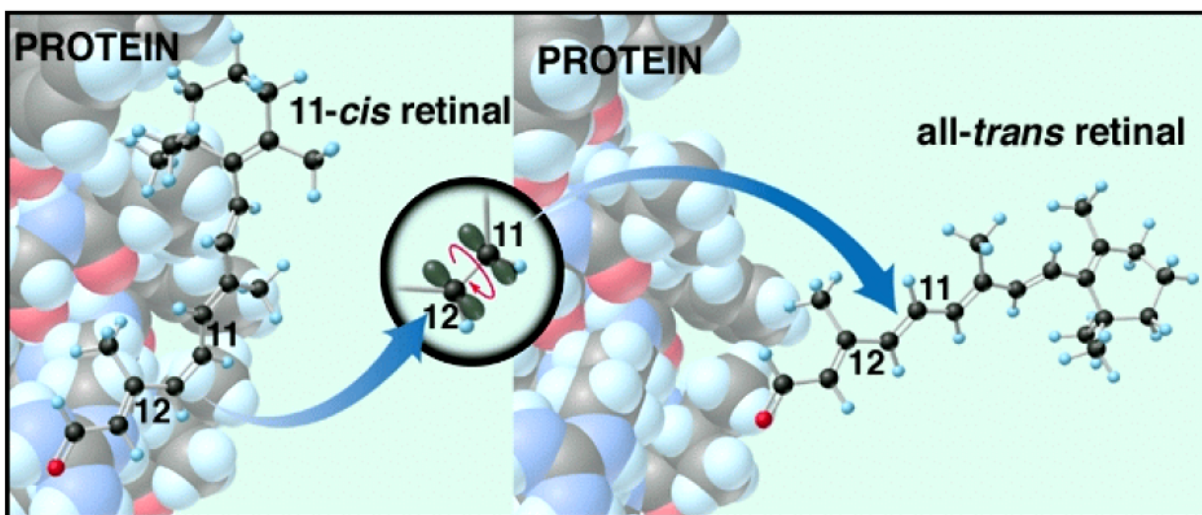
- Also, in ring compounds of 7 carbons or less, due to angles, the double bond within the ring must be of the geometry shown (cis as defined by the ring carbon atoms).



- For every C=C in a molecule, there is a possibility of 2 isomers (the E or the Z). So, for n C=C's in a molecule, there is a maximum of 2^n possible isomers.
- The actual number of isomers is decreased if one or more of the double bonds is symmetrical (*i.e.* has two identical substituents on one of the C=C atoms).
 - $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}=\text{CH}_2$ has three C=C, but the one on the right does not have *E,Z* isomers.
 - Instead of the maximum possible $2^3 = 8$, this compound only has 4 isomeric forms.



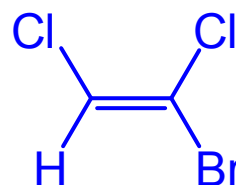
- *cis-trans* isomerism is also physiologically important.
- Vitamin A (retinol) is essential for vision and has four double bonds in the chain. When light strikes the molecule (bound to the protein rhodopsin via its oxidized aldehyde form, retinal), the second double bond in from the OH group undergoes a *cis to trans* isomerization.
- This change in shape causes a signal to be sent from the optic nerve to the brain.

Retinol (all-*trans*-isomer)

M. E and Z Nomenclature for Alkene Stereoisomers

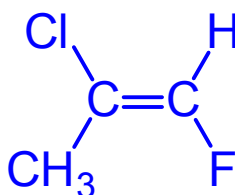
- The *cis/trans* nomenclature used to define stereochemistry in alkenes leads to difficulties.

- For example, is this molecule *cis* or *trans*?



- Whereas, the *E-Z* system is unambiguous nomenclature. The convention uses a set of rules to assign a priority order to the substituents attached to the double bond:

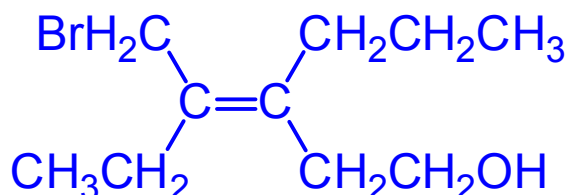
- Atoms directly attached to a C=C atom are arranged in the order of **descending atomic number** (nothing else!!!!)
 - e.g. $I > Br > Cl > S > F > O > N > C > H$
 - For different isotopes of the same element, atomic mass determines order (e.g. $H^2 > H^1$).
 - Rank the atoms (groups) on each C of the double bond
 - Example:



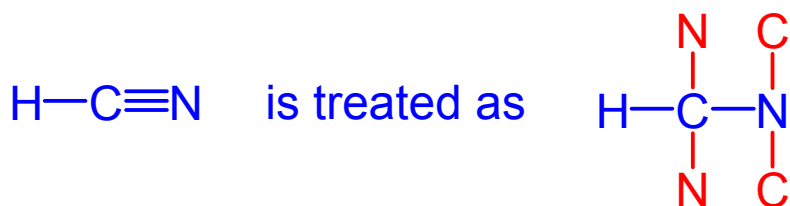
- When rule #1 leads to a “tie” between atoms, continue on to rules #2 and #3.

2. Starting with atoms involved in a “tie,” proceed along the chain to the **first difference** in bonded atoms. The atomic number at that point determines priority.

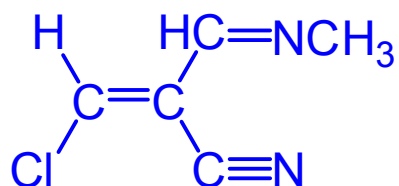
○ Example:



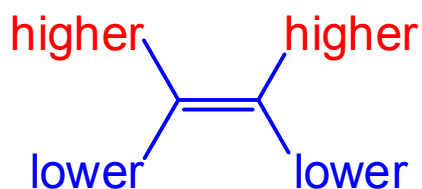
3. For atoms attached by double or triple bonds, they are given single-bond equivalencies so that they can be treated like singly bonded groups. Replace each p-bond with two single bonds to “phantom” atoms identical to the real atoms at both ends of the p-bond.



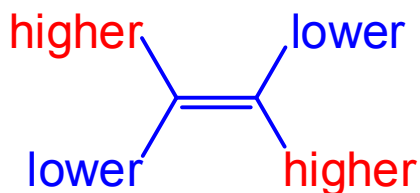
○ Example:



- Then we can assign a **configuration label** to the isomer: If two groups of higher priority are on the same sides of the double bond, then the C=C stereoisomer is *Z* (*zusammen*). If the two groups are on opposite sides of the double bond, then *E* (*entgegen*).



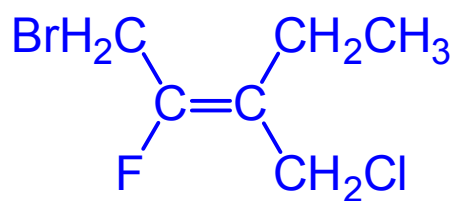
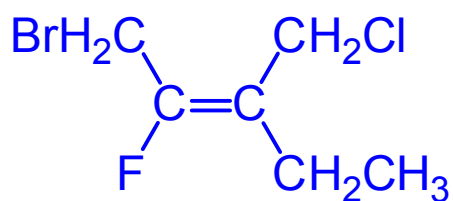
Z (*zusammen*)



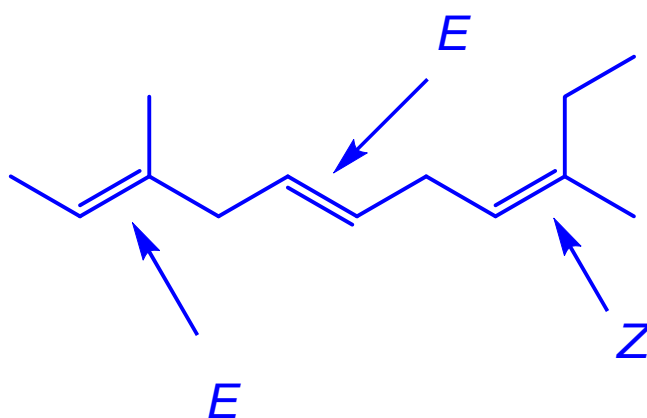
E (*entgegen*)

- Realize that you must compare groups on each of the C in the C=C bond independently, so don't automatically pick the groups with priorities 1 and 2.

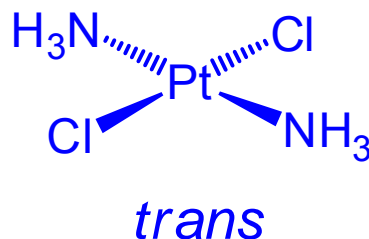
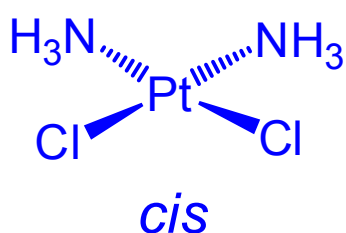
- Remember that *Z* rhymes with same, *i.e.* zame zide!
 - e.g.* assign *E* or *Z* to these stereoisomers



- If there is more than one double bond, give labels to each double bond.



- Interesting fact: some inorganic molecules also exist as geometric (*cis-trans*) isomers. Example: **Pt(NH₃)₂Cl₂**
- This molecule exists in a square planar arrangement of the atoms around the Pt center.
- In one isomer (*cis*) the two Cl are adjacent to each other, and in the *trans* isomer they are on opposite sides.



- These two isomers cannot be interconverted by conformational change, and they are therefore classified as stereoisomers.
- The *cis* isomer is sold under the name *cisplatin*, a strong chemotherapy agent used to treat bladder, testicular and certain types of sarcoma cancers.
- The *trans* isomer has no chemotherapy effects.