
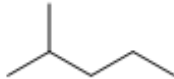


Ch3 Alkanes and their Stereochemistry

- Alkanes are the simplest family of hydrocarbons.
- They contain only single bonds with C and H.
- They can be straight chains, branched, or cyclic (with rings).
- Anything other than H attached to a C on the chain is called a substituent or functional group.
- A [functional group](#) will have the same kind of chemical characteristics regardless of what it is attached to, and the chemistry of every organic molecule is determined by the functional groups it contains. See Table 3.1 for structures and names for common functional groups.
- For instance, hydrocarbon molecules with C=C (double bonds) are called alkenes. Hydrocarbon molecules with C≡C (triple bonds) are called alkynes. Rings with six C's and three alternating double bonds are called arenes, or aromatic.
- A functional group could also be an electronegative atom. Organic molecules with OH (hydroxyl group) are called alcohols. Alkyl halides have F, Cl, Br, or I attached to a C. Amines have NH₂, NHR, or NR₂ attached to a C, where R is a hydrocarbon functional group. A carbon/oxygen double bond (C=O) is called a carbonyl. Carbonyl compounds include aldehydes, ketones, carboxylic acids, esters, and amides.

Alkane Isomers

- Alkane molecules are saturated, that is they have only single bonds.
- The molecules possess the maximum possible number of H's, and their formula is C_nH_{2n+2}.
- The C's are all sp³, with four sp³ orbitals forming σ bonds with tetrahedral geometry.
- Aliphatic means saturated as well, and is derived from the Greek word for phat.
- The C's can be attached to both H's and C's.
- Since a C can be bonded with up to four other C's, multiple structures are possible.
- If all C's are attached in a single row, the molecule is a normal, or straight-chained, alkane. For example, this is n-hexane: 
- If at least one C is attached to three or four other C's, the molecule is a branched alkane, such as 2-methylpentane: 
- If two compounds have the same number of C's and H's, but have different structures, they are called isomers. More specifically, they are constitutional isomers. For instance, n-hexane and 2-methylpentane are constitutional isomers, as both are C₆H₁₄.
- Often, line-bond structures are written with the four bonds 90° apart for simplicity.
- Geometry is actually tetrahedral, with ~109.5° bond angles.

Names for Normal Alkanes

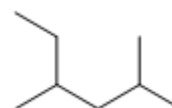
- The first four alkanes are methane, ethane, propane, and butane.
- The larger alkanes use Greek prefixes followed by -ane, such as pentane, hexane, heptane, octane, nonane, decane, etc.

Alkyl Groups

- These are functional groups where a terminal H is removed from an alkane, and this is where the group is attached to a larger (parent) chain.
- The group name is created by replacing the -ane suffix with -yl.
- For instance, -CH₃ is a methyl group and -CH₂CH₃ is an ethyl group.
- If an H is removed from an internal C, the naming is different. Some common names are used, such as (CH₃)₂CH- is called an isopropyl group.
- The C's can be classified by the number of C's attached to it. A primary (1°) C is bonded to only one other C, such as in RCH₃ (where R is an alkyl group). A secondary (2°) C is bonded to two other C's, such as in R₂CH₂. A tertiary (3°) C is bonded to three other C's, such as in R₃CH. A quaternary (4°) C is bonded to four other C's, such as in R₄C.
- For instance, RCH₂OH is a primary alcohol, and R₂CHOH is a secondary alcohol.

Naming Alkanes

- Systematic nomenclature uses IUPAC (Int'l Union of Pure and Applied Chemists) rules:
 1. Find the parent. This is the longest chain. If there is more than one chain with the same length, the parent is the one that has the most branch points.
 2. Number C's in parent chain, starting with #1 as the end that is closest to a branch point.
 3. Identify and number the substituents. Name the substituent as an alkyl group. Precede alkyl group name with the number of the C it is attached to. Use number prefixes and commas between numerals for multiple identical groups. If there are two substituents on the same C, they will have the same number.
 4. Write the compound name as a single word with dashes before and after numbers. Place the alkyl groups at the beginning as prefixes, and place them in alphabetical order. The parent name will be at the end.
 5. Complex (branched) substituents are named as if they are compounds, except that their names end in -yl. Number the sub-branches so that the C attached to the parent is the substituent's #1 C.
- For example, the molecule below has six C's on the longest chain, so the parent is hexane. Also, the right side is #1, because it is closer to a branch point. This molecule is 2,4-dimethylhexane, and its condensed structure is CH₃CH₂CH(CH₃)CH₂CH(CH₃)₂.

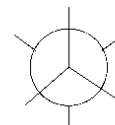


Properties of Alkanes

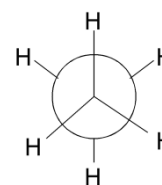
- Alkanes are also called paraffins, which derived is from Latin, and means little chemical affinity. Essentially, alkanes are fairly inert.
- Alkanes will react with O_2 (combustion) or $Cl_2 / Br_2 / I_2$ (halogenation).
- Combustion essentially means they are being burned in a furnace or engine, and the products are CO_2 and H_2O .
- Halogenation occurs if UV light is also present, and creates a mixture of alkyl halides.
- MP's and BP's increase as molar mass increases for normal alkanes because dispersion forces (instantaneous dipoles) increase as molar mass increases. Also, long chains become entangled together, so that vaporization is more difficult.
- Branching decreases BP because it reduces the molecules' surface area, and therefore reduces the dispersion forces.

Alkane Stereochemistry

- Essentially, σ bonds are cylindrically symmetrical, so that the attached atoms can rotate like a propeller on a shaft.
- As we rotate one of the two C's in a carbon-carbon bond, the resulting configurations (or conformations) can be depicted using sawhorse representations and Newman projections (right).

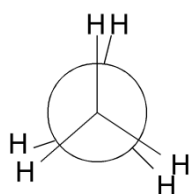


- The Newman projection depicts two carbons bonded together, along with their six substituents (three each).
The front C is the point in the middle, while the rear C is the circle.
- Each C has three other atoms attached in addition to the second C.
The two C's together have six other atoms attached, three on each C.
- If the Newman projection shows the six atoms equally spaced, the configuration is staggered.
- Staggered H atoms are far enough apart that they do not interact, so that staggered conformations have the lowest energy.
- For example, this is a staggered ethane (C_2H_6) molecule:



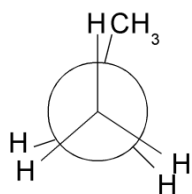
Torsional Strain (Eclipsing)

- If the Newman projection shows the two sets of three atoms superimposing, the configuration is eclipsed.
- Two eclipsed atoms create torsional strain due to an unfavorable interaction between their orbitals. This strain results in a higher energy (less stability).
- Two eclipsing H's raise E by 4.0 kJ/mol.
- If a C and an H are eclipsing, they raise E by 6.0 kJ/mol.
- If two C's eclipsing, they raise E by 11.0 kJ/mol.
- If ethane (C_2H_6) is eclipsed, there are three sets of eclipsing H's: $3 \times 4.0 \text{ kJ} = 12.0 \text{ kJ}$. So, the eclipsed conformation is 12.0 kJ higher than staggered.
- If propane (C_3H_8) is eclipsed, there are two sets of eclipsing H's, and there is one C that eclipses an H. This conformation is $(2 \times 4.0) + 6.0 = 14.0 \text{ kJ}$ higher than staggered.
- Butane has two eclipsed conformations. The higher energy conformation has the two end C's eclipsing each other, and also has two sets of eclipsing H's: $11.0 + (2 \times 4.0) = 19.0 \text{ kJ}$. The other has both end C's eclipsing H's instead: $(2 \times 6.0) + 4.0 = 16.0 \text{ kJ}$.



Eclipsed Ethane

$$3 \times 4.0 \text{ kJ} = 12.0 \text{ kJ}$$

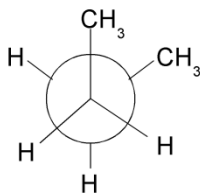


Eclipsed Propane

$$(2 \times 4.0 \text{ kJ}) + 6.0 \text{ kJ} = 14.0 \text{ kJ}$$

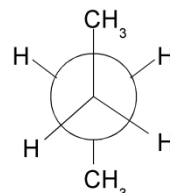
Steric Strain (Gauche)

- If two C's are adjacent (60° apart) in a staggered conformation, then E is raised due to steric strain. This is caused by e^{-1}/e^{-1} repulsion from the H atoms on the two C's (the H e^{-1} 's are too close). The interaction is called gauche, and E is 3.8 kJ/mol higher than when they are not adjacent.
- If the two C's are not adjacent, they must be 180° apart, and this staggered configuration is called anti.
- Long hydrocarbon chains tend to exist mainly in staggered anti configurations, because this is the lowest energy (most stable). Other conformations occur, but the molecules need to gain energy for this to happen.



Gauche Butane (C_4H_{10})

$$\text{Steric Strain} = 3.8 \text{ kJ}$$



Anti Configuration

$$\text{No Steric Strain}$$