

3. Alkanes and Cycloalkanes (text 3.1 – 3.11)

A. Structure and Nomenclature

- Straight- or branched-chain compounds of C and H are termed acyclic hydrocarbons or *alkanes*. They have the general formula C_nH_{2n+2} .
- Why do boiling points increase with molecular size?

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

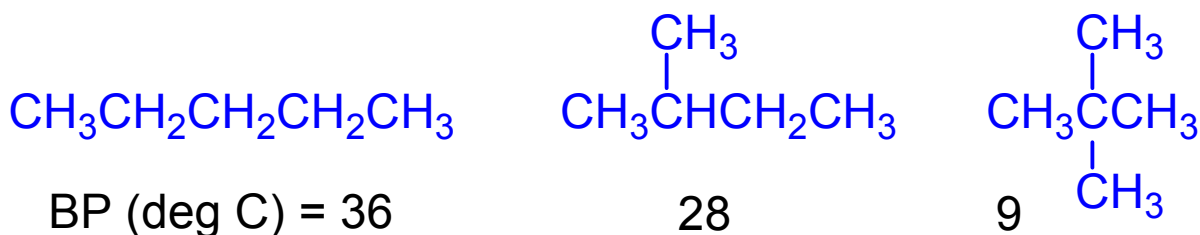
B. Constitutional (Structural) Isomerism

- Compounds with several atoms may be connected in various sequences (atom connectivity). This gives different compounds, known as **constitutional isomers**, that have the same molecular formula but different bonding sequence.

- The number of possible isomers rapidly increases with molecular size, since there would be more possible combinations of bonding sequences. This structural diversity is key to the centrality of organic chemistry in biological systems.

CH ₄	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		

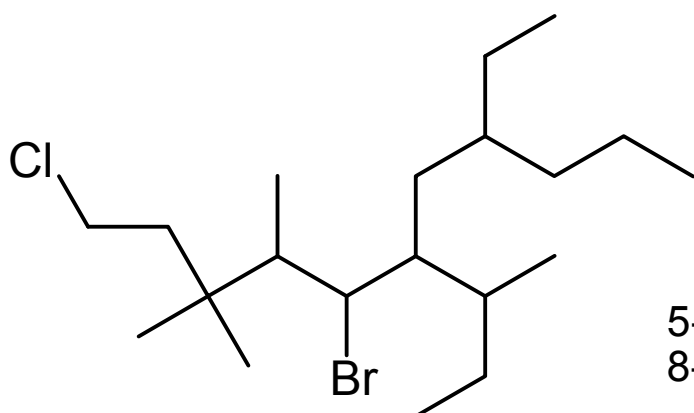
- Constitutional isomerism results in compounds of the same formula, but with different chemical and physical properties, e.g. the boiling points of various pentanes (C₅H₁₂).



- Self-study: review constitutional isomers from first-year chemistry and practice drawing them.

C. Nomenclature

- Alkanes are named according to rules set out by the International Union of Pure and Applied Chemistry (IUPAC).
- Required self study: learn rules in text section 3.4

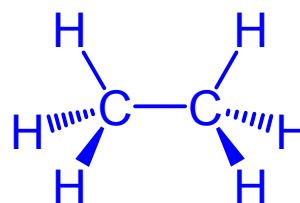


5-bromo-6-sec-butyl-1-chloro-
8-ethyl-3,3,4-trimethylundecane

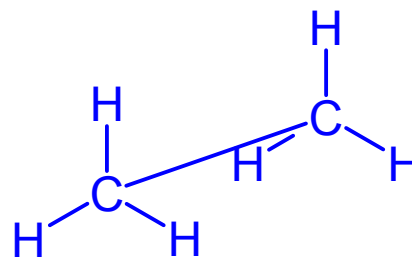
D. 3-D Structure

- Recall the conventions used for drawing a 3-D molecule on a 2-D surface. For example, ethane CH_3CH_3 .

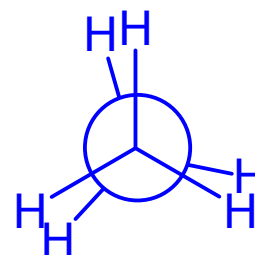
- Dot-Line-Wedge** is most versatile and widely used.



- 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.



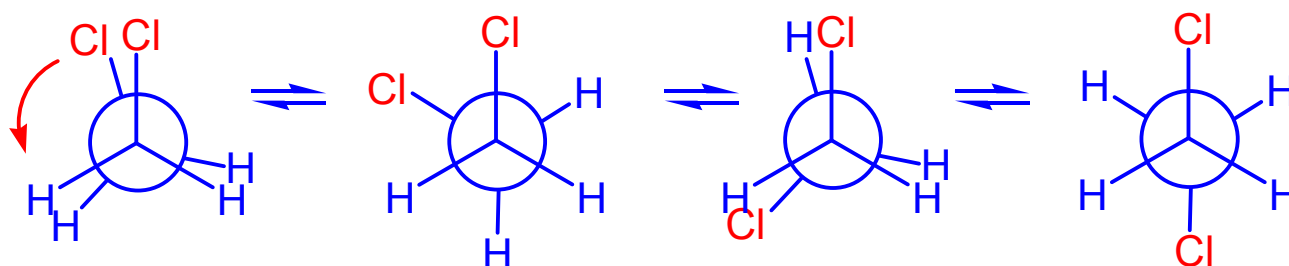
4. **Fischer projections**: useful for molecules with several chiral carbons (more later). C chain written vertically, east-west bonds above plane, north-south below plane. Frequently seen in biochemistry.



E. Molecular Conformations

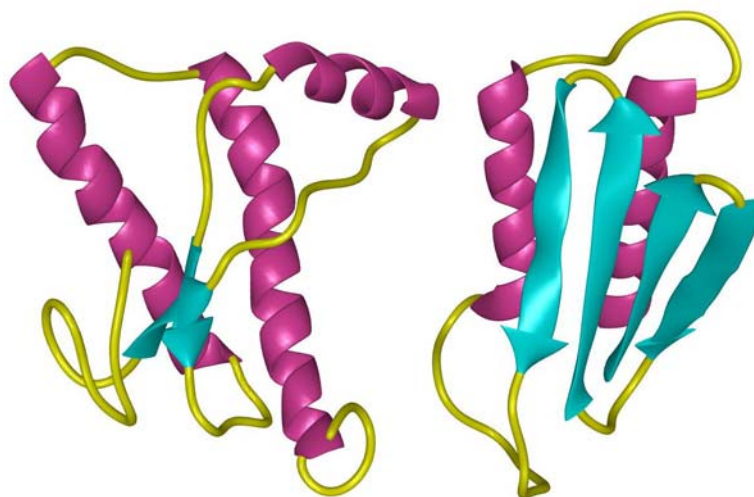
- Single bonds (σ) are able to rotate, which result in different, short-lived *spatial arrangements* of atoms or groups around single bonds. These are termed **conformations** (different shapes of the same constitutional isomer).
- When two atoms or groups are connected by a single bond (σ), they are free to spin about the bond axis. The strength of σ bonds is unaffected by such rotations.

- Newman projections are often used to show conformations, as shown below for 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$).



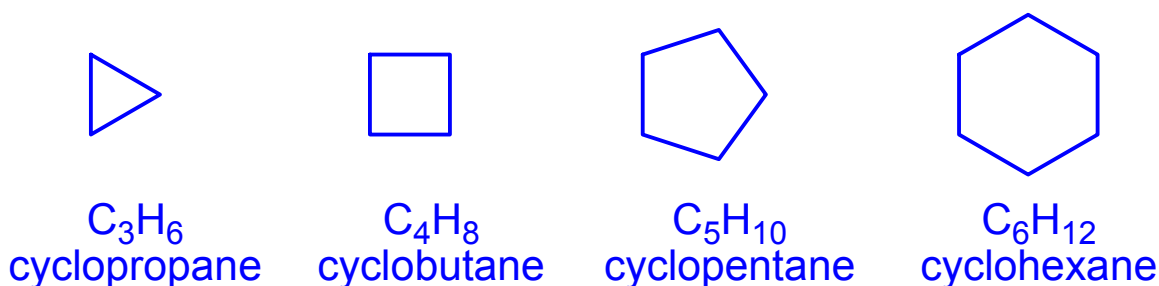
- All representations are the *same* molecule, but in different conformations. However, they are different in energy.
 - Far left: least stable conformation (eclipsed); has the two large chlorine atoms eclipsing each other
 - Far right: most stable conformation (staggered); has the two large chlorine atoms staggered and *anti*
- Because these rapidly interconvert (10^6 s^{-1}) at room temperature, they cannot be isolated and are NOT isomers.

Proteins can switch conformations. "Mad cow disease" (BSE) is believed to be caused by a prion, a harmful conformation of a normally benign protein. The diagram shows two conformations of the same prion. The one on the right (30% α -helix) is infectious, but the other (43% α -helix) is not.

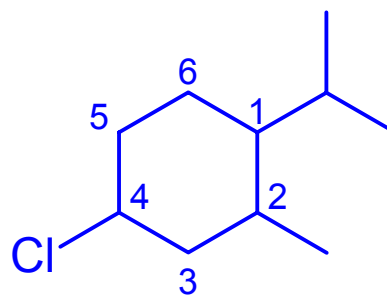


F. Cycloalkanes

- Cycloalkanes have the general formula C_nH_{2n} .
- 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 a bit out of the plane to reduce the eclipsed interactions, even though this increases angle strain (make a model of cyclohexane).



- Naming: the ring is numbered sequentially, with numbers chosen so that the **sum** of substituent numbers gives the lowest possible value, *i.e.* 4-chloro-1-isopropyl-2-methylcyclohexane.



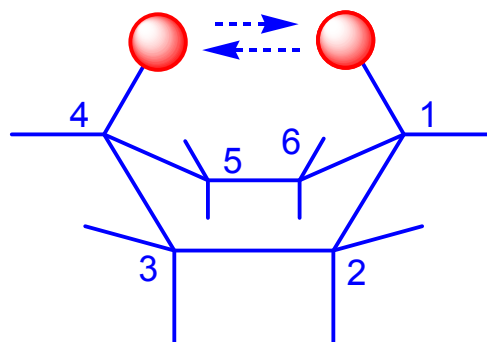
- Cyclohexanes drawn as polygons represent top views. However, side views of the ring reveal conformations.

G. Cyclohexane Conformations

- There are two distinct conformations in which all carbons have normal tetrahedral geometry (all bonds 109.5°). Review cyclohexane from first-year chemistry.

1. Boat Conformation

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

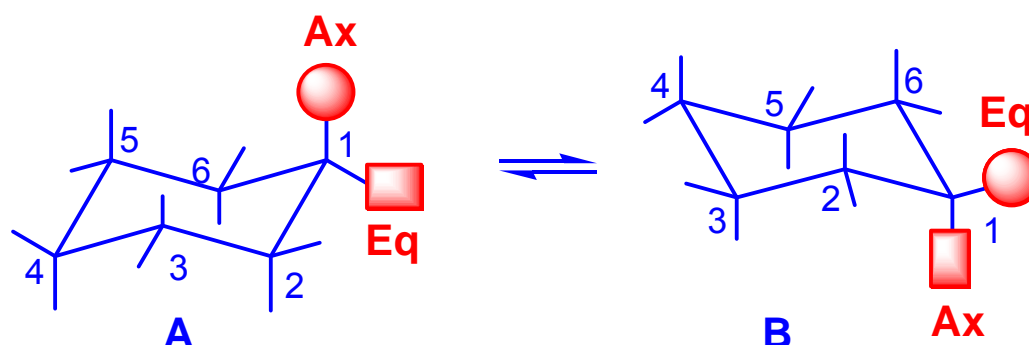


- Such interactions are not favourable, and thus, the boat conformation is present in the conformation equilibrium mixture in very small amounts (typically $< 0.1\%$).

2. Chair Conformation

- The six substituents directed straight up and down are **axial**. The other six (outward) are **equatorial** and 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.
- Notice the alternating pattern.** If the substituents at one carbon are axial down and equatorial up, the adjacent carbon's substituents are axial up and equatorial down.

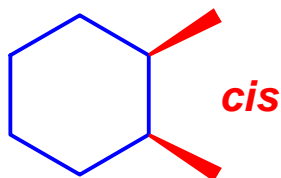
- Recall that every chair conformation (A) can change by bond rotation to an equivalent chair (B).



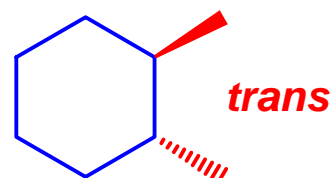
- This has some important implications:**
 - When A changes to B, all axial substituents become equatorial, and all equatorial ones become axial.
 - Of the two possible chairs, the one favoured (*i.e.* more stable) will be the one where large substituents are placed in the equatorial positions (less crowded).
- Thus, for cyclohexane rings with more than one 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.



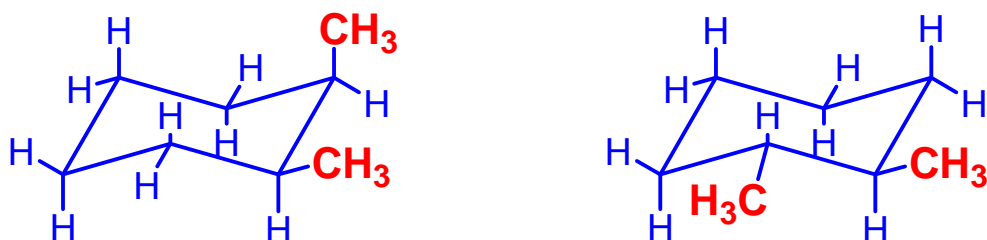
BP = 130 °, MP = -50 °



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.
- Alkenes can also have *cis-trans* isomers (more later).
- This is one type of **stereoisomerism**. Stereoisomers have the *same molecular formula and the same bonding sequence*, but have different, non-interconverting 3D architectures.
- Usually, but not always, *trans* isomers are more stable, since the large groups are further away (reduced *steric* interactions/hindrance).
- Like all isomers, *cis-trans* isomers do NOT interconvert at room temperature. However, they can exist in a usual number of conformations.

- It is possible to recognize *cis-trans* relationships even when drawn in the chair form. Two substituents that both lie above (or both below) the ring are *cis*. If one is above and the other is below, they are *trans*.

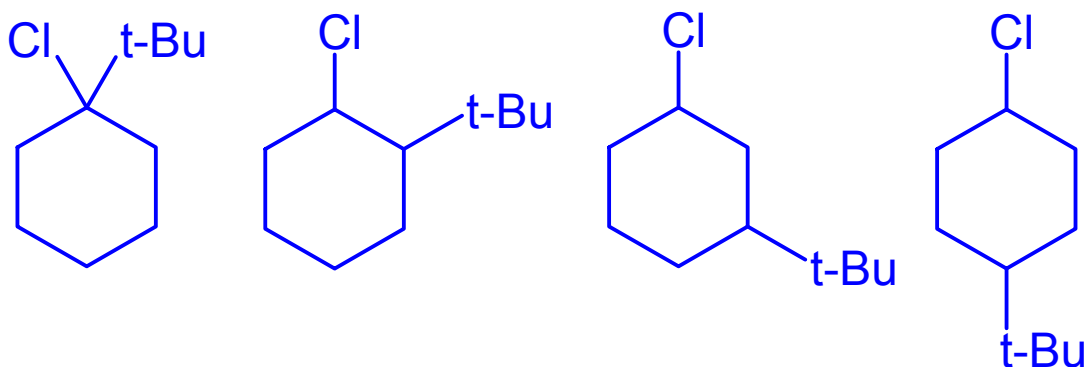


I. Stereochemical Summary (Up To Now)

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

1. Constitutional Isomerism

- For example, cyclohexane with a Cl and a *tert*-butyl group, known as t-Bu or $(\text{CH}_3)_3\text{C}-$. There are 4, and only 4 constitutional isomers.

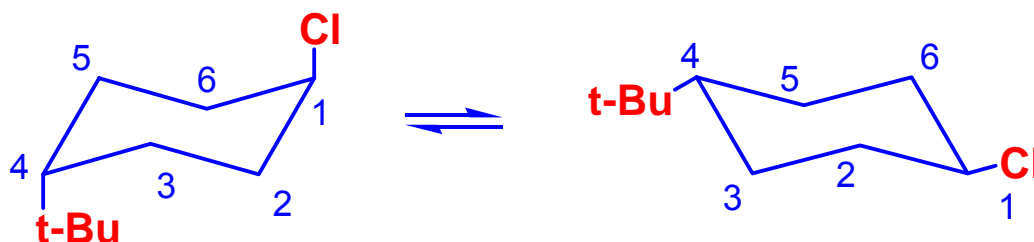


2. *cis-trans* Isomerism

- Different spatial arrangements of groups on rings, e.g. for 1-*tert*-butyl-4-chlorocyclohexane.



- 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-chloro-4-*tert*-butylcyclohexane.



- Example: draw *cis*-1-chloro-3-methylcyclohexane in its most stable conformation.

J. Alkane Properties and Reactions

1. Properties

- Alkanes are non-polar (all C-C and C-H bonds) and are usually insoluble in polar solvents (e.g. water).
- Relatively low BP and MP due to a lack of intermolecular attractive forces. BP and MP increase with molar mass.

2. Reactions

- Alkanes and cycloalkanes are generally unreactive due to the strength and non-polarity of C-C and C-H bonds. However, they react exothermically with O₂ to form CO₂ and H₂O by combustion (oxidation).
- The products of combustion (CO₂ and H₂O) are the starting materials for photosynthesis. The burning of fossil fuels (e.g. natural gas and petroleum), is making use of the chemical energy stored in them by photosynthetic reactions hundreds of millions of years ago.

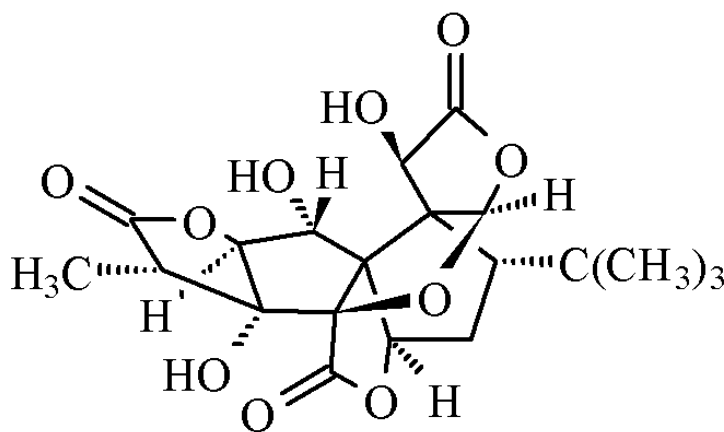
Summary

- Textbook pages 60-89, q. 16, 19, 20, 22 – 24, 29, 33, 37, 39, 41, 54, 55
- Midterms:

2005 #10 – 14	2006 #11 – 15
2007 #11 – 14	2008 #11 – 16

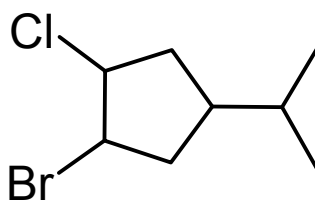
In lecture notes, we learn the basics of org chem using simple molecules to illustrate the structural and theoretical concepts. However, the goal of this course is to help you extend the fundamental principles to the molecules of life.

Living organisms are pretty good at putting lots of chemical diversity into its molecules. For example, consider the natural product ginkgolide B, the active compound in extracts of the ginkgo tree. See if you can i) identify all the functional groups present, ii) count up the total number of rings in the compound (be alert!), and iii) count the number of *cis-trans* relationships in the rings.



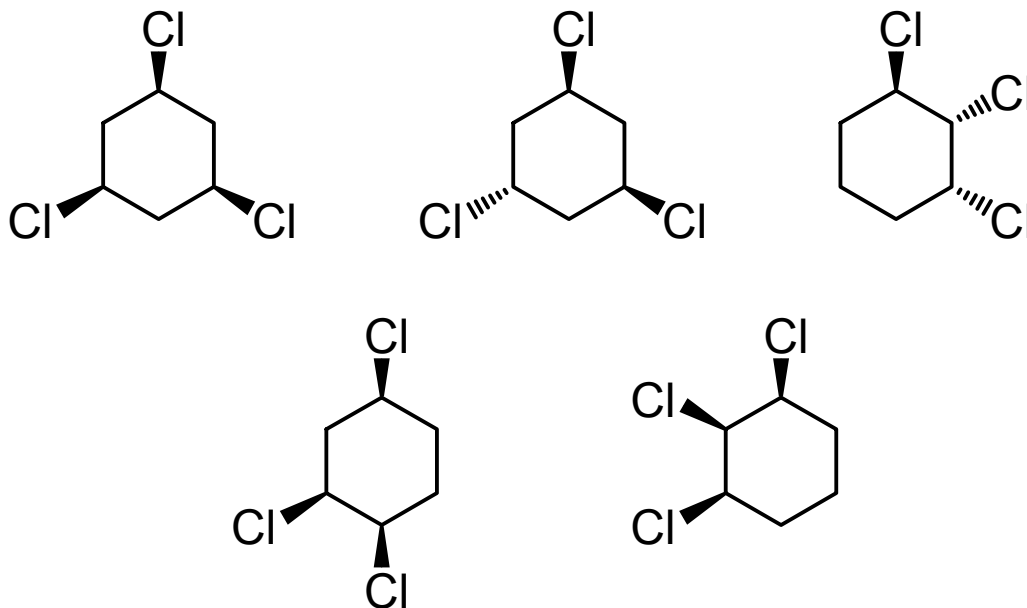
ginkgolide B

- Past test: What is a correct IUPAC name for this molecule?

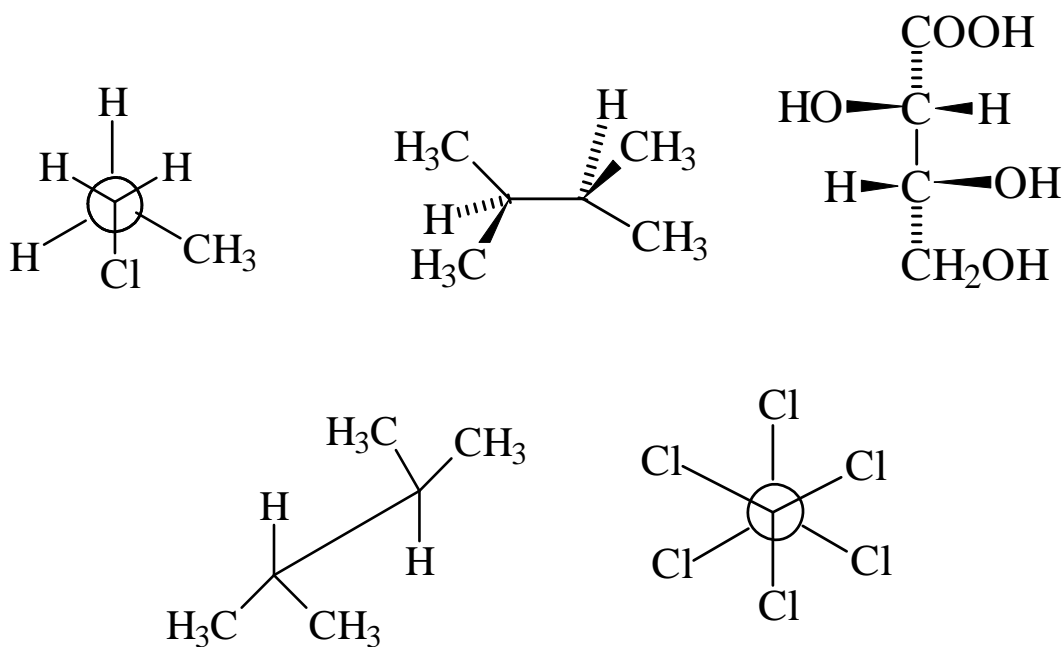


- 1-bromo-2-chloro-3-isopropylcyclopentane
- 2-bromo-1-chloro-4-isopropylcyclopentane
- 1-isopropyl-3-chloro-4-bromocyclopentane
- 1-isopropyl-3-bromo-4-chlorocyclopentane
- 1-bromo-5-chloro-3-isopropylcyclopentane

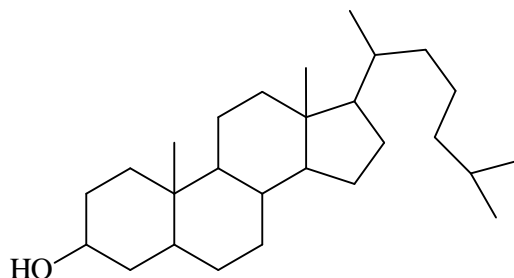
- Which one of the following molecules can form a conformation in which all chlorine atoms are equatorial?



- Which one of the following is *not* a staggered conformation?



- MCAT Questions: Refer to the structure of 3- β -cholestanol to answer the next two questions.



- How many tertiary carbons are present in 3- β -cholestanol?
A. 3 B. 5 C. 7 D. 9
- What type of alcohol is 3- β -cholestanol?
A. primary B. secondary C. tertiary D. quaternary