LOGIC BLOOM · CHEMISTRY · CLASS 11 AND 12

Isomerism

Structural · Geometrical · Optical · Conformational

NEET, JEE Main and JEE Advanced

Two compounds, one molecular formula, and completely different behaviour. That is the whole subject. This set works through every kind, from simply rewiring a chain to molecules that are chiral without owning a single chiral carbon.

11 Sections | 10 Diagrams | Advanced Tier | Trap Alerts | Fact Sheet

Logic Bloom
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Simplest way to understand the NCERT.

Contents

0 How to Read This Set

Sections 1 to 9 are the full syllabus for **NEET and JEE Main**. Sections 10 and 11 are the **JEE Advanced** layer. There a molecule can be chiral with no chiral carbon at all, and you are asked how to separate one enantiomer from the other.

THE WHOLE CHAPTER IN ONE LINE

Same formula. Ask whether the CONNECTIVITY differs, or only the arrangement in space.

Different connectivity means structural isomers. Same connectivity but a different 3D arrangement means stereoisomers. Every later question is just a sharper version of that one test.

THINK IT THROUGH

WHY THIS CHAPTER PAYS FOR ITSELF

- It is examined directly, and it is also the **language** of every organic mechanism you will meet afterwards.
- Reaction questions constantly ask whether a product is racemic, which product predominates, or which conformer reacts. None of that is answerable without this chapter.
- Almost all of it is reasoning, not recall, so it rewards understanding rather than memory.

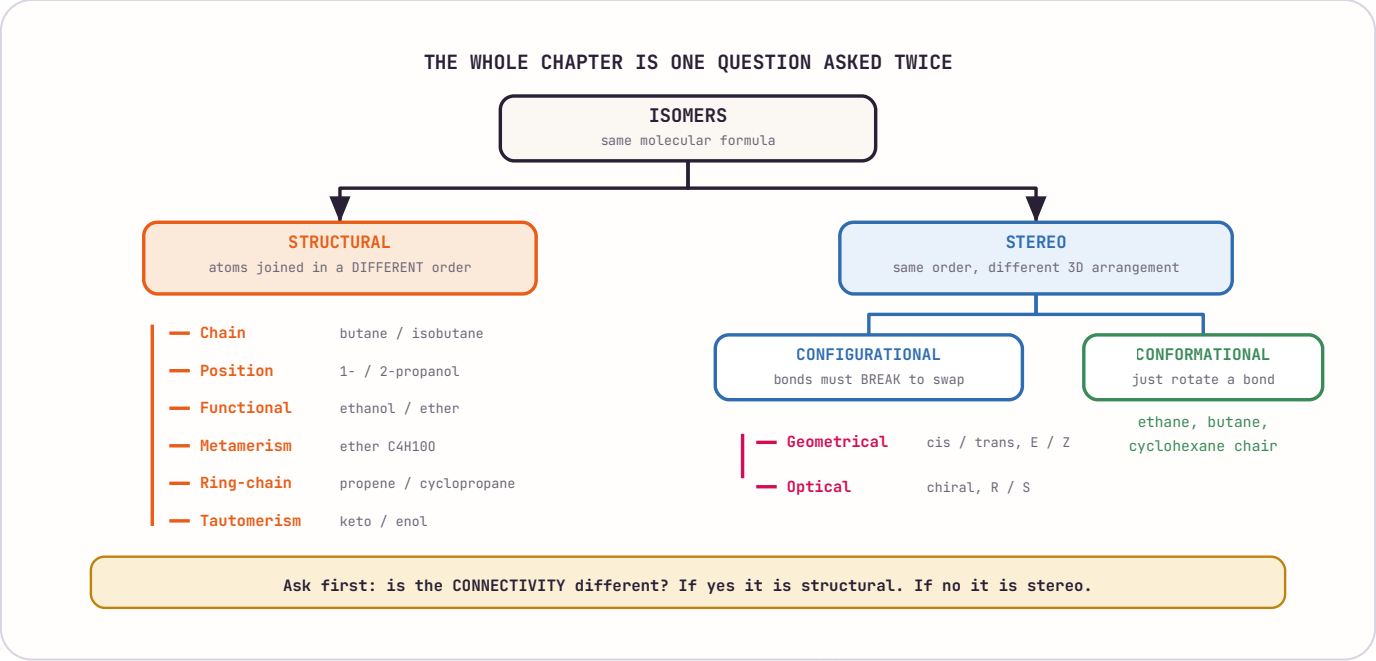
TRAP ALERT

THE HABIT THAT FIXES THIS CHAPTER

- Never eyeball two structures and guess. Count.
- **Count the carbons, then count what each carbon carries.** If the lists differ, the connectivity differs and they are structural isomers.
- If the lists match, you are in stereochemistry. Now look for a double bond, a ring, or a carbon holding four different groups.

1 The Isomerism Map

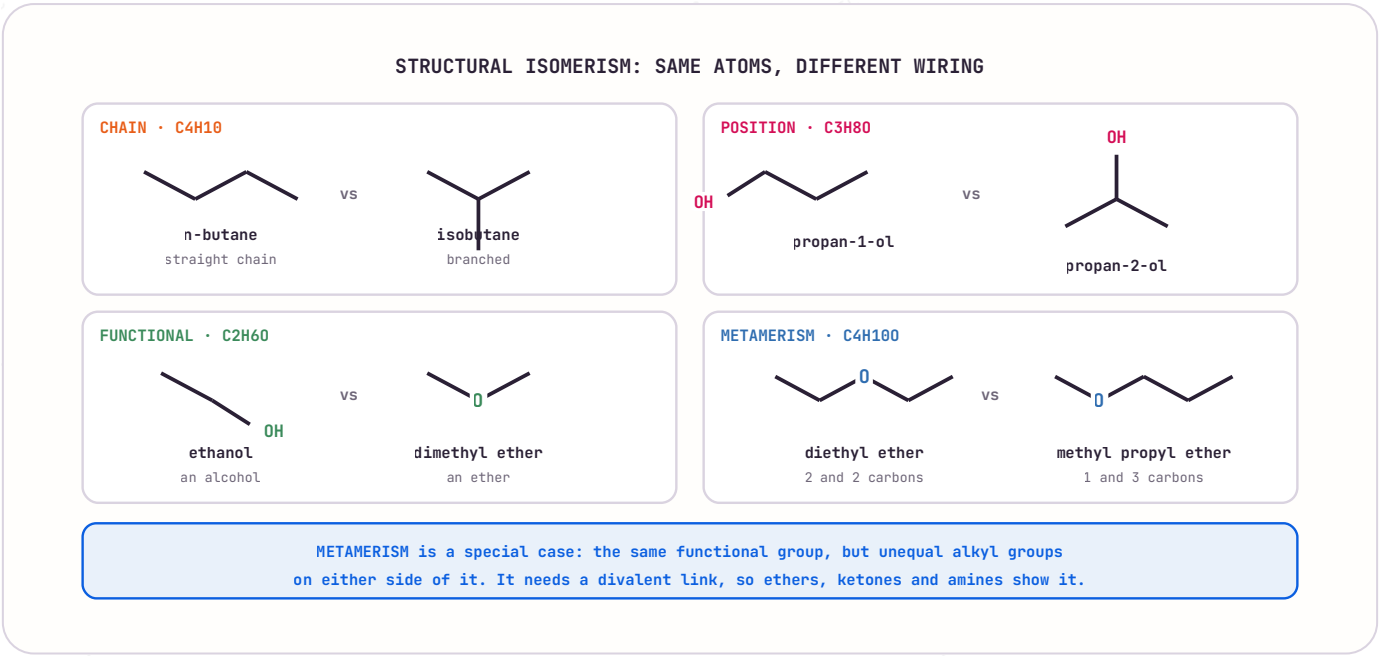
Learn this shape first. Nearly every question begins by asking you to place a pair of structures somewhere on it.



Two branches from one question. Structural changes the wiring; stereo keeps the wiring and moves atoms in space.

TERM	MEANS
Isomers	same molecular formula, different compounds
Structural	the atoms are joined in a different order
Stereoisomers	same order of joining, different arrangement in space
Configurational	you must **break a bond** to turn one into the other
Conformational	you only need to **rotate a single bond**
Enantiomers	stereoisomers that are non-superimposable mirror images
Diastereomers	stereoisomers that are **not** mirror images

2 Structural Isomerism



Four kinds, each drawn as the real structures rather than described in words.

TYPE	WHAT CHANGES	EXAMPLE
Chain	the carbon skeleton branches differently	n-butane and isobutane, C_4H_{10}
Position	the same group sits on a different carbon	propan-1-ol and propan-2-ol
Functional	the functional group itself is different	ethanol and dimethyl ether
Metamerism	unequal alkyl groups on either side of a divalent link	diethyl ether and methyl propyl ether

THINK IT THROUGH

COUNTING CHAIN ISOMERS WITHOUT DRAWING THEM ALL

- C_4H_{10} has 2, C_5H_{12} has 3, C_6H_{14} has 5, C_7H_{16} has 9.
- Work down: take the longest chain first, then shorten it by one and place the spare carbon in every distinct position.
- **Do not count the same skeleton twice.** A methyl at position 2 of pentane and a methyl at position 4 are the same molecule, read from the other end.

3 Tautomerism and Ring-Chain Isomerism

Tautomerism

A special structural isomerism. The two forms sit in a **dynamic equilibrium**, and they change into one another by moving a single hydrogen atom.

```
keto form CH3-CO-CH3  ⇌  enol form CH3-C(OH)=CH2
```

COMPOUND	PERCENTAGE ENOL	WHY
propanone	0.00025%	nothing stabilises the enol
cyclohexanone	0.02%	slightly more favourable
acetylacetone	80%	conjugated, and held by an internal hydrogen bond
phenol	100%	the keto form would destroy the aromatic ring

TRAP ALERT

TAUTOMERS ARE NOT RESONANCE STRUCTURES

- Resonance structures differ only in where the **electrons** are drawn. They are not real, separate species, and nothing moves.
- Tautomers differ in where an **ATOM** sits, here a hydrogen. Both are real molecules and can in principle be isolated.
- Resonance is shown with a double headed arrow. Tautomerism is shown with equilibrium arrows.

Ring-chain isomerism

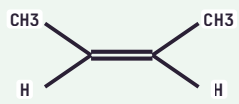
One isomer is an open chain, the other a ring. They match in formula because forming a ring costs exactly the same two hydrogens as forming a double bond.

```
C3H6 : propene CH2=CH-CH3  and  cyclopropane
```

4 Geometrical Isomerism

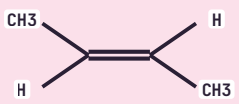
GEOMETRICAL ISOMERISM: THE DOUBLE BOND WILL NOT LET GO

CIS · but-2-ene



both methyls on the SAME side

TRANS · but-2-ene



on OPPOSITE sides

WHEN IT HAPPENS

1. rotation must be restricted
   (a C=C, a C=N, or a ring)
2. each doubly bonded atom must
   carry TWO DIFFERENT groups

PROPERTIES

CIS has the higher dipole and
so the higher BOILING point

TRANS packs better, so it has the
higher MELTING point

Restricted rotation locks the groups in place, so two different compounds exist.

BOTH CONDITIONS MUST HOLD

- **Rotation must be restricted**: a C=C, a C=N, an N=N, or a ring.
- **Each doubly bonded atom must carry two DIFFERENT groups.** If either atom holds two identical groups, there is only one compound.

How the two differ in the laboratory

PROPERTY	CIS	TRANS	REASON
Dipole moment	higher	lower or zero	in trans the bond moments cancel
Boiling point	higher	lower	stronger dipole attraction
Melting point	lower	**higher**	trans is more symmetrical, so it packs better
Solubility in water	higher	lower	follows the dipole
Stability	lower	**higher**	cis suffers steric crowding on one side

THINK IT THROUGH

MALEIC AND FUMARIC ACID, THE STANDARD PAIR

- **Maleic acid is cis**: melting point 135 °C, and water soluble. On heating it **forms an anhydride**. Both -COOH groups sit on the same side, so they can reach each other.
- **Fumaric acid is trans**: melting point 287 °C, and far less soluble. It **cannot form an anhydride**, because the two groups point away from each other.
- Maleic is the stronger **first** acid (pK_{a1} 1.9 against 3.0), because the mono-anion is held by an internal hydrogen bond.
- But maleic is the **weaker second** acid (pK_{a2} 6.1 against 4.4). That same hydrogen bond makes the second proton hard to pull off.

▶ PLAY

CIS AND TRANS STILL LOOKING IDENTICAL?

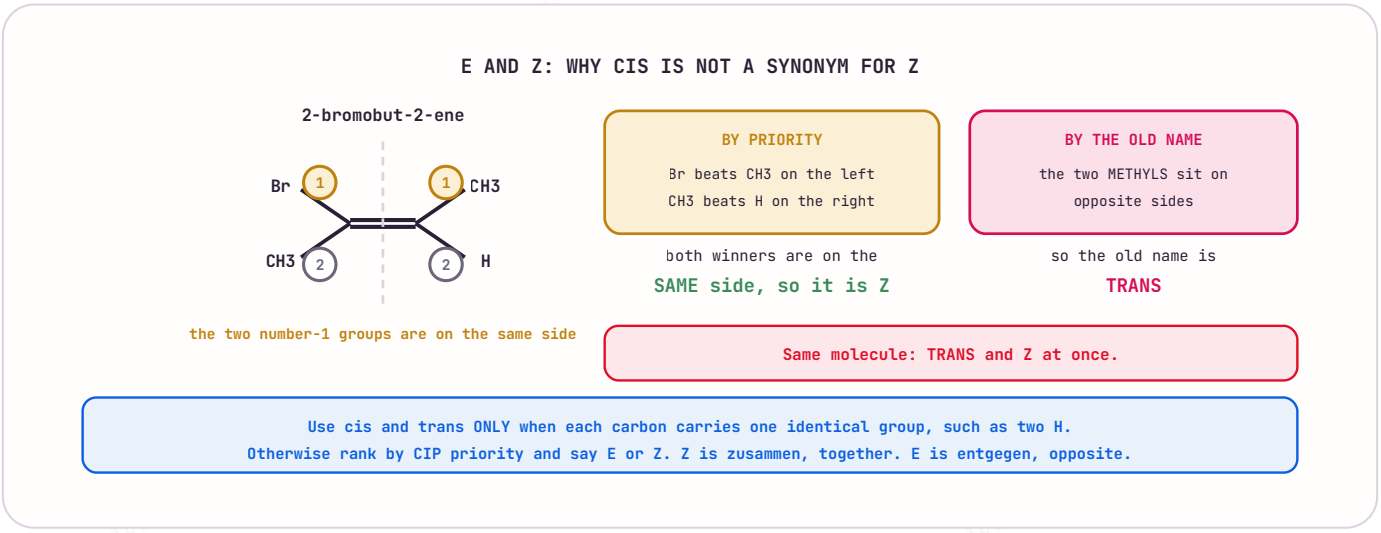
Rotate the molecule yourself and watch it refuse.

Grab the double bond, try to twist it, and see why the two forms can never interconvert without breaking it. **logicbloom.co.in/download** · Free to start.

SCAN

5 E and Z: The System That Never Fails

Cis and trans work only when each carbon happens to carry one identical group. When all four groups differ, the old names become meaningless and you must rank by priority instead.



The same molecule is trans by the old name and Z by priority. The two systems are not synonyms.

THE RULE

Rank the two groups on **each** carbon by CIP priority.

Z (zusammen, together) means the two winners are on the **same** side.

E (entgegen, opposite) means they are on **opposite** sides.

Counting geometrical isomers

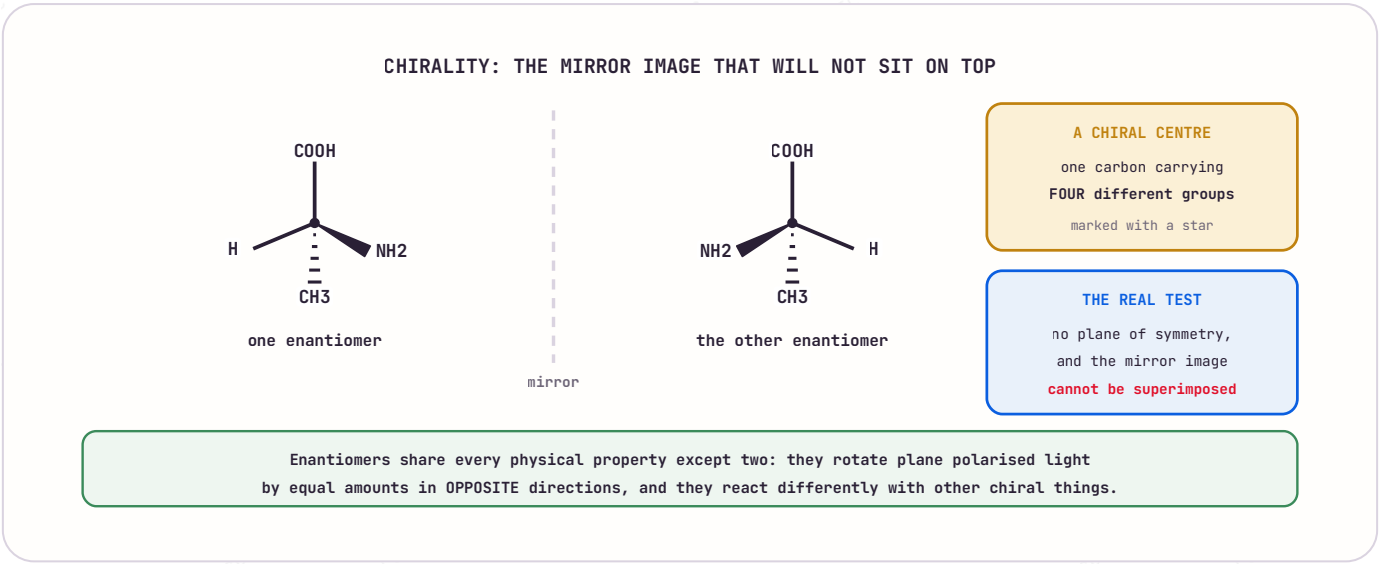
For a chain with n double bonds, each of which qualifies, there are 2^n geometrical isomers. If the molecule is symmetrical some of those coincide, so count carefully rather than applying the formula blindly.

TRAP ALERT

THREE PLACES STUDENTS LOSE THE MARK

- **Assuming cis always equals Z.** It does not, as the diagram above proves.
- Forgetting that **rings** also restrict rotation, so 1,2-dimethylcyclopropane has cis and trans forms too.
- Ranking by size rather than by atomic number. Priority is decided by the **atom**, not by how bulky the group looks.

6 Chirality and Optical Activity



Four different groups on one carbon, and the mirror image can never be laid on top.

The vocabulary, in order

TERM	MEANING
Chiral	not superimposable on its own mirror image
Chiral centre	a carbon carrying four **different** groups, marked with a star
Enantiomers	the two non-superimposable mirror images
Optically active	rotates the plane of plane polarised light
Dextrorotatory (+) or d	rotates the plane to the **right**
Laevorotatory (-) or l	rotates the plane to the **left**
Racemic mixture (±)	50:50 of both enantiomers, so it is optically **inactive**
Racemisation	converting a pure enantiomer into that 50:50 mixture

SPECIFIC ROTATION

$[\alpha] = \alpha_{observed} / (l \times c)$

l is the tube length in decimetre, c the concentration in g/mL. Specific rotation is a constant for a substance; the observed rotation is not.

THINK IT THROUGH

WHAT ENANTIOMERS DO AND DO NOT SHARE

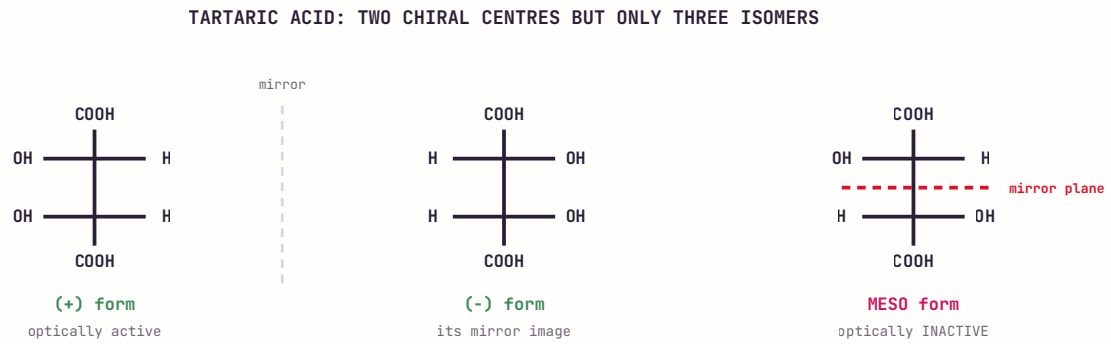
- **Identical**: melting point, boiling point, density, solubility in ordinary solvents, and every spectrum you will meet at this level.
- **Different**: the direction they rotate polarised light, and how they react with other chiral things.
- That second point matters. One enantiomer of a drug can heal while the other does nothing, and your body digests one sugar but not its mirror image.

TRAP ALERT

A RACEMIC MIXTURE IS NOT A MESO COMPOUND

- A **racemic mixture** is TWO compounds in a jar, in equal amounts. Separate them and each half is optically active.
- A **meso compound** is ONE compound. Nothing can be separated, and it is inactive no matter what you do to it.
- Both read zero on the polarimeter, which is exactly why the question is worth asking.

7 Meso Compounds and Counting Stereoisomers



A MESO compound has chiral centres yet is achiral overall. The top half rotates light one way, the bottom half rotates it back by exactly the same amount, so the two cancel inside one molecule. That is why 2 centres give 3 isomers here, not 4.

Two chiral centres, yet only three compounds exist, because one of the four is its own mirror image.

HOW MANY STEREOISOMERS?

No symmetry possible: $\mathbf{2^n}$ for n chiral centres.

Molecule with two identical halves, n **even**: total 2^{n-1}, of which $2^{(n/2)-1}$ are meso.

Molecule with two identical halves, n **odd**: total 2^{n-1}, of which $2^{(n-1)/2}$ are meso.

COMPOUND	CENTRES	TOTAL	ACTIVE	MESO
butan-2-ol	1	2	2	0
2,3-dibromopentane	2 (ends differ)	4	4	0
tartaric acid	2 (ends the same)	**3**	2	1
2,3-dichlorobutane	2 (ends the same)	**3**	2	1
2,3,4-trihydroxyglutaric acid	3 (ends the same)	**4**	2	2

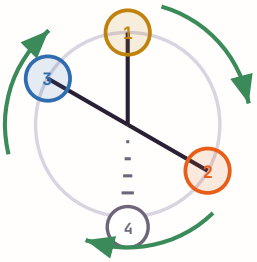
THINK IT THROUGH

HOW TO SPOT A MESO COMPOUND IN TWO SECONDS

- Draw it as a Fischer projection with the chain vertical.
- Look for a **horizontal mirror line** through the middle. If the top half is the exact reflection of the bottom half, it is meso.
- In practice: the same groups on the same side, top and bottom. Both OH on the left in the diagram above is the (+) form; one left and one right is the meso form.
- **A meso compound has chiral centres but is achiral overall.** That sentence is the whole idea.

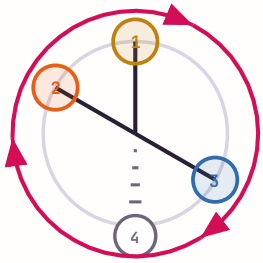
8 R and S Configuration

ASSIGNING R AND S: POINT THE LOWEST PRIORITY AWAY, THEN STEER



R · rectus

clockwise



S · sinister

anticlockwise

THE CIP RULES

1. higher atomic number wins
2. tie? look one atom further out, and compare the sets
3. **a double bond counts twice**
4. isotopes: heavier wins

IF 4 POINTS AT YOU

read the direction as usual, **then REVERSE the answer.**

R and S describe the arrangement. (+) and (-) describe measured rotation. Neither predicts the other.

Put the lowest priority behind, then read 1 to 2 to 3. Clockwise is R and anticlockwise is S.

The CIP rules, applied in order

RULE	HOW IT WORKS
1. Atomic number	the atom directly attached with the higher atomic number wins
2. Go one step out	if tied, compare the sets of atoms attached to each, highest first
3. Multiple bonds	a double bond counts the atom **twice**, a triple bond three times
4. Isotopes	if still tied, the heavier isotope wins, so D beats H

THE STANDARD PRIORITY ORDER, WORTH MEMORISING

$-I > -Br > -Cl > -SH > -F > -OCH_3 > -OH > -NO_2 > -NH_2 > -COOH > -CONH_2 > -CHO > -CH_2OH > -C_6H_5 > -CH{=}CH_2 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3 > -H$

THINK IT THROUGH

WHY COOH BEATS CHO BEATS CH2OH

- All three start with carbon, so rule 1 ties and you go one step out.
- **-COOH**: that carbon holds O, O and O once the double bond is duplicated.
- **-CHO**: it holds O, O and H.
- **-CH_2OH**: it holds O, H and H.
- Compare the sets in order and the answer falls out. **(O,O,O) beats (O,O,H) beats (O,H,H).**

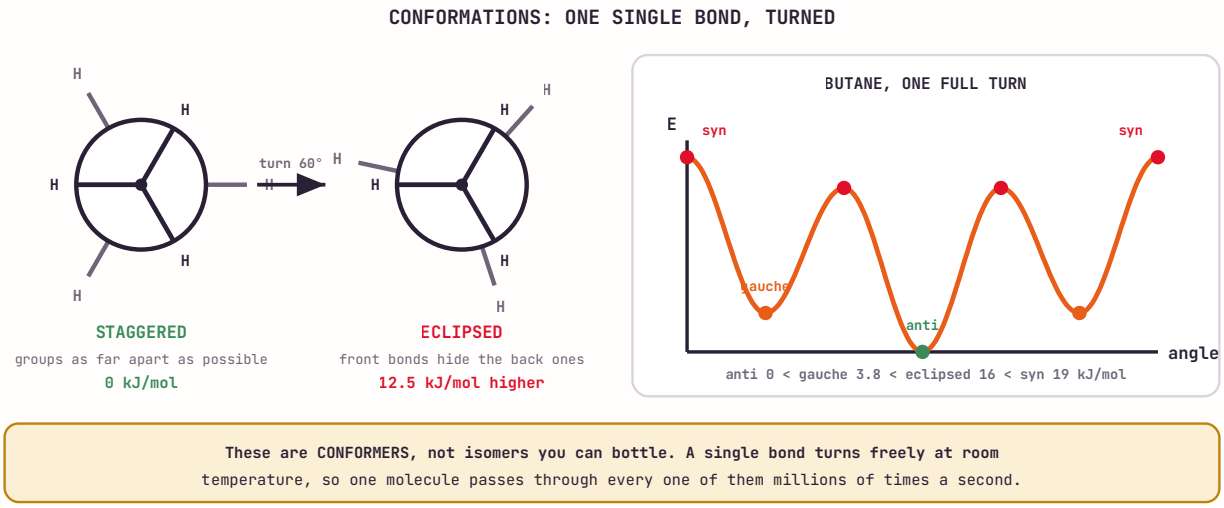
TRAP ALERT

R AND S HAVE NOTHING TO DO WITH (+) AND (-)

- **R and S describe the arrangement in space.** You work them out on paper.
- **(+) and (−) describe measured rotation.** You get them from a polarimeter.
- An R compound may be either (+) or (−). Knowing one tells you nothing about the other.
- If the lowest priority group points **towards** you, read the direction normally and then reverse your answer.

9 Conformational Isomerism

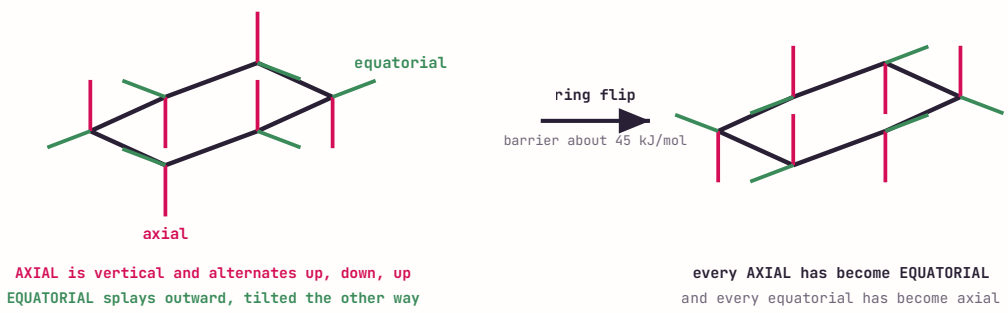
Rotate a single bond and the shape changes without breaking anything. The shapes you pass through are **conformers**. They are real, but they cannot be bottled separately at room temperature.



Ethane on the left. Butane on the right, drawn through a complete turn.

CONFORMER	DIHEDRAL ANGLE	RELATIVE ENERGY	NOTE
anti	180°	0 kJ/mol	the most stable, methyls furthest apart
gauche	60° and 300°	3.8 kJ/mol	staggered, but the methyls are crowded
eclipsed	120° and 240°	16 kJ/mol	methyl against hydrogen
syn or fully eclipsed	0°	19 kJ/mol	methyl directly against methyl, the worst

Cyclohexane



The chair, its two kinds of bond, and what a ring flip does to them.

FORM	ENERGY ABOVE THE CHAIR	COMMENT
chair	0 kJ/mol	completely staggered, no strain, by far the commonest
twist boat	23 kJ/mol	a shallow minimum, so it does exist briefly
boat	30 kJ/mol	eclipsed bonds plus a flagpole clash
half chair	45 kJ/mol	not a form at all, it is the barrier being climbed

THINK IT THROUGH

WHICH SIDE DOES A SUBSTITUENT CHOOSE?

- An axial group points straight up or down, into the space above the ring. There it clashes with the two other axial groups on the same face. That is **1,3-diaxial strain**.
- So a bulky group prefers **equatorial**. The bigger it is, the stronger the preference.
- Methyl prefers equatorial by 7.3 kJ/mol, which is 95 percent equatorial. **tert**-butyl prefers it by 20.5 kJ/mol, which locks the ring completely.

TIER 2

The JEE Advanced layer

Everything so far is complete for NEET and JEE Main. Advanced asks for chirality without a chiral carbon. It also asks how enantiomers differ from diastereomers, and how you would separate them.

10 Beyond the Chiral Carbon

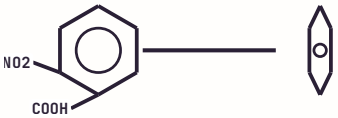
A chiral carbon is the commonest source of chirality, but it is not the requirement. The real requirement is simply that the molecule has **no plane of symmetry**.

CHIRAL WITHOUT A SINGLE CHIRAL CARBON

ALLENE

the left pair lies flat on the page, **the right pair sticks out at 90°**

BIPHENYL



bulky groups at the ortho positions **stop the two rings turning flat**

THE REAL RULE

Chirality needs NO **plane of symmetry.**

A chiral carbon is the commonest way to get that. It is not the only way.

Here the whole molecule is twisted, so the mirror image still will not sit on top of it.

Allene is chiral only when BOTH ends carry two different groups. Biphenyl is chiral only when the ortho groups are bulky AND each ring is unsymmetrically substituted.

Two molecules with no chiral carbon anywhere, both of which are chiral.

SYSTEM	CHIRAL WHEN	CALLED
Allene $R_2C=C=CR_2$	both ends carry two different groups	axial chirality
Biphenyl	ortho groups are bulky **and** each ring is unsymmetrical	atropisomerism
Spirane	the two rings are perpendicular and each is unsymmetrical	axial chirality
trans-cyclooctene	the ring is too small to let the chain pass through	planar chirality

TRAP ALERT

THE CUMULENE RULE, ASKED ALMOST EVERY YEAR

- Count the double bonds in a row. An **EVEN** number, as in allene with two, leaves the two end groups in **perpendicular** planes, so you get optical isomerism.
- An **ODD** number, as in an ordinary alkene with one, leaves the end groups **coplanar**. So you get cis and trans instead.
- So allene gives enantiomers and butadiene-type cumulenes give geometrical isomers. The question turns entirely on counting the double bonds.

THINK IT THROUGH

OTHER THINGS THAT BLOCK A CHIRAL CARBON FROM MAKING A CHIRAL MOLECULE

- A **meso** arrangement, as in section 7. Centres are present, symmetry cancels them.
- A carbon with a **lone pair**, such as an amine, inverts millions of times a second. So a simple amine cannot be resolved, even though it looks chiral on paper.
- **Always test for the plane of symmetry rather than counting stars.**

11 Diastereomers, Optical Purity and Resolution

Enantiomers against diastereomers

	ENANTIOMERS	DIASTEREOMERS
Relationship	mirror images	**not** mirror images
Every centre	**all** centres inverted	**some** centres inverted, not all
Melting and boiling point	identical	**different**
Solubility	identical	**different**
Separation	very hard, needs a chiral reagent	easy, ordinary crystallisation works
Optical rotation	equal and opposite	different, and unrelated

OPTICAL PURITY, ALSO CALLED ENANTIOMERIC EXCESS

optical purity = (observed rotation / rotation of the pure enantiomer) × 100

A mixture of 75% R and 25% S has an excess of 50%, so it shows half the rotation of the pure R compound. The remaining 50% behaves as a racemate.

Resolution: separating a racemate

THINK IT THROUGH

WHY YOU CANNOT SIMPLY CRYSTALLISE IT

- The two enantiomers have identical solubility, so no ordinary method can tell them apart.
- The trick is to react the racemate with a **single pure enantiomer** of something else, often a natural acid or base.
- The products are now **diastereomers**, which have different solubilities and **can** be crystallised apart.
- Split them, then remove the added reagent, and you have the two pure enantiomers.
- Pasteur did the first resolution in 1848, picking tartrate crystals apart by hand under a lens.

TRAP ALERT

ERYTHRO AND THREO, SYN AND ANTI

- When two adjacent centres carry similar groups, the isomers get these older names.
- **Erythro**: in the Fischer projection the two similar groups lie on the **same** side. It resembles the meso arrangement.
- **Threo**: they lie on **opposite** sides.
- Modern papers prefer syn and anti, but Indian exam papers still use erythro and threo, so recognise both.

▶ PLAY

STEREOCHEMISTRY STILL FEELS ABSTRACT?

Build the molecule and turn it over yourself.

Rotate an enantiomer in three dimensions and try to lay it on its mirror image. The moment it refuses, the idea lands. **logicbloom.co.in/download** · Free to start.

SCAN

★ Isomerism · Fact Sheet

Every rule for revision day. Print this page alone.

THE FIRST TEST

Different connectivity = STRUCTURAL

Same connectivity = STEREO
Ask this before anything else.

STRUCTURAL TYPES

Chain, position, functional,

metamerism, ring-chain, tautomerism.

METAMERISM

Same group, unequal alkyl

groups either side of it.
Ethers, ketones, amines.

GEOMETRICAL NEEDS

Restricted rotation, AND

two different groups on each doubly bonded atom.

CIS VS TRANS

cis: higher bp, higher dipole

trans: higher mp, more stable trans packs better.

CIS IS NOT Z

Rank by CIP, then say E or Z.

2-bromobut-2-ene is trans AND Z at once.

CHIRALITY

No plane of symmetry.

A chiral carbon carries FOUR different groups.

COUNTING

2^n with no symmetry.

Symmetric ends: 2^{n-1} total, some of them meso.

MESO

Has chiral centres yet is achiral.

Internal mirror plane.
Tartaric acid: 3 isomers, not 4.

RACEMATE VS MESO

Racemate: TWO compounds, separable.

Meso: ONE compound, never separable.
Both read zero rotation.

R / S

Lowest priority to the back,

then 1 to 2 to 3.
Clockwise R, anticlockwise S.

R/S VS (+)/(-)

R/S is arrangement on paper.

(+)/(−) is measured rotation.
Neither predicts the other.

BUTANE ENERGIES

anti 0 < gauche 3.8

< eclipsed 16 < syn 19 kJ/mol.

CYCLOHEXANE

chair 0 < twist boat 23

< boat 30 < half chair 45.
Bulky groups go EQUATORIAL.

CUMULENE RULE

EVEN double bonds: optical.

ODD double bonds: geometrical.
Allene has two, so it is chiral.

RESOLUTION

React with one pure enantiomer,

making DIASTEREOMERS, then crystallise them apart.

Logic Bloom

Simplest way to understand the NCERT.

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★ STEREOCHEMISTRY STILL NOT CLICKING?

Play it. Then practice it.

Open Isomerism in the Logic Bloom app. Turn a molecule over in three dimensions, try to lay it on its mirror image. Flip a cyclohexane ring and watch every axial bond become equatorial. Then drill the counting until it is automatic. Free to start.

SCAN → PLAY · READ · PRACTICE