STEREOISOMERISM - GEOMETRICAL ISOMERISM

Geometric isomerism (also known as cis-trans isomerism or E-Z isomerism) is a form of stereoisomerism. This page explains what stereoisomers are and how you recognise the possibility of geometric isomers in a molecule.

Further down the page, you will find a link to a second page which describes the E-Z notation for naming geometric isomers. You shouldn't move on to that page (even if the E-Z notation is what your syllabus is asking for) until you are really confident about how geometric isomers arise and how they are named on the cis-trans system.

The E-Z system is better for naming more complicated structures but is more difficult to understand than cis-trans. The cis-trans system of naming is still widely used - especially for the sort of simple molecules you will meet at this level. That means that irrespective of what your syllabus might say, you will have to be familiar with both systems. Get the easier one sorted out before you go on to the more sophisticated one!

What is Geometric Isomers?

In stereoisomerism, the atoms making up the isomers are joined up in the same order, but still manage to have a different spatial arrangement. Geometric isomerism is one form of stereoisomerism.

Geometric (cis / trans) isomerism: How geometric isomers arise

These isomers occur where you have restricted rotation somewhere in a molecule. Think about what happens in molecules where there is unrestricted rotation about carbon bonds - in other words where the carbon-carbon bonds are all single. The next diagram shows two possible configurations of 1,2-dichloroethane.

![Diagram of 1,2-dichloroethane isomers](image)

These two models represent exactly the same molecule. You can get from one to the other just by twisting around the carbon-carbon single bond. These molecules are not isomers.

If you draw a structural formula instead of using models, you have to bear in mind the possibility of this free rotation about single bonds. You must accept that these two structures represent the same molecule:

\[
\begin{align*}
\text{H} & \quad \text{Cl} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{C} & \quad \text{H} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

But what happens if you have a carbon-carbon double bond - as in 1,2-dichloroethene?
These two molecules aren't the same. The carbon-carbon double bond won't rotate and so you would have to take the models to pieces in order to convert one structure into the other one. That is a simple test for isomers. If you have to take a model to pieces to convert it into another one, then you've got isomers. If you merely have to twist it a bit, then you haven't!

In one, the two chlorine atoms are locked on opposite sides of the double bond. This is known as the \textit{trans} isomer. (\textit{trans} : from latin meaning “across” - as in transatlantic).

In the other, the two chlorine atoms are locked on the same side of the double bond. This is known as the \textit{cis} isomer. (\textit{cis} : from latin meaning “on this side”)

\textit{trans}-1,2-dichloroethene \hspace{1cm} \textit{cis}-1,2-dichloroethene

The most likely example of geometric isomerism you will meet at an introductory level is \textit{but-2-ene}. In one case, the CH$_3$ groups are on opposite sides of the double bond, and in the other case they are on the same side.

\textit{trans}-but-2-ene \hspace{1cm} \textit{cis}-but-2-ene

\textbf{How to recognise the possibility of geometric isomerism}

You obviously need to have restricted rotation somewhere in the molecule. Compounds containing a carbon-carbon double bond have this restricted rotation. (Other sorts of compounds may have restricted rotation as well, but we are concentrating on the case you are most likely to meet when you first come across geometric isomers.)

\textbf{What needs to be attached to the carbon-carbon double bond?}
Although we’ve swapped the right-hand groups around, these are still the same molecule. To get from one to the other, all you would have to do is to turn the whole model over.

You won’t have geometric isomers if there are two groups the same on one end of the bond - in this case, the two pink groups on the left-hand end.

So, there must be two different groups on the left-hand carbon and two different groups on the right-hand one. The cases we’ve been exploring earlier are like this:

But you could make things even more different and still have geometric isomers:

Here, the blue and green groups are either on the same side of the bond or the opposite side.

Or you could go the whole hog and make everything different. You still get geometric isomers, but by now the words cis and trans are meaningless. This is where the more sophisticated E-Z notation comes in.
**At A Glance:** To get geometric isomers you must have:

- restricted rotation (often involving a carbon-carbon double bond for introductory purposes);
- two different groups on the left-hand end of the bond and two different groups on the right-hand end. It doesn't matter whether the left-hand groups are the same as the right-hand ones or not.

**The effect of geometric isomerism on physical properties**

The table shows the melting point and boiling point of the cis and trans isomers of 1,2-dichloroethene.

<table>
<thead>
<tr>
<th>isomer</th>
<th>melting point (°C)</th>
<th>boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis</td>
<td>-80</td>
<td>60</td>
</tr>
<tr>
<td>trans</td>
<td>-50</td>
<td>48</td>
</tr>
</tbody>
</table>

You will notice that:

- the trans isomer has the higher melting point;
- the cis isomer has the higher boiling point.

This is common. You can see the same effect with the cis and trans isomers of but-2-ene:

<table>
<thead>
<tr>
<th>isomer</th>
<th>melting point (°C)</th>
<th>boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-but-2-ene</td>
<td>-139</td>
<td>4</td>
</tr>
<tr>
<td>trans-but-2-ene</td>
<td>-106</td>
<td>1</td>
</tr>
</tbody>
</table>

**Why is the boiling point of the cis isomers higher?**

There must be stronger intermolecular forces between the molecules of the cis isomers than between trans isomers.

Taking *1,2-dichloroethene* as an example:

Both of the isomers have exactly the same atoms joined up in exactly the same order. That means that the van der Waals dispersion forces between the molecules will be identical in both cases.

The difference between the two is that the cis isomer is a polar molecule whereas the trans isomer is non-polar.

*Both molecules contain polar chlorine-carbon bonds, but in the cis isomer they are both on the same side of the molecule. That means that one side of the molecule will have a slight negative charge while the*
other is slightly positive. The molecule is therefore polar.

Because of this, there will be dipole-dipole interactions as well as dispersion forces - needing extra energy to break. That will raise the boiling point.

A similar thing happens where there are CH₃ groups attached to the carbon-carbon double bond, as in cis-but-2-ene.

Alkyl groups like methyl groups tend to "push" electrons away from themselves. You again get a polar molecule, although with a reversed polarity from the first example.

E/Z Stereoisomerism (Geometrical/Geometric cis/trans Isomerism)

The IUPAC recommend that the term geometrical/geometric isomerism is NOT used but to use the stereoisomerism classification E/Z stereoisomerism or E-Z isomerism. The E/Z notation is replacing the limited cis/trans notation in assigning names to a particular stereoisomer. However cis/trans nomenclature is in widespread use so it will be acknowledged in parallel with the E/Z convention where appropriate.

In molecules of the same molecular formula, exhibit E/Z stereoisomerism, spatially different molecules (E/Z isomers) exist because of the inhibited/restricted rotation about at least one bond due to too high an energy requirement (don't say rotation is impossible, its the energy barrier that causes the existence of two distinct isomers!)

A simple example: but-2-ene:

The (trans) \[ \text{CH}_3\text{C}=\text{C}\text{H} \]

and the \[ \text{CH}_3\text{C}=\text{C}\text{H}_3 \]

(cis) \[ \text{H}\text{C}=\text{C}\text{H} \]

forms of but-2-ene.
However, in order for E/Z stereoisomers to exist there must be two different atoms/groups attached to both carbon atoms of the C=C carbon carbon double bond (see diagram below) or two adjacent carbons in a substituted cycloalkane.

The three most common situations you are likely to encounter are >C=C< or a >C=N- double bond and around a C-C single bond in cycloalkanes. In both cases the energy required is too high to allow free rotation around the double bond BUT free rotation is possible around single bonds (C-C, C-O etc.) e.g. alkyl groups around the C-C single bonds in non-cyclo linear/branched alkanes.

If two identical atoms/groups are attached to the same carbon, you cannot have geometrical isomers e.g. those with $R_2C=C< or R_2C=N- where R = R$.

The 'old' nomenclature term cis often means the same substituents are on the same side of the double bond and trans when they are on opposite sides. Under the E/Z notation cis is now Z and trans is now E. In a sense cis/trans isomers were a special case of a substituent and a hydrogen atom on each carbon of the C=C double bond. E/Z configuration assignment is absolutely necessary when there 3 or 4 different substituents on the C=C group (again, see the diagram below)

The Z isomer is where both highest priority groups are on the same side of the double bond (includes all cis configurations of the old convention).

The E isomer is where the two highest priority atoms/groups are diagonally opposite each other on different sides of the plane of the double bond system (includes all trans isomers of the old convention).

(Note: In terms of the two highest priority atoms or groups, E, 'on opposite sides', comes from the German word entgegen, meaning 'opposite' and the Z 'on the same side' comes from the German word zusammen meaning 'together')

Case study: Isomers of C₄H₈, cis/trans but-2-ene

Priority order: -CH₃ > H (since at. no. of 6 > 1 for hydrogen)

1. Cis-but-2-ene (cis) (bpt 4°C)

   \[
   \text{CH}_3\quad \text{C} = \text{C} \quad \text{CH}_3
   \]

   (Cis-2-butene)

   The Z isomer has the two highest priority groups on the same side of the plane of the C=C double bond.

2. Trans-but-2-ene (trans) (bpt 1°C)

   \[
   \text{CH}_3\quad \text{C} = \text{C} \quad \text{CH}_3
   \]

   (Trans-2-butene)

   The E isomer has the two highest priority groups on opposite sides of the carbon = carbon double bond.

(1) and (2) are very similar physically (e.g. colourless gases and very low bpt) and chemically (e.g. alkene electrophilic addition reactions).

Note that there are four other physically similar isomers of C₄H₈ namely, (3) 2-methylpropene (bpt -7°C, chain isomer), (4) but-1-ene (bpt -6°C, position of C=C isomer), (5) methylcyclopropane and (6) cyclobutane (bpts 5°C and 13°C, 5 and 6 are alkane functional group isomers of alkenes 1 to 4), BUT none of (3) to (6) can form geometrical isomers.
E-3-methylpent-2-ene (trans)

Z-3-methylpent-2-ene (cis)

Two identical groups are attached to one of the carbon atoms of the double bond.

4,4-dimethylpent-2-ene.

Z-4,4-dimethylpent-2-ene and E-4,4-dimethylpent-2-ene

Case study: trans/cis or Z/E-but-2-ene-1,4-dioic acid, HOOC-CH=CH-COOH (butenedioic acids, old names given below). Substituent group priority -COOH > H

On heating the trans form (1) fumaric acid, now called E-but-2-ene-1,4-dioic acid, it proves difficult to change it into the cyclic anhydride (3) below.

Z-but-2-ene-1,4-dioic acid (2) cis form, maleic acid

H₂O

However, if the Z(cis) form (2) is heated, it readily changes into the cyclic acid anhydride (3). Not only does the restricted rotation about the C=C bond cause the existence of geometrical isomers, but in this case you can only readily get the elimination of water when the two -OH groups are on the same side of the planar >C=C< system, as in the cis form (2). In the trans form (1) the elimination reaction is stereoelectronically hindered because the -OH so far apart. However, both (1) and (2) undergo the same electrophilic addition reactions of the ‘alkene’ double bond, >C=C< and the same reactions of the carboxylic acid group -COOH.
Case study: Physical properties of cis/trans or Z/E-1,2-dichloroethene

The $\text{C}^+\text{-Cl}^-$ bond is polar due to the **difference in electronegativity** between carbon and chlorine ($\text{Cl} > \text{C}$).

(1) **Z-1,2-dichloroethene** (cis) $d = 1.265 \text{cm}^3$, mpt $-80 ^\circ \text{C}$, bpt $60 ^\circ \text{C}$, dipole moment 1.89D, with both Cls on the same side of the C=C bond, the combined effect of the two polar C-Cl bonds makes it a much more polar molecule and raises the bpt compared to (2), but not the mpt.

(2) **E-1,2-dichloroethene** (trans) $d = 1.259 \text{cm}^3$, mpt $-50 ^\circ \text{C}$, bpt $48 ^\circ \text{C}$, dipole moment 0.00D, the effect of the C-Cl polar bonds cancel each other out giving a relatively non-polar molecule, this and there is **positional isomer** (3) shown below.

(3) $d = 1.218 \text{cm}^3$, mpt $? ^\circ \text{C}$, bpt $32 ^\circ \text{C}$, dipole moment 1.30D?. **1,1-dichloroethene**, is a **positional** isomer of the two geometrical isomers and cannot exhibit geometrical isomerism because two identical groups (H's or Cl's) are attached to the same carbon of the double bond.

All three isomers are chemically similar e.g. the electrophilic addition reactions of alkenes.

Case study: Di-substituted cycloalkanes

Cis and trans isomers can exist in 1,2-disubstituted cyclopropanes and cyclobutanes because the -C-C- ring structure inhibits rotation about the C-C bonds. If the 1,2-substituents are on the same side of the plane of the triangle/square of carbon atoms you get the Z (cis) form, if the are on opposite sides you get the E (trans) form.

(1) **Cl Cl 1,2-dichlorocyclopropane** can give E/Z isomers and the group priority is Cl > H

**Z-1,2-dichlorocyclopropane** (cis), both highest priority groups on the same side of the 'plane' of the cyclopropane ring.
and E-1,2-dichlorocyclopropane (trans), the highest priority groups are on opposite sides of the 'plane' of the cyclopropane ring.

(2) 1,1-dichlorocyclopropane is a positional isomer of C₃H₄Cl₂, and cannot exhibit geometrical isomerism.

(3) Br -- Br 1,2-dibromocyclobutane, likewise can give ...

(4) or (9) 1,1-dibromocyclobutane, is a positional isomer of C₄H₆Br₂ and cannot exhibit E/Z (geometrical) isomerism because the two bromine atoms are attached to the same carbon.

(5) 1,3-dibromocyclobutane is also positional isomer of C₄H₆Br₂ and can exhibit E/Z (geometric) isomerism.

with the two Br atoms on same side of the plane of the C₄ ring.

and E/trans Br with the two Br atoms on each side of the plane of the cyclobutane ring.
Case study: Isomerism in azo (-N=N-) and R₂C=N-X compounds

Organic (or inorganic) compounds of the structure R-N=N-R' (e.g. aromatic azo dyes) can exist as cis and trans isomers in just the same way as alkenes, where R or R' = H, alkyl, aryl group etc. R can be different or the same as R'.

Stereochemically, the lone pairs on the nitrogen effectively behave as an atom bonding pair of electrons in determining the trigonal planar orientation of the -N= bonds and the lone pair of electrons on the nitrogen. Three groups of electrons around an atom X, always give a trigonal planar arrangement around the central atom >X-. The double bond, N=N or C=N, ensures that too high an energy is required for ready rotation about the double bond.

Examples of -N=N- systems:

(1) (Z/cis) \[ R'N=N\text{-}R \] and (2) (E/trans) \[ R\text{-}N=N\text{-}R' \] (all R-N=N-R' bond angles are about 120°)

Examples of >C=N- systems

Carbonyl compounds like aldehydes and ketones undergo condensation reactions of the type

\[ RR'\text{C}=O + H_2N\text{-}X \implies RR'\text{C}=N\text{-}X + H_2O \]

where R is different to R' and = H, alkyl or aryl etc. geometrical isomers can occur.

and when X= H (ammonia), alkyl (aliphatic primary amine), aryl (aromatic primary amine), OH (hydroxylamine), NH₂ (hydrazine), NHC₆H₄(NO₂)₂ (2,4-dinitrophenylhydrazine). If for (3) and (4) if in priority R' > R (e.g. CH₃CH₂ > CH₃)

(3) (Z/cis) \[ R\text{-}C=\text{N-}R' \] and (4) (E/trans) \[ R'\text{-}C=\text{N-}R \]

(i.e. R' as a higher ranking group than R) When R = R' i.e. (5) \[ R\text{-}C=\text{N-}R \] geometrical isomerism is not possible. (Note: all >C=N-X angles are about 120°)

Case Study: Dienes can also exhibit E/Z stereoisomerism

H - C \[ \equiv \equiv \text{Z-buta-1,3-diene (cisoid)} \] and \[ \text{E-buta-1,3-diene (transoid)} \]