

Geometrical Isomerism

GEOMETRICAL ISOMERISM IS EXHIBITED BY A WIDE VARIETY OF COMPOUNDS

They may be classified into following groups :

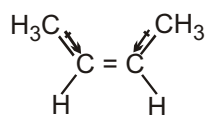
- (i) Compounds containing a double bond : $C = C$, $C = N$, $N = N$.
- (ii) Compounds containing a cyclic structure – homocyclic, heterocyclic and fused ring systems.
- (iii) Compounds which may exhibit geometrical isomerism due to restricted rotation about a single bond
- (iv) Bicyclo compound.

NOMENCLATURE OF GEOMETRICAL ISOMERS

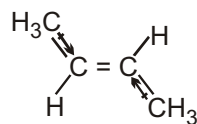
When geometrical isomerism is due to the presence of one double bond in a molecule, it is easy to name the geometrical isomers if two groups are identical, e.g., in molecules (I) and (IV), (I) is the cis-isomer and (II) the trans ; similarly (III) is cis and (IV) is trans.

cis isomer (cis is Latin for "on this side"). trans isomer (trans is Latin for "across").

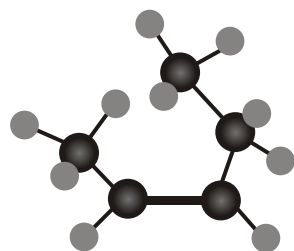
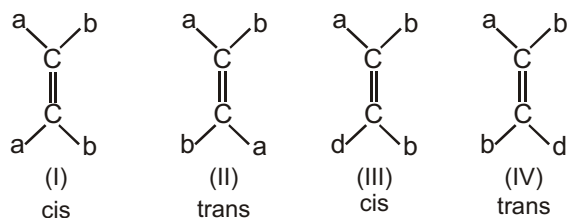
The *cis isomer* has its substituents on the same side of the ring; the *trans isomer* has its substituents on opposite sides of the ring. (A solid wedge represents a bond that points out of the plane of the paper toward the viewer and a hatched wedge represents a bond that points into the plane of the paper away from the viewer.)



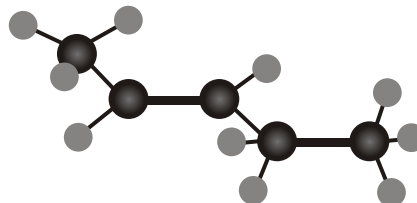
the cis isomer
bp 3.7 °C
= 0.33 D



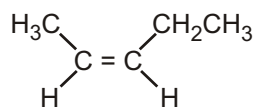
the trans isomer
bp = 0.9 °C
= 0 D



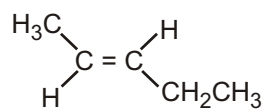
cis-2-pentene



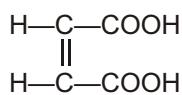
trans-2-pentene



cis-2-pentene

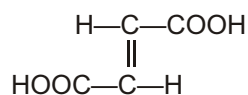


trans-2-pentene



Maleic acid
(cis)

and

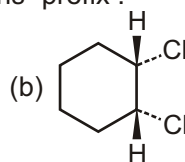
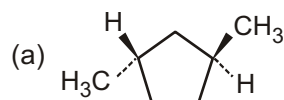


Fumaric acid
(trans)

NAMING CYCLOALKANES

Solved Example

- Name the following substances, including the cis- or trans- prefix :



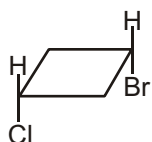
Strategy

In these views, the ring is roughly in the plane of the page, a wedged bond protrudes out of the page, and a dashed bond recedes into the page. Two substituents are cis if they are both out of or both into the page, and they are trans if one is out of and one is into the page.

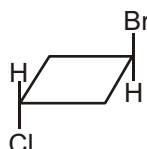
Ans. (a) *trans*-1,3-Dimethylcyclopentane

(b) *cis*-1,2-Dichlorocyclohexane

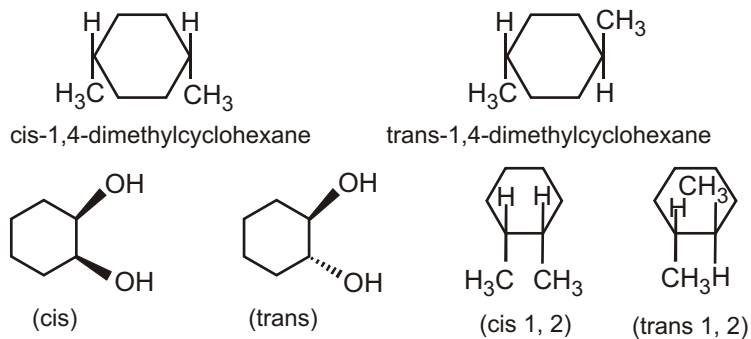
Solved Example



cis-1-bromo-3-chlorocyclobutane

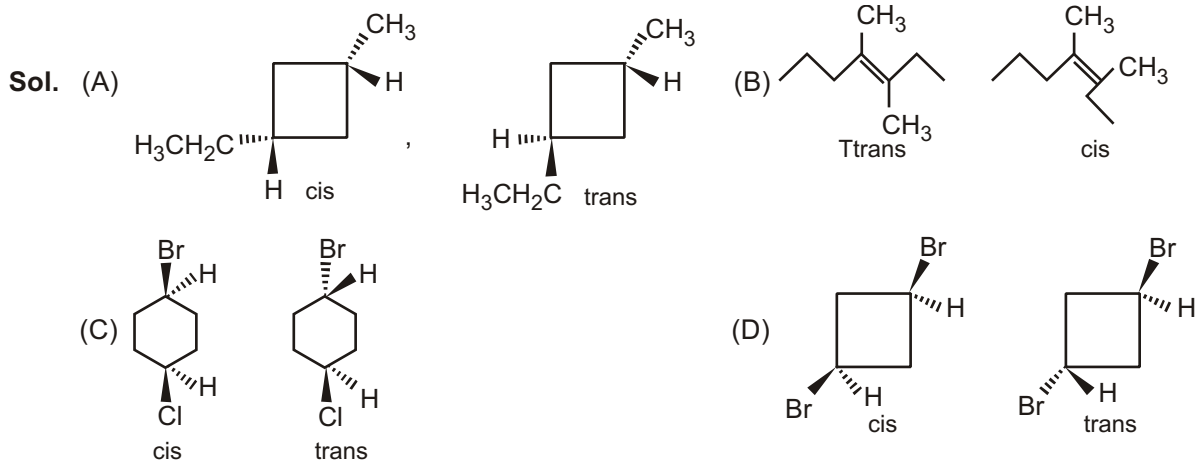


trans-1-bromo-3-chlorocyclobutane

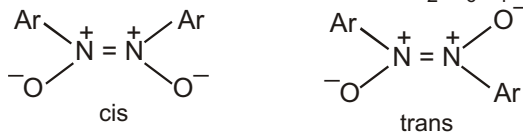


Solved Example

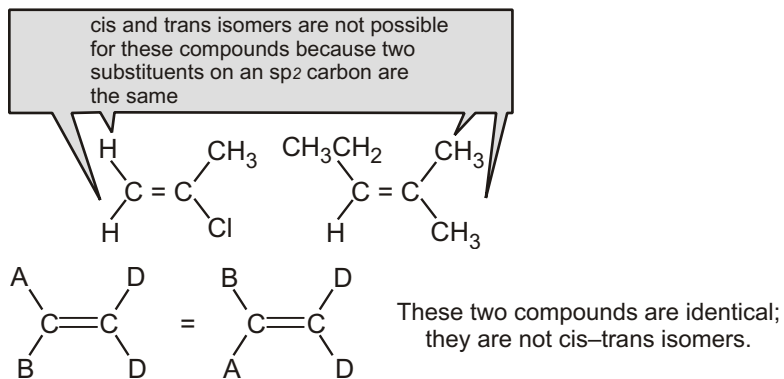
- Draw the cis and trans isomers for the following compounds :
- | | |
|---------------------------------|----------------------------|
| (A) 1-ethyl-3-methylcyclobutane | (B) 3,4-dimethyl-3-heptene |
| (C) 1-bromo-4-chlorocyclohexane | (D) 1,3-dibromocyclobutane |



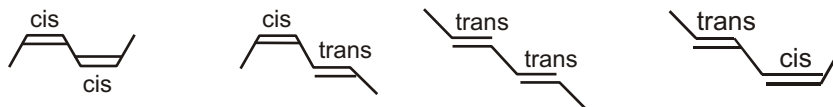
Harley-Mason have offered evidence to show that they have isolated the three theoretically possible geometrical isomers of o-nitroacetophenone azine (Ar = o-NO₂ C₆H₄-) :



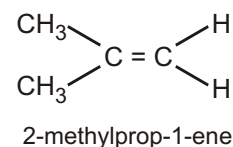
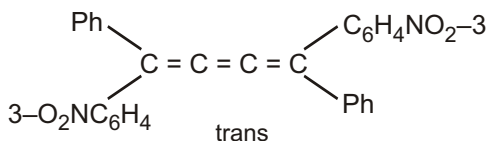
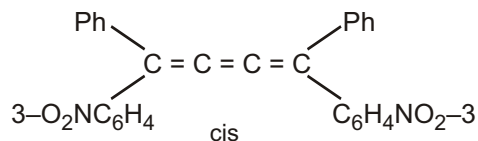
If one of the sp^2 carbons is attached to two identical substituents, then the compound cannot have cis and trans isomers.



CIS & TRANS IN CONJUGATED DIENE



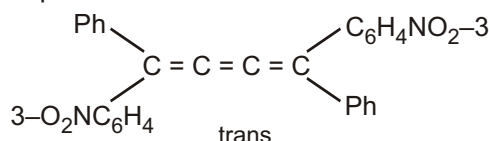
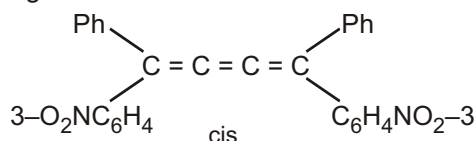
Alkenes like propene and 1-butene do not show geometrical isomerism



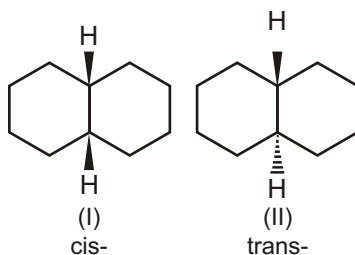
DIFFERENTIATING PROPERTIES OF CIS-TRANS ISOMERISM

- (i) Dipole moment: Usually dipole moment of cis is larger than the trans-isomer.
- (ii) Melting point: The steric repulsion of the group (same) makes the cis isomer less stable than the trans isomers hence trans form has higher melting point than cis.
- (iii) Different chemical properties: Syn-addition makes cis forms into meso and trans into d and l, anti addition makes cis into d - l and trans into meso.

Geometrical isomerism is also exhibited by cumulenes provided that the number of adjacent double bonds is odd, e.g., 1, 4-di-3nitrophenyl-1-4-diphenylbutatriene exists in two forms. On the other hand, cumulenes containing an even number of double bonds exhibit optical isomerism.



GEOMETRICAL ISOMERS OF DECALINE



□ NOTE:



(a)



(b)

(a) and (b) will not show geometrical isomerism

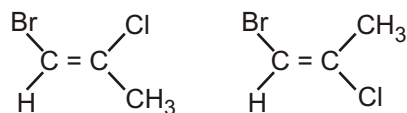
ALKENES STEREOCHEMISTRY AND THE E, Z DESIGNATION

If all the four groups/ atoms attached to C = C double bond are different, then Cis and trans nomenclature fails in such cases and a new nomenclature called E and Z system of nomenclature replace it.

The group / atom attached to carbon - carbon double bond is given to higher rank, whose atomic number is higher. If the two higher ranked group are across, it is called E form (E stands for the German word entgegen meaning thereby opposite) and the two higher ranked groups are on the same side, they are called Z-form (Z stands for German word Zusammen meaning thereby on the same side).

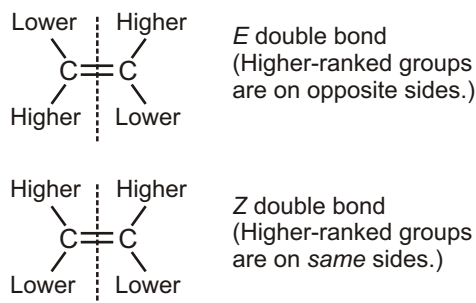
The cis–trans naming system used in the previous section works only with disubstituted alkenes—compounds that have two substituents other than hydrogen on the double bond. With trisubstituted and tetrasubstituted double bonds, a more general method is needed for describing double-bond geometry. (Trisubstituted means three substituents other than hydrogen on the double bond; tetrasubstituted means four substituents other than hydrogen.)

But how would you determine cis and trans isomers for a compound such as 1-bromo-2-chloropropene ?



Which isomer is cis and which is trans ?

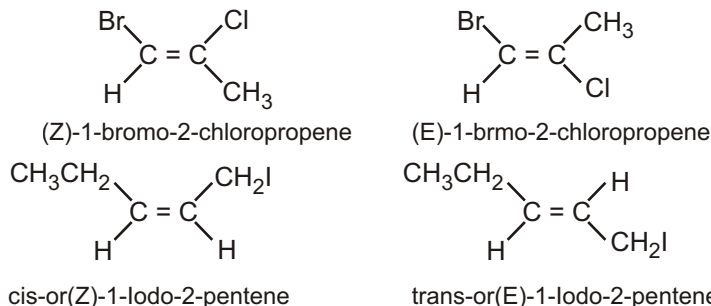
For a compound such as 1-bromo-2-chloropropene, the cis–trans system of nomenclature cannot be used because there are four different substituents on the two vinylic carbons. The E, Z system of nomenclature was devised for these kinds of situations. In order to name an isomer by the E, Z system, first determine the relative priorities of the two groups bonded to one of the sp^2 carbons and then the relative priorities of the two groups bonded to the other sp^2 carbon. (Rules for assigning relative priorities are explained next.) If the high-priority groups are on the same side of the double bond, the isomer is said to have the Z configuration (Z is for *zusammen*, German for "together"). If the high-priority groups are on opposite sides of the double bond, the isomer has the E configuration (E is for *entgegen*, German for "opposite").



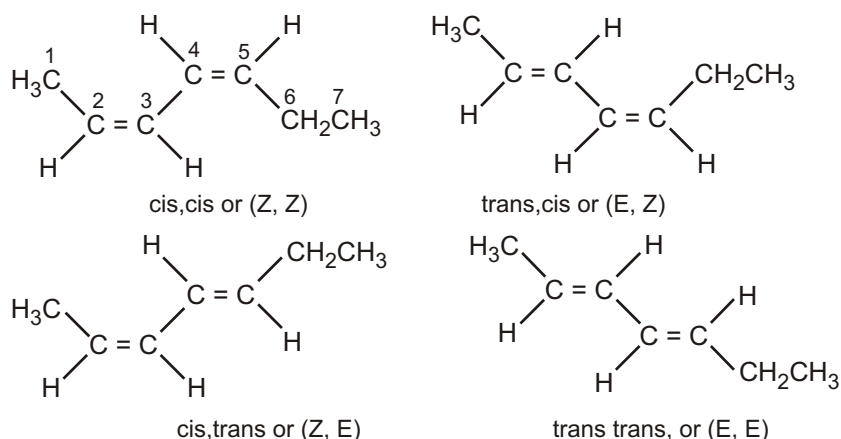
RULES TO DETERMINE THE PRIORITIES OF THE GROUPS BONDED TO THE sp^2 CARBONS

Rule 1.

The relative priorities of the groups depended on the atomic numbers of the atoms bonded directly to a particular sp^2 carbon. The greater the atomic number, the high the priority. For example, in 1-bromo-2-chloropropene, one of the sp^2 carbons is bonded to a bromine and to a hydrogen. Bromine has a greater atomic number than hydrogen, so bromine has the higher priority. The other sp^2 carbon is bonded to a chlorine and to a carbon. Chlorine has a greater atomic number than carbon, so chlorine has the higher priority. The isomer on the left has the high-priority groups (Br and Cl) on the same side of the double bond, so it is the Z isomer. The isomer on the right has the high-priority atoms on opposite sides of the double bond, so it is the E isomer.

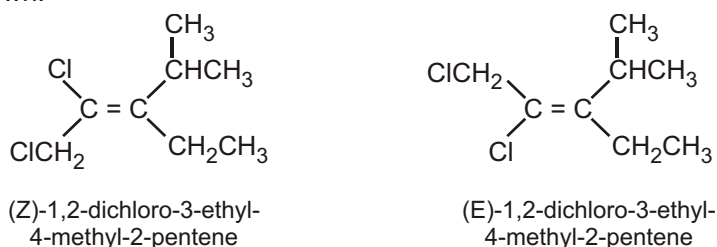


Both double bonds meet the conditions for geometric isomers and there are four diastereomers of 2,4-heptadiene.



Rule 2.

If the two substituents on an sp^2 carbon have the same atomic number (there is a tie), the atomic numbers of the atoms that are attached to the "tied" atoms must be considered. In the following pair of isomers, both atoms bonded to one of the sp^2 carbons are carbons (from an ethyl group and an isopropyl group), so there is a tie at this point. One carbon is bonded to C, C, and H (the isopropyl group); the other is bonded to C, H, and H (the ethyl group). One C cancels in each of the two groups, leaving C and H in the isopropyl group and H and H in the ethyl group. Carbon has a greater atomic number than hydrogen, so the isopropyl group has a higher priority than the ethyl group. The other sp^2 carbon is bonded to a chlorine and to a chloromethyl group. Chlorine has a greater atomic number than carbon, so the chloro group has the higher priority. The E and Z isomers are as shown.

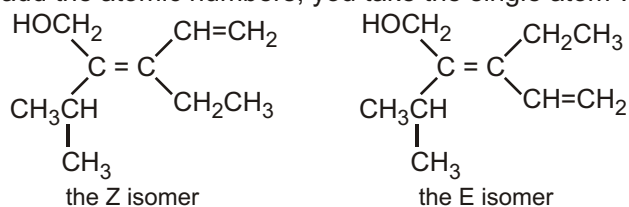


Rule 3.

If an atom is doubly bonded to another atom, the priority system treats it as if it were singly bonded to two of those atoms. If an atom is triply bonded to another atom, the priority system treats it as if it were singly bonded to three of those atoms. One of the sp^2 carbons in the following pair of isomers is bonded to an ethyl group and to a vinyl group. Because the atoms immediately bonded to the sp^2 carbon are both carbons, there is a tie. The carbon of the ethyl group is bonded to C, H and H. The carbon of the vinyl group is bonded to an H and doubly bonded to a C. Therefore, the first carbon of the vinyl group is considered to be bonded to C, C, and H. Consequently, the vinyl group has a higher priority than the ethyl group. Both atoms that are bonded to the other sp^2 carbon are carbons, too, so there is a tie there as well. The carbon of the hydroxymethyl group is bonded to O, H, and H, and the carbon of the isopropyl group to C, C, and H. Of these six atoms, oxygen has the greatest atomic number, so the hydroxymethyl group has the higher priority.

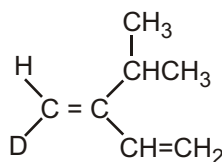
• Mistake to avoid

Notice that you do not add the atomic numbers; you take the single atom with the greatest atomic number.

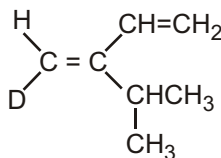


Rule 4.

In the case of isotopes (atoms with the same atomic number but different mass numbers), the mass number is used to determine their relative priorities.



the Z isomer



the E isomer

Notice that in all these examples you never count the atom bonded to the s bond from which you originate. In differentiating between the isopropyl and vinyl groups in the last example, you did count the atom bonded to the p bond from which you originated.

Rule 5.

If the atom in consideration is further attached to an atom via a double bond, then it is treated as if it is attached to two such atoms.

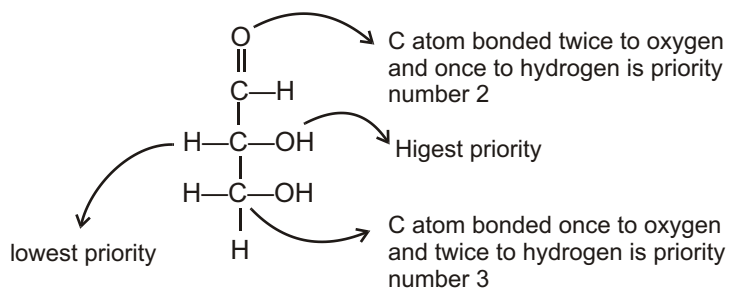
For example, $-\text{C}=\text{C}-$ may be treated as $\begin{array}{c} | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$ and $-\text{C}=\text{O}$ is treated as $\begin{array}{c} | \\ -\text{C}-\text{O} \\ | \quad | \\ \text{O} \quad \text{C} \end{array}$, that is, the atom at

the end of the extreme end of the multiple bond is like as if it is equal to equivalent number of single bonds.

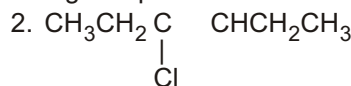
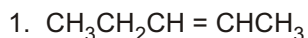
Thus $-\text{C} \equiv \text{C}-$ is treated as $\begin{array}{c} \text{C} \quad \text{C} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$

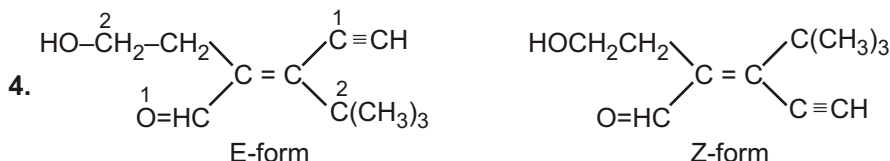
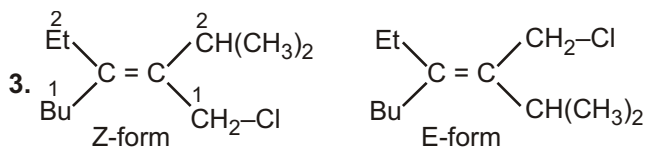
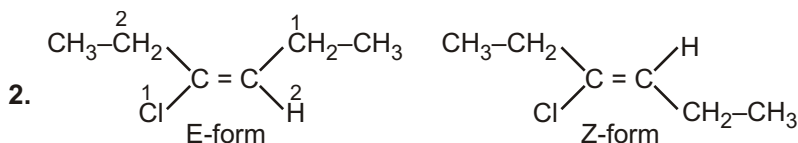
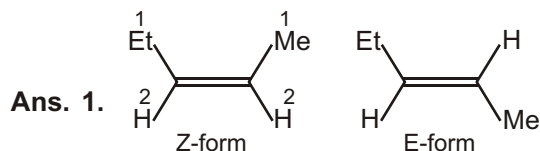
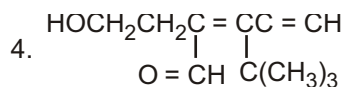
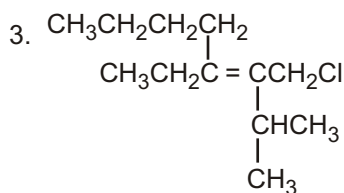
$-\text{C} \equiv \text{N}-$ is treated as $\begin{array}{c} \text{N} \quad \text{C} \\ | \quad | \\ -\text{C}-\text{N}- \\ | \quad | \\ \text{N} \quad \text{C} \end{array}$

$-\text{C}(=\text{O})-\text{H}$ is treated as $\begin{array}{c} \text{O}-\text{C} \\ | \\ -\text{C}-\text{H} \\ | \\ \text{O} \end{array}$

**Solved Example**

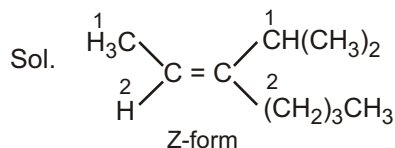
► Draw and label the E and Z isomers of each of the following compounds.





Solved Example

- Draw the structure of (Z)-3-isopropyl-2-heptene.

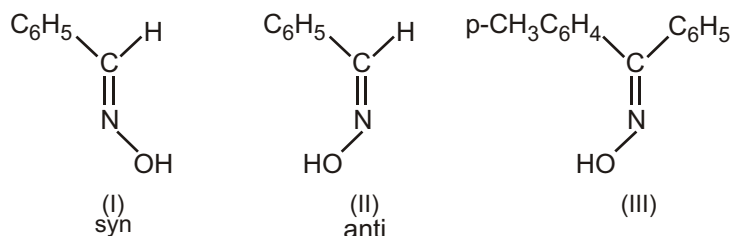


The priority order is followed as

I, Br, Cl, SO_3H , SH, F, COOR, OR, OH, NO_2 , NR_2 , NHCOR, NHR, NH_2 , CO_2R , COOH, CONH_2 , CHO, CH_2OH , CN, CR_3 , C_6H_5 , CHR_2 , CH_2R , CH_3 , D, H.

NOMENCLATURE OF THE OXIMES

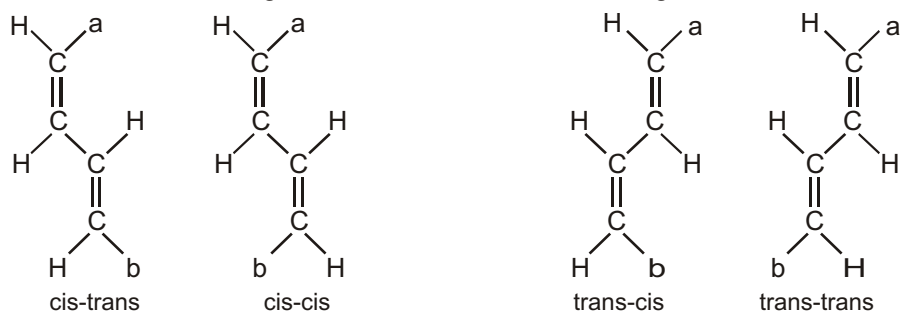
In oxime chemistry the terms syn and anti are used instead of the terms cis and trans. When dealing with aldoximes, the syn-form is the one in which both the hydrogen atom and the hydroxyl group are on the same side; when these groups are on opposite sides, the configuration is anti. Thus (I) is syn- and (II) is anti-benzaldoxime. With ketoximes, the prefix indicates the spatial relationship between the first group named and the hydroxyl group. Thus III may be named as syn- p-tolyl phenyl ketoxime or anti-phenyl p-tolyl ketoxime.

Solved Example

The E – Z system of nomenclature is also applied to oximes. Thus, the syn-oxime (I) is named benzaldehyde (E) - oxime or (E) - benzaldehyde oxime ; (II) is the corresponding (Z) oxime. The group with the greater priority (phenyl) is taken as being cis with respect to the hydroxyl group. Since p-tolyl has priority over phenyl, (III) is (Z) p-tolyl phenyl ketoxime.

TOTAL NUMBER OF GEOMETRICAL ISOMERS

If a compound has two double bonds, e.g., $\text{CHa} = \text{CH} - \text{CH} = \text{CHb}$, four geometrical isomers are possible :



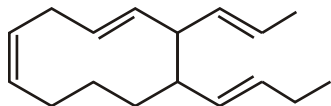
The number of geometrical isomers is 2^n , where n is the number of double bonds.

This formula applies only to molecules in which the ends are different

If the ends are identical, e.g., $\text{CHa} = \text{CH} - \text{CH} = \text{CHa}$, then the number of stereoisomers is $2^{n-1} + 2^{p-1}$, where $p = n/2$ when n is even, and $p = (n + 1)/2$ when n is odd.

Solved Example

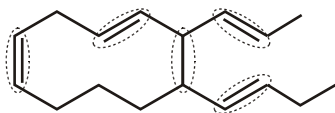
- X = Total number of possible geometrical isomers of the below compound.



The value of $\frac{X}{4}$ is :

Ans. 8

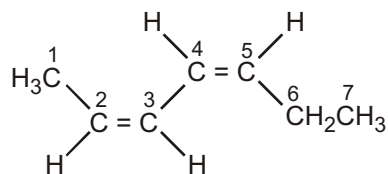
Sol.



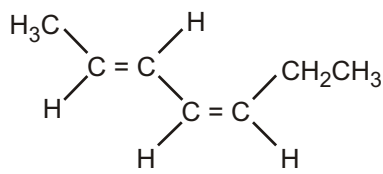
Bonds which are circled show geometrical isomers thus value of $n = 5$; Total G.I. = $2^5 = 32$

The value of $\frac{X}{4} = \frac{32}{4} = 8$

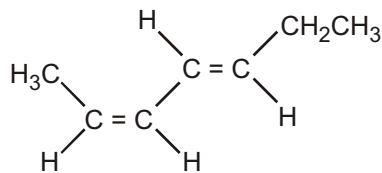
Solved Example



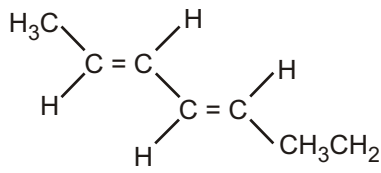
cis,cis or (Z, Z)



trans,cis or (E, Z)



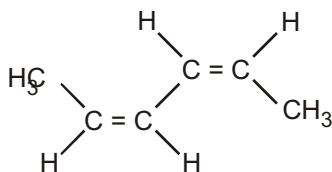
cis,trans or (Z, E)



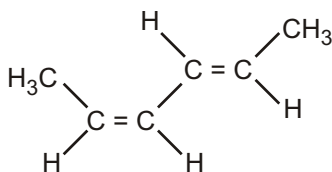
trans, trans or (E, E)

❑ **NOTE:** That cis and trans and E and Z are listed in the same order as the bonds are numbered.

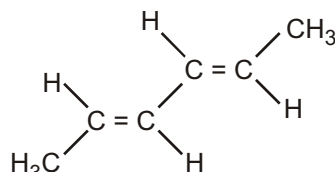
Solved Example



cis,cis-2,4-Hexadiene or
(Z,Z)-2,4-Hexadiene



cis,trans-2,4-Hexadiene or
(Z,E)-2,4-Hexadiene

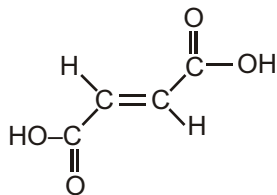


trans,trans-2,4-Hexadiene or
(E,E)-2,4-Hexadiene

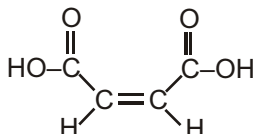
✓ SPECIAL TOPIC

MALEIC AND FUMARIC ACID

The cis isomer is called Maleic acid, and the trans isomer is called Fumaric acid. Fumaric acid is an essential metabolic intermediate in both plants and animals, but maleic acid is toxic and irritating to tissues.



fumaric acid, mp 287°C
essential metabolite



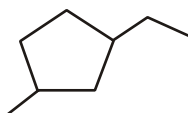
maleic acid, mp 138°C
toxic irritant

► Whether the following compound will show G.I. ?

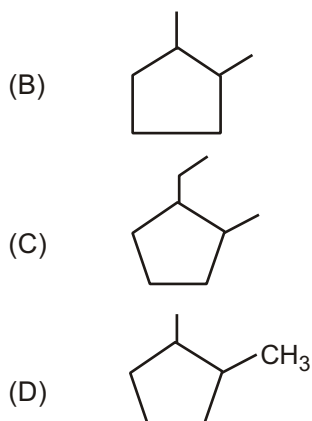
Sol.

Compound

(A)



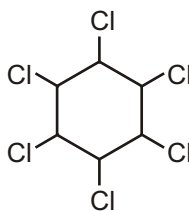
Geometrical Isomerism



EXERCISE

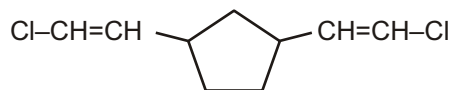
SINGLE CHOICE QUESTIONS

1. Number of geometrical isomers of the given compound are:



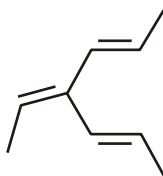
- (A) 6 (B) 7 (C) 8 (D) 9

2. Number of geometrical isomers of the given compound are:



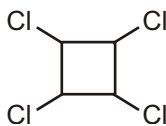
- (A) 2 (B) 4 (C) 6 (D) 8

3. Number of geometrical isomers of the given compound are:



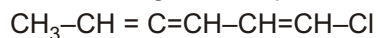
- (A) 1 (B) 2 (C) 3 (D) 4

4. Number of geometrical isomers of the given compound are:



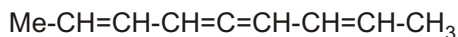
- (A) 1 (B) 2 (C) 3 (D) 4

5. Number of geometrical isomers of the given compound are:



- (A) 1 (B) 2 (C) 3 (D) 4

6. Total number of geometrical isomers possible for given compounds are:

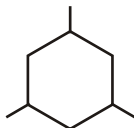


- (A) 16 (B) 8 (C) 4 (D) 2

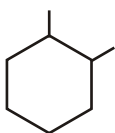
7. Find total number of Geometrical isomerism of following compounds.



has x geometrical isomers



has y geometrical isomers



has z geometrical isomers

What is the value of x+y+z?

- (A) 16 (B) 8 (C) 4 (D) 10

8. Find total number of Geometrical isomerism of following compounds.

- (A) 0 (B) 8 (C) 4 (D) 2

9. Which of the following compounds will exhibit geometrical isomerism :

- (A) 1-Phenyl-2-butene (B) 3-Phenyl-1-butene
(C) 2-Phenyl-1-butene (D) 1,1-Diphenyl-1-propene.

10. The number of isomers for the compound with molecular formula C_2BrClFI is :

- (A) 2 (B) 3 (C) 5 (D) 6

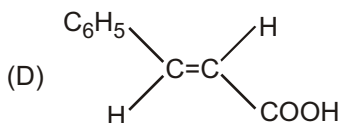
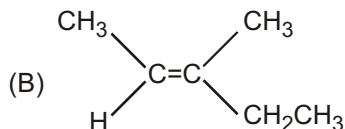
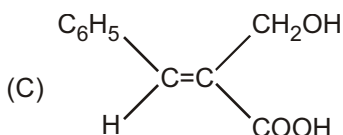
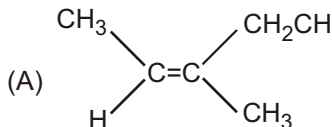
11. Maleic acid and fumaric acid are :

- (A) Position isomers (B) Geometric isomers
(C) Enantiomers (D) Functional isomers.

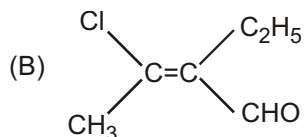
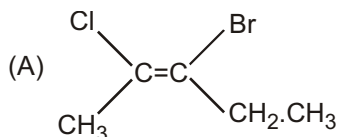
12. Which of the following compounds does not exhibit geometric isomerism :

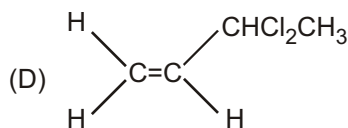
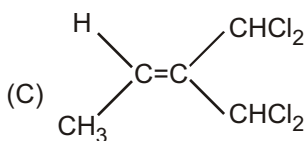
- (A) 1,1-Dichloro-2-butene (B) 1,2-Dichloro-2-butene
(C) 1,1-Dichloro-1-butene (D) 2,3-Dichloro-2-butene.

13. The Z-isomer among the following is



14. Which of the following is an 'E' isomer?





15. Which of the following statements about cis-trans isomerism is/are correct ?

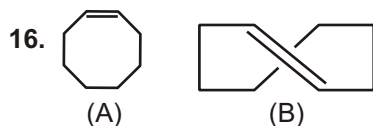
- (1) All alkenes exhibit cis-trans isomerism.
- (2) But-2-ene exhibits, cis-trans isomerism.
- (3) A pair of cis-trans isomers may be optically active

(A) (1) only

(B) (2) only

(C) (1) and (3) only

(D) (2) and (3) only



Relationship between (A) and (B) is :

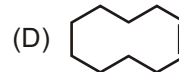
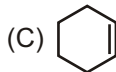
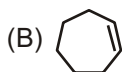
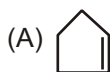
(A) Diastereomers

(B) Enantiomer

(C) Identical

(D) Structural isomer

17. Geometrical isomerism is possible in :



18. Which of the following compounds could exhibit geometrical isomerism?

- (1) 3,4-dimethylhex-3-ene
- (2) 2-methylpent-2-ene
- (3) 1,6-dichlorohex-3-ene

(A) (1) and (2) only

(B) (1) and (3) only

(C) (2) and (3) only

(D) (1), (2) and (3)

19. Which of the following compounds has/have a pair of geometrical isomers ?

- (1) $\text{CH}_3\text{CH}=\text{CH}_2$
- (2) $\text{CH}_3\text{OCCH}=\text{CHCOCH}_3$
- (3) $\text{CH}_2\text{BrCH}=\text{CHCH}_2\text{Cl}$

(A) (1) only

(B) (2) only

(C) (1) and (3) only

(D) (2) and (3) only

20. Which of the following statements concerning geometrical isomers is/are correct ?

- (1) The cis isomer has a higher melting point than the trans isomer.
- (2) A pair of geometrical isomers has the same functional group.
- (3) Any organic compounds with a carbon-carbon double bond have geometrical isomers.

(A) (1) only

(B) (2) only

(C) (1) and (3) only

(D) (2) and (3) only

21. Which of the following are the types of structural isomers?

- (1) Geometrical isomerism
- (2) Functional group isomerism

(3) Chain isomerism

(A) (1) and (2) only

(B) (1) and (3) only

(C) (2) and (3) only

(D) (1), (2) and (3)

22. Which of the following statements concerning a pair of geometrical isomers are correct ?

(1) They have different boiling points and melting points.

(2) They have the same relative molecular mass

(3) Their atoms are joined in the same order.

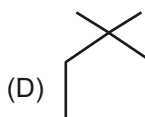
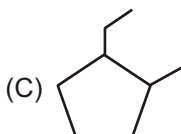
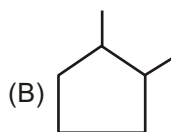
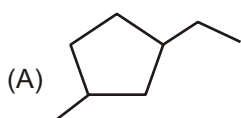
(A) (1) and (2) only

(B) (1) and (3) only

(C) (2) and (3) only

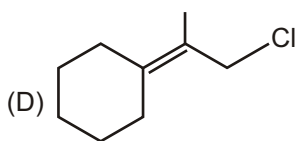
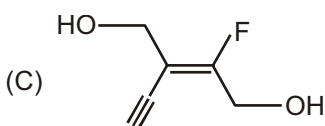
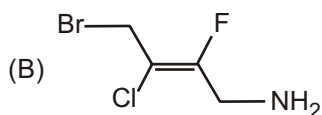
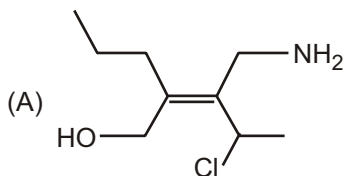
(D) (1), (2) and (3)

23. Which of the cycloalkane is not capable to show cis-trans isomerism ?

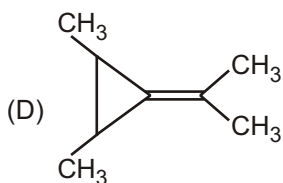
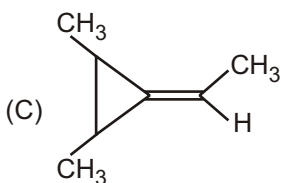
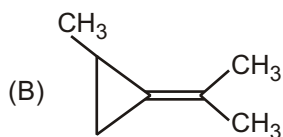
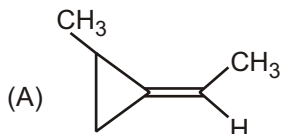


MULTIPLE CHOICE QUESTIONS

1. Which alkane has the Z configuration along '=' bond :

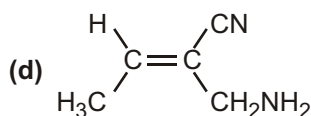
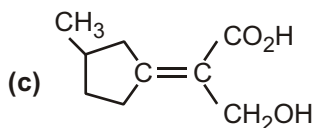
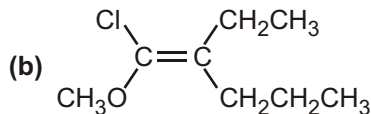
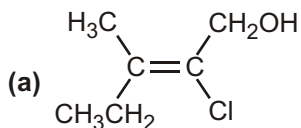


2. Among the following compounds, which can show geometrical isomerism ?

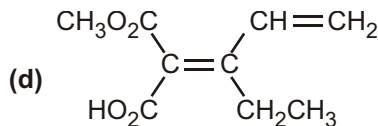
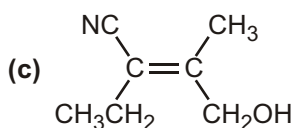
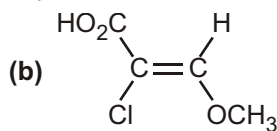
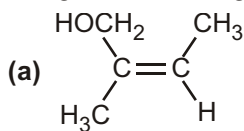


UNSOLVED EXAMPLE

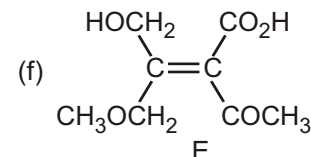
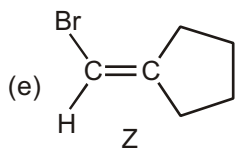
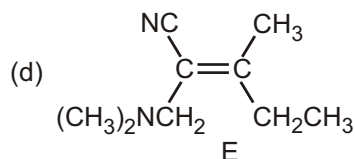
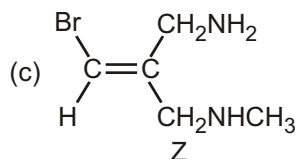
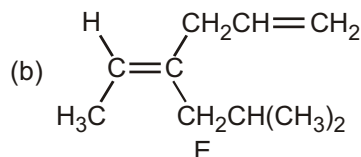
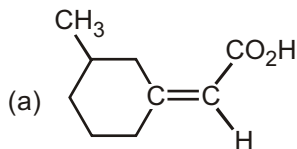
1. Assign E or Z configuration to the following alkenes :



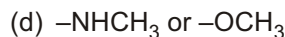
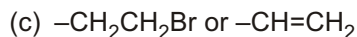
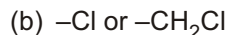
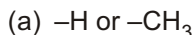
2. Assign E or Z configuration to each of the following compounds :



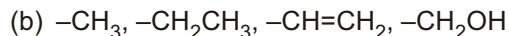
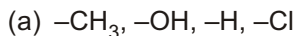
3. Which of the following E, Z designations are correct, and which are incorrect ?



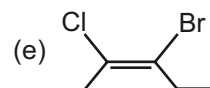
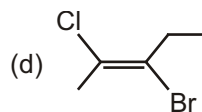
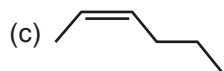
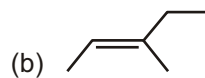
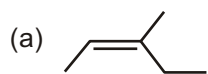
4. Which member in each of the following sets ranks higher?



5. Rank the substituents in each of the following sets according to the sequence rules:



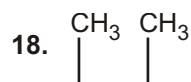
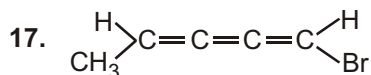
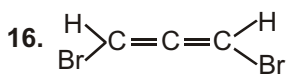
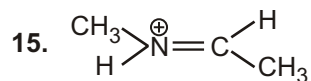
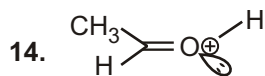
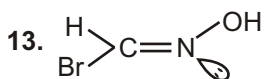
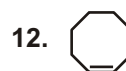
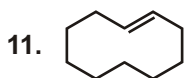
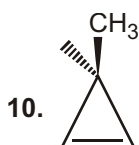
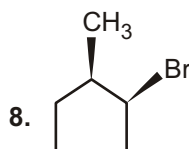
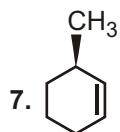
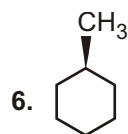
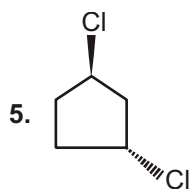
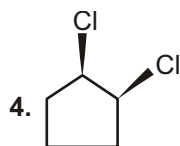
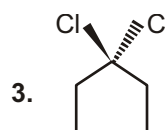
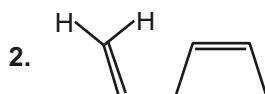
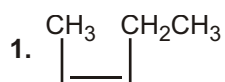
6. Write (E) and (Z) configuration of the following :

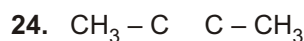
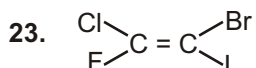
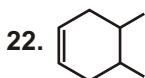
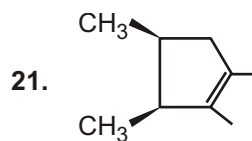
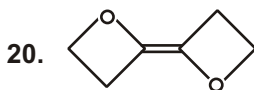
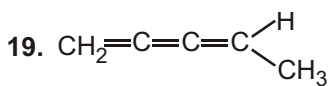


WORKSHEET-1

Q. (To find Geometrical isomerism)

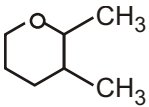
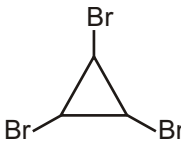
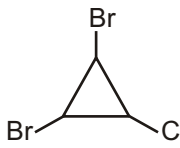
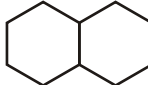

Identify which of the compound show geometrical isomerism?





WORKSHEET-2

(Total Geometrical Isomers)

S.N.	Compound	Total number of Geometrical Isomers possible.
1.	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{CH}_3$	
2.	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	
3.	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$	
4.	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Br}$	
5.	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$	
6.	$\text{CH}_3-(\text{CH}-\text{CH}_3)_n-\text{Ph}$	
7.		
8.		
10.		
11.		
12.		
13.	$\text{CH}_3-\text{CH}=\text{CH}_2$	

Answers

Single Choice Questions

1. (C)	2. (C)	3. (D)	4. (D)	5. (B)	6. (C)	7. (B)	8. (D)
9. (A)	10. (D)	11. (B)	12. (C)	13. (A)	14. (B)	15. (D)	16. (A)
17. (D)	18. (B)	19. (D)	20. (B)	21. (C)	22. (D)	23. (D)	

Multiple Choice Questions

1. (A, C)

2. (A, C, D)

1. According to CIP rule

