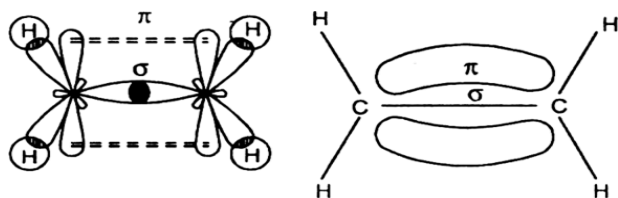
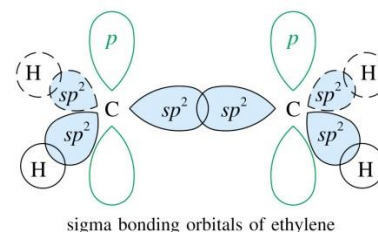


Alkenes

Kumud Bala

Acyclic unsaturated hydrocarbons containing a carbon-carbon double bond are called alkenes. They are also called olefins (Greek: olefiant= oil forming). The lower members of this class are ethene (ethylene), propene (propylene), etc.

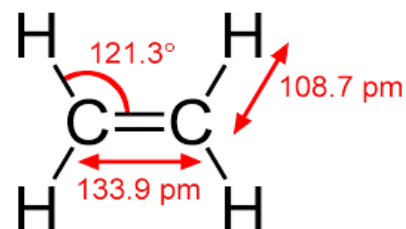
Structures of double bond- The carbon-carbon double bond in alkenes consists of one strong carbon-carbon σ -bond with a bond dissociation energy of 348 kJ/mole and a weak π -bond with a bond dissociation energy of 251 kJ/mole. The sigma bond is formed by head-on overlapping of sp^2 hybridized orbitals while the π -bond is formed by lateral or sideways overlapping of the two 2p-orbitals of the two carbon atoms.



(a) Formation of ethylene molecule

(b) Molecular orbital structure of ethylene

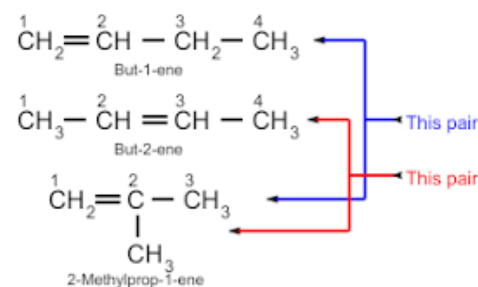
To have an effective overlap, the p-orbitals move little closer, therefore, a double bond is



shorter (134 pm) than single bond (154 pm). Further, due to poor overlapping between the two p-orbitals, a π -bond is always weaker than σ -bond. In other words, presence of the π -bond makes alkenes behave as a source of loosely held electrons. Therefore, alkenes are readily attacked by reagents or compounds which are in search of electrons. Such reagents are called electrophiles or electrophilic reagents. Further, the presence of π -bond makes alkenes less stable and more reactive than alkanes and hence readily change into compound containing single bond by adding electrophilic reagent.

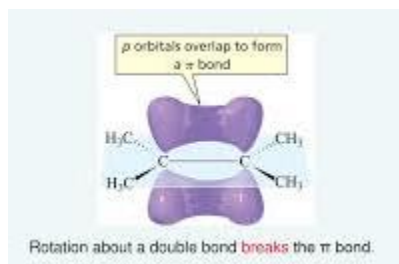
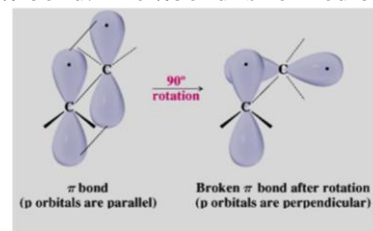
Isomerism of alkenes: Alkenes show both structural isomerism and stereoisomerism.

(a) Structure isomerism: Ethene and propene can have only one structure but alkenes containing four or more carbon atoms can show both position and chain isomerism. For example, the formula C_4H_8 can represent the following three isomers:



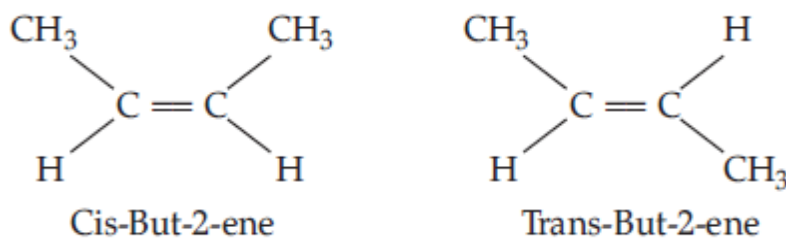
(b) Stereoisomerism: Isomers which have the same structure formula but have different relative arrangement of atoms or groups in space are called stereoisomers (Greek: stereo = space, meros = part) and the phenomenon is called stereoisomerism. Since each different spatial arrangement of atom which characterizes a particular stereoisomer is called its configuration, therefore, stereoisomers have the same molecular structure but different configurations. Stereoisomerism is of the following three types: (i) conformational isomerism (ii) optical isomerism (iii) geometrical isomerism

Geometrical isomerism: We know that double bond consists of a σ - bond and π -bond. The π bond is formed by sideways overlapping of unhybridized p-orbitals of two carbon atoms above and below the plane of carbon atoms. If now one of the carbon atoms of the double bond is rotated with respect to the other, the p- orbitals will no longer overlap and the π -bond should break. But the breaking of a π -bond requires 251 kilo joule per mole of energy which is not provided by the collision of molecules at room temperature. Consequently, the rotation about a carbon -carbon double bond is not free but it is strongly hindered or restricted.



A π -bond prevents free rotation of the carbon atoms of the double bond with respect to each other. Due to this hindered rotation, the relative positions of the atoms or a groups attached to the carbon atoms of the double bond get fixed. For example, H_a and H_b cannot exchange their positions by rotation of C_1 with respect to C_2 without breaking the π - bond.

As a result many substituted alkenes can exist in two distinct isomers which differ from each other only in the relative positions of atoms or groups in space around the double bond. For example, but-2-ene can exist in the following two forms:

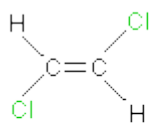


Both these isomers have same structure formula but differ in the relative spatial arrangement of hydrogen atom and methyl groups around the double bond. Such isomers which have the same structural formula but differ in the relative

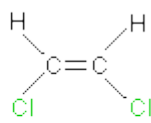
spatial arrangement of atoms or groups around the double bond are called geometrical isomers, and the phenomenon is called geometrical isomerism. The geometrical isomerism is a type of space or stereoisomerism. Isomers in which the similar atoms or groups lie on the same side of the double bond is called cis- isomer whereas the isomer in which the similar atoms or groups lie on the opposite sides of the double group is called trans-isomer. It is because of this reason that geometrical isomerism is also called cis-trans isomerism.

Properties of geometrical isomers: Due to different arrangement of atoms or groups in space these isomers differ in their physical properties such as melting point, boiling point, dipole moment and solubility etc.

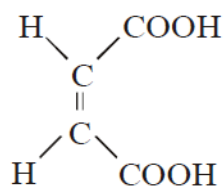
Melting points: In general the melting point of trans -isomer is higher than that of the corresponding cis-isomer. In the trans -isomer the two similar atoms are groups lie on the opposite sides of a double bond. Therefore, these molecules are symmetrical and hence pack well in the crystal lattice. On the other hand, in the cis-isomer, the two similar atoms or groups lie on the same side of the double bond. Therefore, these molecules are unsymmetrical and hence do not pack well in the crystal lattice. As a result intermolecular forces of attraction holding the molecules of a trans -isomers in the crystal lattice are much stronger than those holding the molecules of a cis- isomer. Consequently, the melting point of a trans isomer is much higher than that of the corresponding cis- isomer. For example, the melting point of cis-but-2-ene (134K) is lower than that of trans- but-2-ene (167K). Similarly the melting point of cis- 1, 2 dichloroethene (193K) is lower than that of trans- 1, 2 dichloroethene(223K) and that of maleic acid (cis-isomer) (403K) is lower than that of fumaric acid (trans -isomer) 575K.



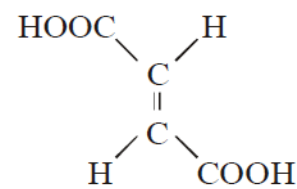
trans-1,2-dichloroethene



cis-1,2-dichloroethene



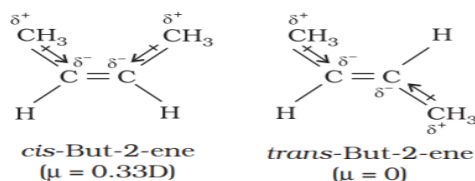
(*Cis*-form)
(Maleic acid)



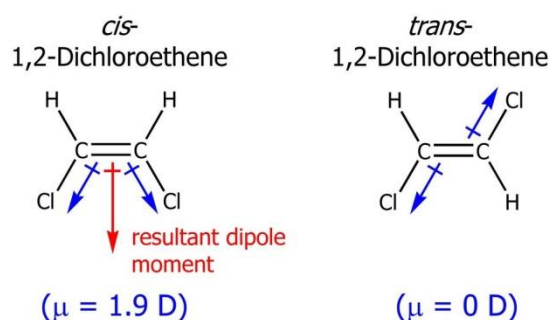
(*trans*-form)
(Fumaric acid)

Solubility: In general, the solubility of a *cis*-isomer is higher than that of corresponding *trans*-isomer. This is due to the reason that the molecules of a *cis*-isomer being less symmetrical, are weakly held in the crystal lattice than the corresponding more symmetrical *trans*-isomers. As a result, lesser amount of energy is required to break the crystal lattice of the *cis*-isomer and consequently the solubility of the *cis*-isomer maleic acid (79g/100ml H₂O) is higher as compared to that of the *trans*-isomer fumaric acid (0.7g/100ml H₂O) in the same solvent.

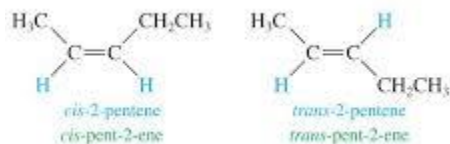
Dipole moments: In general, *cis*-isomer of an alkane is found to be more polar than the *trans*-isomer. For example, the dipole moment of *cis*-but-2-ene is 0.33D while that of *trans*-but-2-ene is zero. Thus, *trans*-but-2-ene can be said to be non-polar. This may be explained as follows:



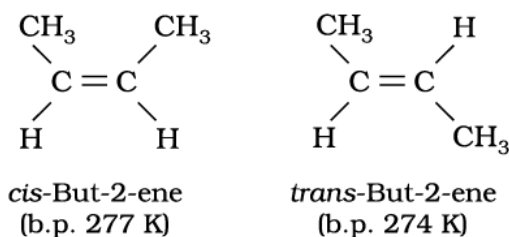
In case of *cis*-but-2-ene, the dipole moments of two C-CH₃ bonds are inclined at an angle of 60° and hence have a resultant equal to 0.33D. However, in case of *trans*-but-2-ene, the two dipole moments being equal and opposite cancel each other and, therefore, dipole moment of *trans*-but-2-ene is zero. Similarly, *cis*-1, 2- dichloroethene has higher dipole moment than the corresponding *trans* isomer.



It may, however, be noted here that a *trans*-isomer need not necessarily have a zero dipole moment. For example, *trans*-pent-2-ene has a finite dipole moment though much smaller than the corresponding *cis*-isomer. The reason being that the dipole moment of C-CH₃ and C-CH₂CH₃ bonds are not equal. Although these two dipoles oppose each other, they do not exactly cancel out each other and hence *trans*-pent-2-ene has a small but finite dipole moment. Thus, *trans*-pent-2-ene is much less polar than *cis*-pent-2-ene.



Boiling point: Boiling point of the cis-isomers is higher than those of the corresponding trans-isomers. The reason is that the boiling point of isomeric compounds depends upon dipole-dipole interactions. Since, the cis-isomers have higher dipole moment (more polar) than the corresponding trans-isomers (less polar), therefore, the boiling point of cis-isomers are higher than those of their corresponding trans-isomers. For example the boiling point of cis-but-2-ene is higher than that of Trans-but-2-ene.



Assignment

- Out of the following compounds which one would have a zero dipole moment?
 - 1,1 -dichloro ethylene
 - cis-1,2 dichloroethylene
 - trans-1,2 dichloroethylene
 - none of these compound.
- Which of the following compounds exhibit geometrical isomerism?
 - $\text{C}_2\text{H}_5\text{Br}$
 - $(\text{CH})_2(\text{COOH})_2$
 - CH_3CHO
 - $(\text{CH}_2)_2(\text{COOH})_2$
- $(\text{CH}_3)_3\text{CMgCl}$ on reaction with D_2O produces-----
 - $(\text{CH}_3)_3\text{CD}$
 - $(\text{CH}_3)_3\text{OD}$
 - $(\text{CD}_3)_3\text{CD}$
 - $(\text{CD}_3)_3\text{OD}$
- But-2-ene exhibit cis-trans isomerism due to -----
 - rotation around $\text{C}_3\text{-C}_4$ sigma bond
 - restricted rotation around $\text{C}=\text{C}$ bond
 - rotation around $\text{C}_1\text{-C}_2$ bond
 - rotation around $\text{C}_2\text{-C}_3$ double bond
- Which of the following compounds will exhibit geometrical isomerism?
 - 1-phenyl-2-butene
 - 3-phenyl-1-butene
 - 2-phenyl-1-butene
 - 1,1-diphenyl-1-propene
- Which of the following hydrocarbons has the lowest dipole moment?
 - $\text{CH}_3\text{H} > \text{C} = \text{C} < \text{H} \text{CH}_3$
 - $\text{CH}_3\text{C} \equiv \text{CCH}_3$
 - $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$
 - $\text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH}$

ANSWER

1. (C) 2. (B) 3. (A) 4. (B) 5. (A) 6. (B)