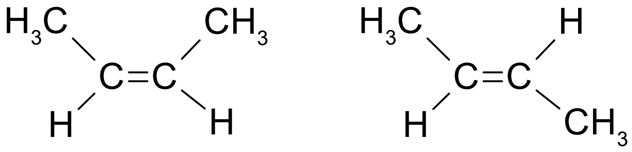
Geometrical isomerism (π – Diastereoisomerism)

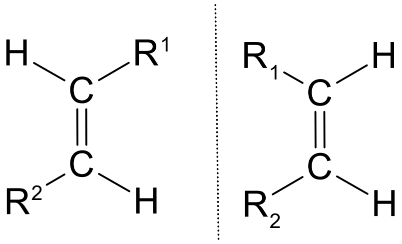
Rotation about a multiple bond is restricted. This restricted rotation gives rise to isomerism if the multiple bond is suitably substituted. This type of isomerism due to restricted rotation around the multiple bond is called **π-diastereomerism**.

The term cis-trans isomerism is applied to isomerism that depends upon the different spatial arrangements of groups or atoms in a molecule around the rigid double bond or a cyclic structure. Depending on the nature of the substituents, the alkenes may exist in more than one form. If the alkene is designated as $C_{ab}=C_{cd}$ then it will exist in two forms so long as $a \neq b$ and $c \neq d$. It does not matter whether a and/or b are the same as c and/or d. The simplest example of *cis–trans* isomerism may be cited in the isomers of but-2-ene. *cis*-but-2-ene and *trans*-but-2-ene have the same connectivity of atoms but spatial arrangement of CH_3 groups around the rigid C=C bond, in each case, is different. They represent a pair of *cis-trans* isomers, since they are not optically active.



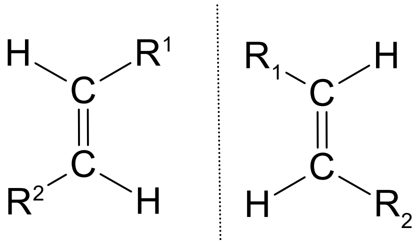
cis-But-2-ene trans-But-2-ene

A pair of *cis–trans* isomers is diastereoisomers in the sense that they are not related to each other by the *mirror image* relationship.



No mirror image relationship: diastereomer

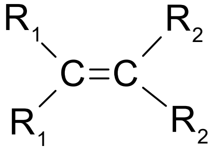
cis–trans isomers in many cases may also be optically active due to the absence of elements of symmetry. It can be argued that cis or *trans* isomers of alkenes may be considered as two-dimensional enantiomers having a two-dimensional non-superimposable mirror images which are produced by reflection, within the plane of the paper, through a straight line which represents a two-dimensional mirror.



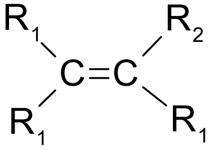
Non-superimposable mirror image in two dimensions

When $R_1=R_2$ (say *cis*-but-2-ene), *cis*-alkene represents a two-dimensional *meso*-compound and *trans*-alkene is two-dimensionally chiral. However, in three dimensions both are achiral molecules and since optical activity always manifests itself in three-dimensional chirality, alkenes are always optically inactive irrespective of the nature of achiral substituents.

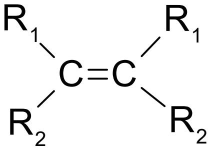
Of the four types of substituted alkenes possible, types I and II cannot exhibit *cis–trans* isomerism but types III and IV can.



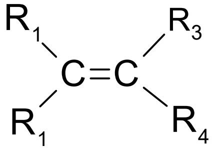
I



II

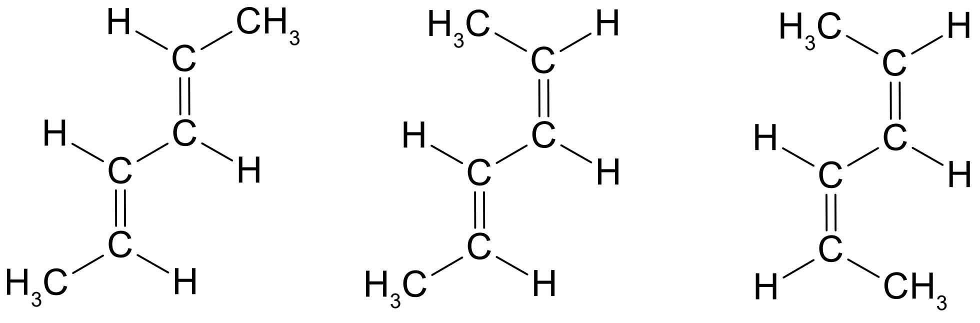


III

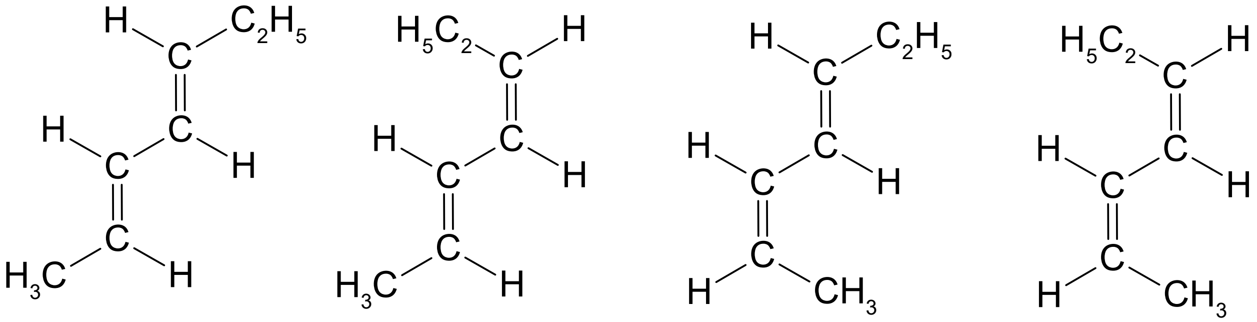


IV

In case of polyenes, the number of *cis–trans* isomers depend on the number of double bonds in a molecule. Normally the number of diastereoisomers is 2^n, where n is the number of double bonds. This formula is applicable to polyenes of the type R^1—(CH═CH)$_n$—R^2. If the general formula of a polyene is R—(CH═CH)$_n$—R (terminal substituents are identical) then the number of stereoisomers is (2n−1 + 2p−1), where $p = n/2$ when n is even, and $p = (n + 1)/2$ when n is odd.



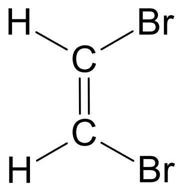
Three diastereomers of hexa-2,4-diene (terminal groups are same)



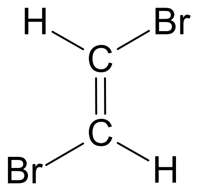
Four diastereoisomers of hepta-2,5-diene (terminal groups are different)

NOMENCLATURE OF *cis–trans* ISOMERS OF COMPOUNDS WITH C=C

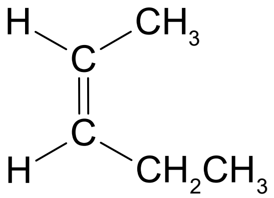
The terms *cis* and *trans* are used to show the relationship between two atoms or groups attached to separate atoms that are connected by a double bond, which may be C=C, C=N, or N=N. Then identical substituents, one on each of the carbon atoms joined by a double bond, are on the same side of the double bond (reference plane), then that isomer is called *cis*-isomer. When they are on the opposite sides of the double bond, it is called *trans*-isomer. The prefixes *cis* and *trans* are written in italics and in lowercase before the name and are separated from the name by a hyphen.



*c*is-1,2-Dibromoethylene

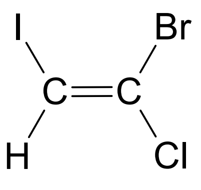


*t*rans-1,2-Dibromoethylene

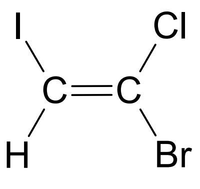


*c*is-Pent-2-ene

When, however, all the four groups on sp^2 carbons are different, *cis*- and *trans*- prefixes cannot be used unambiguously. For example, 1-bromo-1-chloro-2-iodoethylene has two isomers (A and B) but they are difficult to be named as *cis* and *trans*-isomers:



A

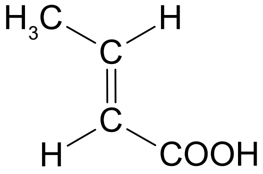


B

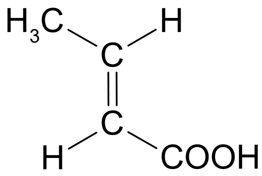
To avoid this difficulty, E-Z system of nomenclature have been introduced.

E–Z system of nomenclature

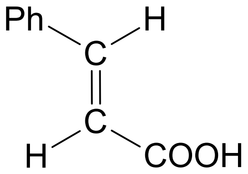
When the groups of higher precedence (according to CIP sequence rule) are on the same side of the double bond, the symbol *(Z)* (German: *Zusammen* meaning together) is used as a stereodescriptor to specify the configuration. The symbol *(E)* (German: *Entgegen* meaning opposite) is used when the groups of higher precedence are on the opposite sides of the double bond. *(E)* and *(Z)* are shown by capital letters in italics and prefixes are placed in parentheses followed by hyphens. Prefixes precede the whole name of the molecule. When necessary, appropriate locants are used before the stereodescriptors *(E, Z)* separated by hyphen.



(*E*)-but-2-enoic acid
CH_3 > H, COOH > H

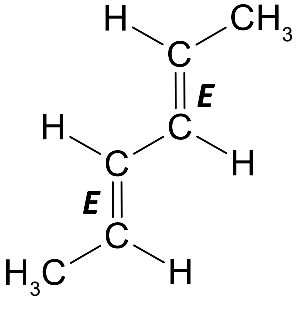


(*Z*)-butenedioic acid
(maleic acid)
COOH > H, COOH > H

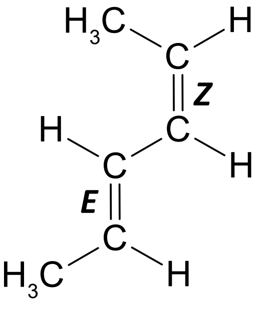


(*E*)-2-phenylpropenoic acid
(cinnamic acid)
(Ph > H, COOH > H)

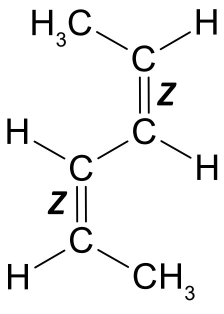
When *cis–trans* isomers contain two or more double bonds, nomenclature is done specifying the configuration of each double bond. For example, hexa-2,4-diene can have the following configurational isomers, each written in *s*-transoid form.



(2*E*,4*E*)-2,4-hexadiene

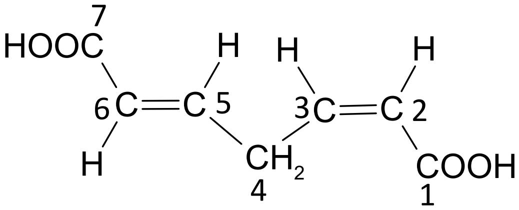


(2Z,4*E*)-2,4-hexadiene



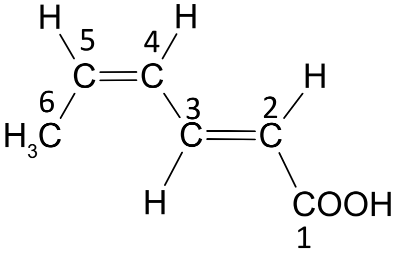
(2Z,4Z)-2,4-hexadiene

When there is a choice in counting the carbon atoms in a molecule having both *(Z)* and *(E)* descriptors, *Z* gets preference over *E*. For example, the diene compound given below should be named as *(2Z,5E)-hepta-2,5-dienedioic acid*. The lower numbers are assigned to the *(Z)* double bond. The alternative name *(2E,5Z)-hepta-2,5-dienedioic acid* is incorrect.



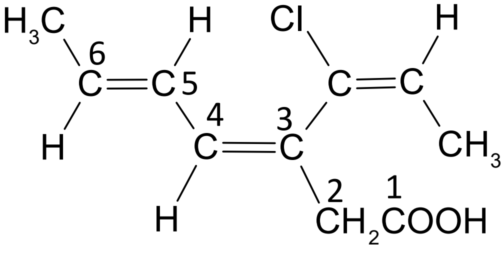
Structure of (2Z,5E)-hepta-2,5-dienedioic acid.

When an unsymmetrical alkadiene compound is considered, IUPAC rules set preference in numbering the carbon atoms and not the *Z* or *E* descriptors. For example, the compound shown below should be named as *(2E,4Z)-hexa-2,4-dienoic acid* and not *(4Z,2E)-hexa-2,4-dienoic acid*.



Structure of (2E,4Z)-hexa-2,4-dienoic acid.

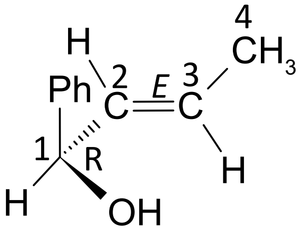
If a molecule contains several double bonds, then each *E* or *Z* prefix is immediately preceded by the lower or less primed locant of the relevant double bond. The *E, Z* prefixes are given at the beginning of the complete name, unless the prefix is related to a double bond within a substituent. The prefixes then form part of the name of the substituent.



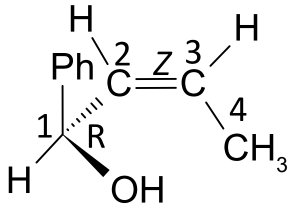
The compound given above should be named as 3-[(*E*)-1-chloropropenyl] -(3*Z*,5*E*)-hepta-3,5-dienoic acid.

Combination of R, S and *E*, *Z* isomerisms in the same molecule

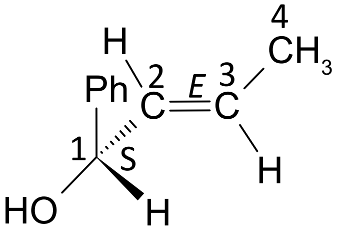
The **cis-trans** isomers, in the true sense, are not optically active but if they develop molecular chirality (with chiral centre or without chiral centre), then they also exhibit optical isomerism. In such cases, both **E, Z-** and **R, S-** stereodescriptors should be used to indicate both diastereoisomeric and enantiomeric configurations of the stereoisomers. If a molecule contains both chiral centre and an appropriately substituted olefinic bond to give **E, *Z*** isomers then four stereoisomers are possible. According to **CIP system**, they may be specified as **(R, *E*), (R, *Z*), (S, *E*), and (S, *Z*)**. An example is given below. $PhC^{*}H(OH)CH{=}CHCH_3$ contains a chiral centre (*) and a suitably substituted double bond capable of giving *E, Z* isomers. Its four possible configurations are shown here:



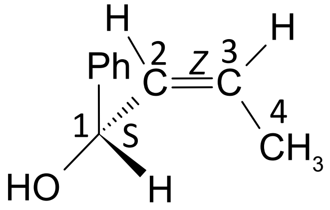
(1R,2*E*)-Phenyl-but-2-en-1-ol



(1R,2Z)- isomer



(1S,2*E*)- isomer



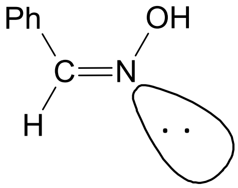
(1S,2Z)- isomer

Cis-trans isomerism of compounds with C=N and N=N

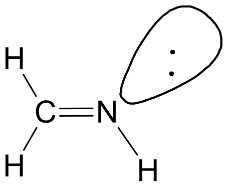
Oximes, hydrazones, and semicarbazides of unsymmetrical carbonyl compounds can exhibit **cis-trans** isomerism due to the presence of the rigid **C=N** moiety. Diazo compounds with the rigid —**N=N**— moiety also exhibit **cis-trans** isomerism. Both the carbon and nitrogen atoms of the **C=N** group in oximes are **sp²** hybridized. This is analogous to the hybridization of the carbon atoms in ethylene. Therefore, the **C=N** double bond consists of one sigma (σ) and one pi (π) bond, while the third **sp²** orbital of nitrogen is occupied by a lone pair of electrons. Thus, oximes are coplanar about the **C═N** and can exhibit **cis-trans** isomerism. A similar case is observed in hydrazones and semicarbazides.

Stereochemical nomenclature of oximes

In oxime chemistry, the terms syn and anti are used. In the case of oximes of aldehydes (aldoximes), the carbon of the C═N group must contain one hydrogen atom, and therefore, the *syn* form is the one in which the hydrogen atom and the hydroxyl group (on the N atom) are on the same side of the double bond. When the H and OH groups are on opposite sides of the double bond, the configuration is *anti*.

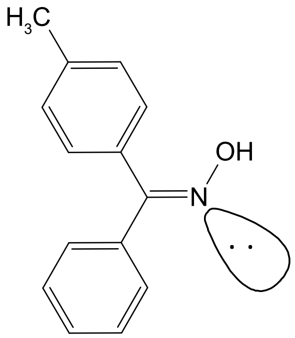


anti-Benzaldoxime

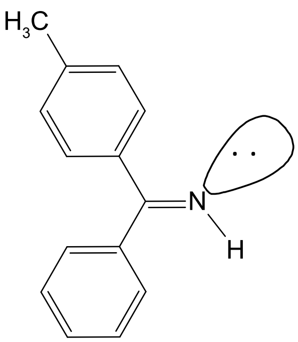


syn-Benzaldoxime

The E-Z system (CIP) can also be used to specify the configurations of oximes. For example, *syn*-p-tolyl phenyl ketoxime is (*Z*)-phenyl p-tolyl ketoxime because the p-tolyl group has priority over phenyl and the hydroxyl group has priority over the lone pair of electrons. The *syn* and *anti*-nomenclature are now abandoned for specifying the configurations of oximes. *E-Z* nomenclature is now used.

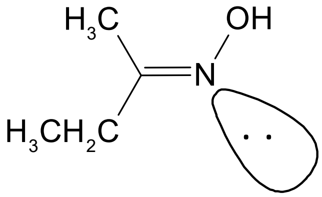


syn-p-tolyl phenyl ketoxime
or
anti-phenyl p-tolyl ketoxime
or
Z-phenyl p-tolyl ketoxime

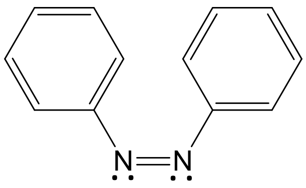


anti-p-tolyl phenyl ketoxime
or
syn-phenyl p-tolyl ketoxime
or
E-phenyl p-tolyl ketoxime

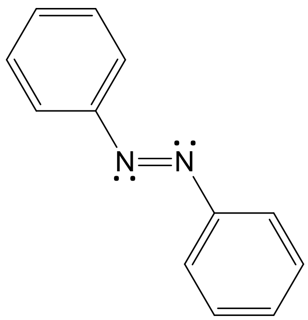
(*E*)-butanone oxime is depicted below.



Azobenzenes having a rigid —N=N— bond can also give rise to cis-trans isomerism. For example, Ph—N=N—Ph can have (*E*) and (*Z*) isomers:



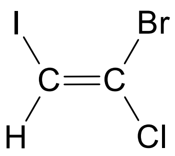
Z-azobenzene

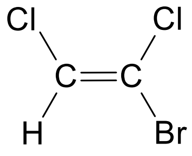


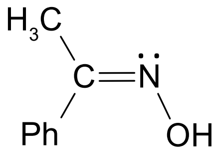
E-azobenzene

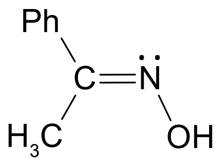
Questions

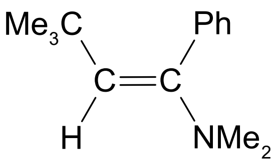
1. Give *E*-*Z* nomenclature to the following:

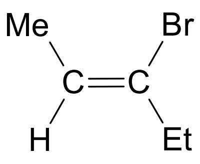


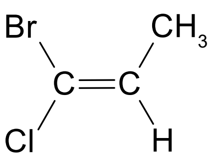


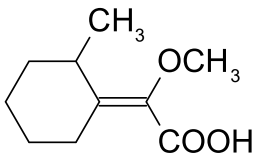












2. Draw the *E* and *Z* isomer of but-2-ene.