

STEREOCHEMISTRY

SEM-1, CC-1 / GE-1

PART-6, PPT-9

Part-6: Configurational Nomenclature

CONTENTS

- *Structure of Alkenes: Nature of cis-trans Isomerism*
- *E, Z-descriptors for alkenes (C=C),*
- *E, Z-descriptors for C=N system (for Oximes, Hydrazones and Semicarbazones) and N=N system (for diazo compounds)*

Dr. Kalyan Kumar Mandal

Associate Professor

St. Paul's C. M. College

Kolkata

Stereochemistry (PART-6, PPT-9)

Configurational Nomenclature

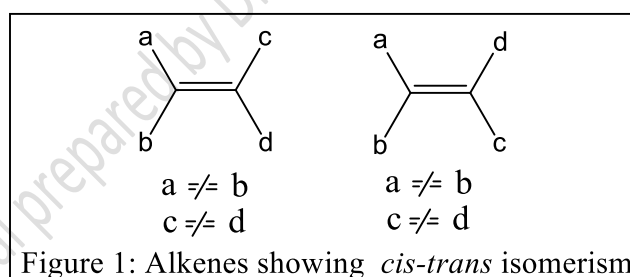
- Structure of Alkenes: Nature of *cis-trans* Isomerism
- *E, Z*-descriptors for alkenes ($C=C$),
- *E, Z*-descriptors for $C=N$ system (for Oximes, Hydrazones and Semicarbazones) and $N=N$ system (for diazo compounds)

Structure of Alkenes:

Nature of *cis-trans* Isomerism

In most alkenes (olefins), the two double-bonded carbon atoms and the four additional ligands attached to them are coplanar (Figure 1). The generally accepted orbital description involves sp^2 hybridized carbon atoms. The carbon atoms are linked to each other and to the attached ligands (a, b and c, d, respectively) by sp^2 hybridized σ - bonds, and they are further linked to a π bond formed by lateral overlap of the remaining p orbitals of the two carbon atoms.

The necessary and sufficient condition for *cis-trans* isomers to exist is that one substituent at each end of the double bond must be nonequivalent; referring to Figure 1 this means $a \neq b$ and $c \neq d$.

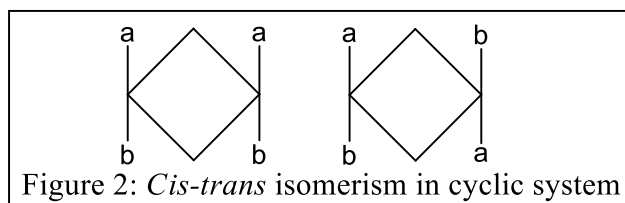


There are no restrictions as to the identity of a, b with c, d; thus $Cab=Cab$ displays *cis-trans* isomerism. The barrier for interconversion of the *cis-trans* isomers be high enough for these isomers to be distinguishable entities. The rotational barriers in alkenes are very much higher than those in alkanes [e.g., $3.6 \text{ kcal mol}^{-1}$ (15.1 kJ mol^{-1}) for the central C-C bond in butane]. Whereas the C-C σ bond energy is about 83 kcal mol^{-1} , the strength of the π bond, with its less favorable lateral overlap, is only 60 kcal mol^{-1} .

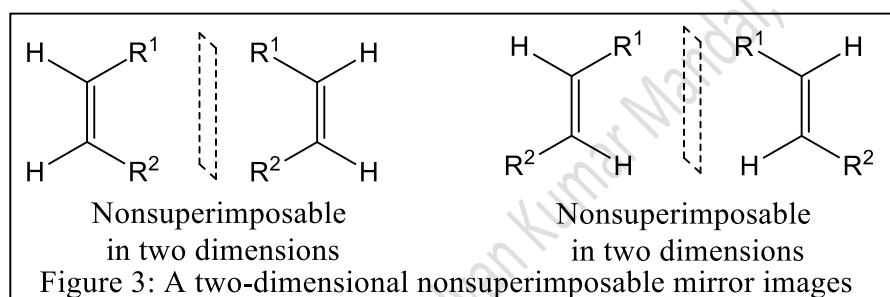
These two energies add up to the generally accepted total energy of a $C=C$ double bond, $143 \text{ kcal mol}^{-1}$.

The activation barrier (E_a) to the thermal isomerization of 2-butene (Figure 1, $cis \rightleftharpoons trans$, $a = c = CH_3$, $b = d = H$), is $\sim 62 \text{ kcal mol}^{-1}$. In the case of $Cab=Nx$ (for oximes, hydrazones and for semicarbazones), or $Nx=Nx$ (for diazo compounds), the missing substituent is the lone

pair of electrons on nitrogen. Since this isomerism owes its existence to the presence of a π -bond, it has been called π -diastereomerism to distinguish it from σ -diastereomerism exhibited by cyclic compounds (Figure 2).



cis-trans Isomerism (sometimes called geometric isomerism) is a type of diastereomerism. The *cis*- and *trans*-isomers are not mirror image stereoisomers (Figure 3). Therefore, they can be considered as two-dimensional enantiomers having a two-dimensional nonsuperimposable mirror images which are produced by reflection, within the plane of the paper, through a straight line which represents a two-dimensional mirror.

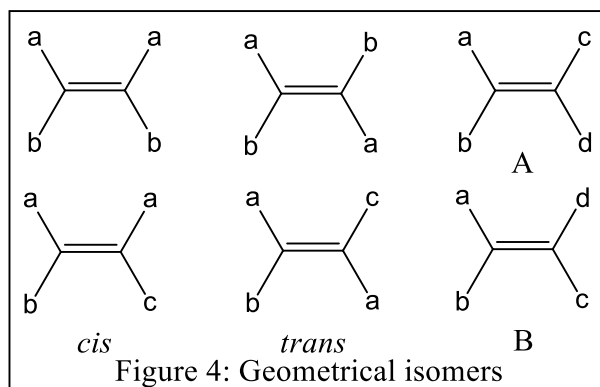


Both the *cis*- and *trans*-isomers of but-2-ene have the same bonding connectivity of atoms but the spatial arrangement around the rigid C=C bond, in each case, is different. They are diastereomers. *cis*- and *trans*-isomers are different compounds and possess different physical and chemical properties. The π -diastereomers are two-dimensional molecules (if one ignores the geometry of the 'a' and 'b' groups), possess a plane of symmetry, and therefore are *achiral*. On the other hand, σ -diastereomers are three-dimensional and may be *chiral*.

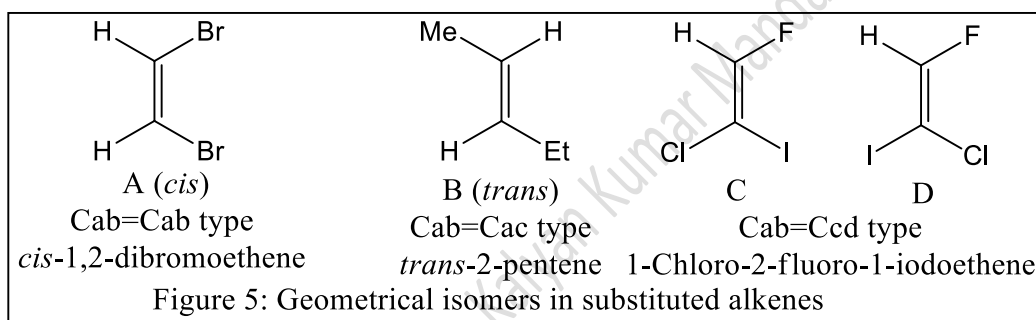
Since, in general, the plane of the double bond is a plane of symmetry, geometrically isomeric olefins do not usually show optical activity. An exception occurs in compounds that contain asymmetric atoms (or other source of dissymmetry) in addition to the double bond. For alkenes of the type, Cab=Cab or Cab=Cac, the terms '*cis*' and '*trans*' are adequate and unambiguous. But if three or four of the substituents are different (of the type Cab=Ccd), this nomenclature leads to ambiguity and sometimes to total confusion.

In the first two cases (i.e., for alkenes of the types Cab=Cab and Cab=Cac), where at least one group attached to the left carbon is equal to one attached to the right carbon, the geometrical isomers are distinguished by the prefixes "*cis*" and "*trans*".

cis being used when the two identical groups are on the same side and *trans* when they are on the opposite sides. The prefixes "*cis*" and "*trans*" are from Latin: "this side of" and "the other side of", respectively.



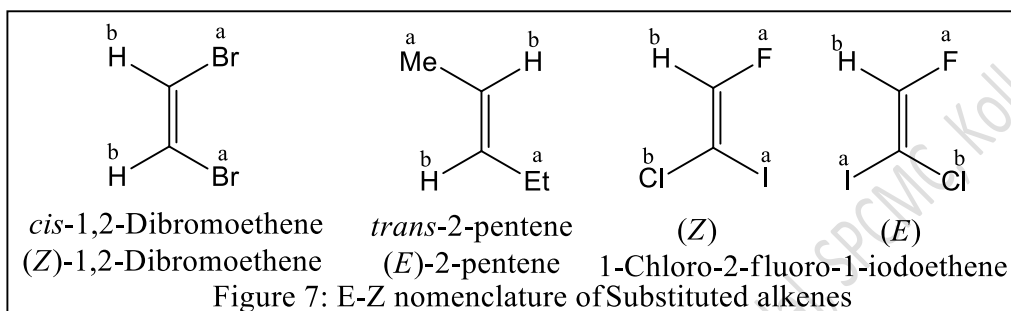
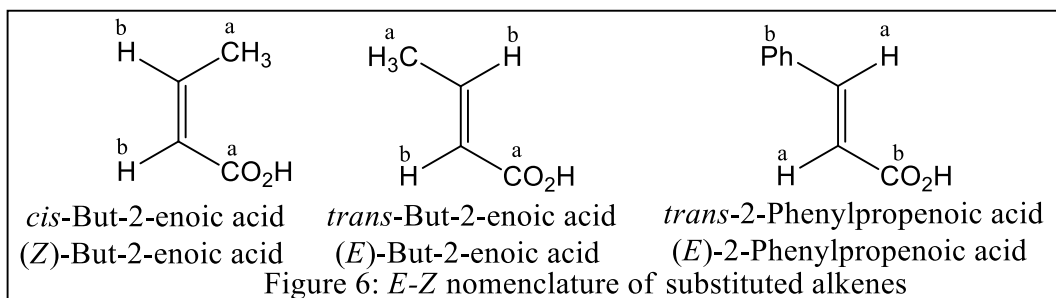
cis- and *trans*- configurational nomenclature is not applicable to alkenes in which all the four ligands attached to the double bonded carbon atoms are different. For example, 1-chloro-2-fluoro-1-iodoethene has two isomers C and D (Figure 5) but they are difficult to be name as *cis*- and *trans*-isomers. In fact, no suitable general symbolism is developed to name such compounds.



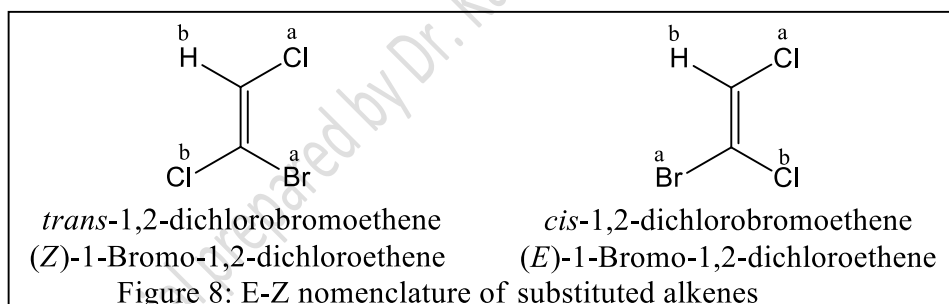
***E/Z* Configurational Nomenclature**

An easy solution to the problem in naming of alkenes with different substituents at the double bond is provided by arranging the pair of ligands at each trigonal carbon in CIP sequence. Then if the groups of higher priority are on the same side, the configuration is *seq-cis* (*sequential-cis*); if they are on the opposite sides, the configuration is *seq-trans* (*sequential-trans*) (CIP 1966).

Later, the system has been modified (Blackwood et al., 1968), the terms being replaced by two shorter symbols '*Z*' (from German *zusammen* meaning 'together') and '*E*' (from German *entgegen* meaning 'opposite'). The two arrangements shown in Figure 6 are called '*Z*' and '*E*' depending on whether the atoms of highest priority in the Cahn-Ingold-Prelog sequence are on the same side or on opposite sides of the double bond. The descriptors *E* and *Z* are always italicized. When the descriptor (*E* or *Z*) is part of a name, it is placed in parentheses in front of the name followed by a hyphen.

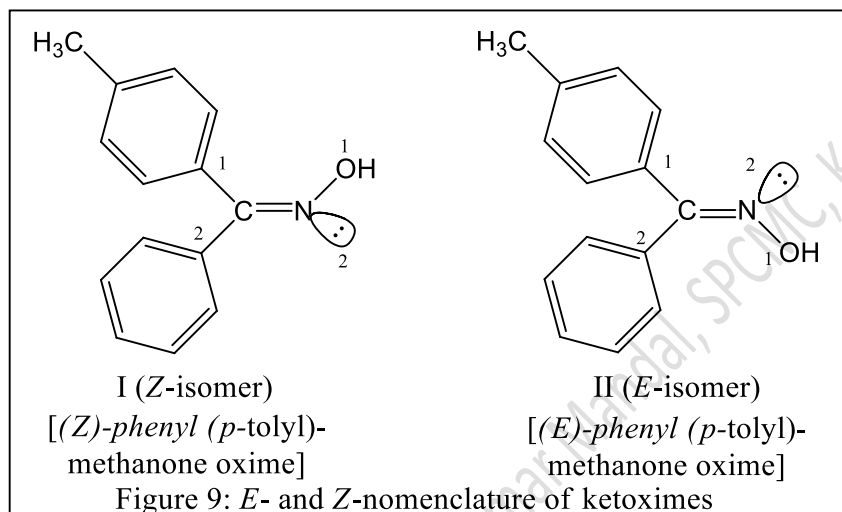


E, Z nomenclature is more meaningful than *cis-trans* nomenclature because it is applicable to all cases and is free from ambiguity. It is important to realize that in cases where *cis* and *trans* can be used, *Z* does not always correspond to *cis* and *E* does not necessarily correspond to *trans*. Thus structures A and B in Figure 8 are called (*Z*)-1-bromo-1,2-dichloroethene and (*E*)-1-bromo-1,2-dichloroethene, respectively. Here, atoms of higher priority on each of the olefinic carbons determine the type of descriptors.



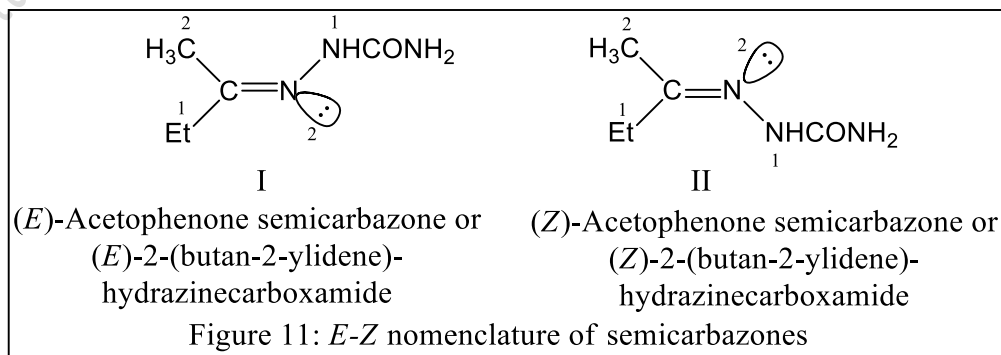
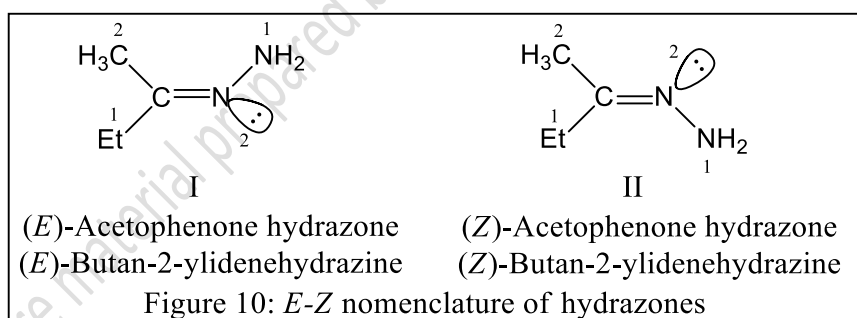
E/Z Stereochemical Nomenclature of Oximes

The *E-Z* system (CIP) can also be used to specify the configurations of oximes. For example, *syn-p*-tolyl ketoxime is (*Z*)-phenyl-*p*-tolyl ketoxime because *p*-tolyl group has priority over phenyl and hydroxyl group has priority over the lone pair of electrons. *Syn* and *anti*-nomenclature are now abandoned for specifying the configurations of oximes. The nomenclature is illustrated in Figure 9.



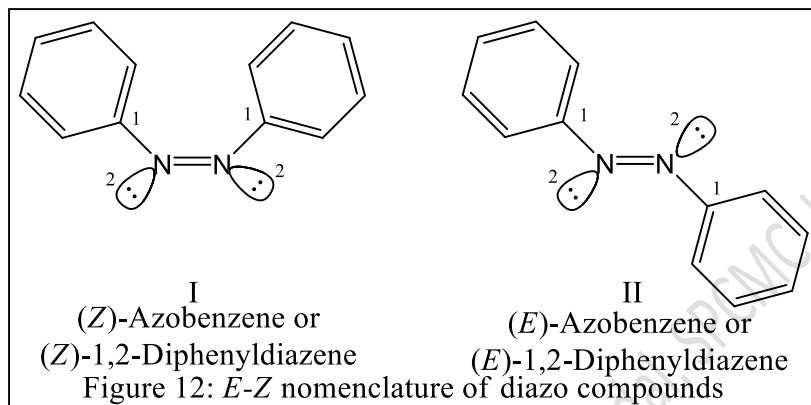
Stereochemical Nomenclature of Hydrazones and Semicarbazones

Semicarbazones and hydrazones of aldehydes (except HCHO) and unsymmetrical ketones ($R-CO-R^1$) also exhibit *cis-trans* isomerism. Examples are given below.



Stereochemical Nomenclature Diazo Compounds

A doubly bonded nitrogen may play the same part in geometrical isomerism as a doubly bonded carbon. Azobenzenes having rigid $-N=N-$ bond can also give rise to *cis-trans* isomerism. For example, azobenzene (Ph-N=N-Ph) can give *E*- and *Z*-isomers as shown in Figure 12.



Lecture material prepared by Dr. Kalyan Kumar Manu, IIT Kolkata