

CHAPTER 9 SPECIFICATION OF CONFIGURATION AND CONFORMATION

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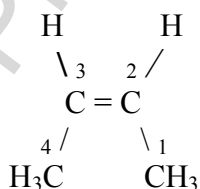
P-90 Introduction

This section is concerned only with the main principles for specification of configuration and conformation of organic compounds. The spatial structure of an organic compound is systematically indicated by one or more affixes added to a name that does not itself prescribe stereochemical configuration or conformation; such affixes are generally called stereodescriptors. Thus stereoisomers, such as *cis/trans* isomers and enantiomers, have names that differ only in the stereodescriptors used. By contrast, certain retained names imply their own stereochemical description, for example, maleic acid (recommended only for general nomenclature), cholesterol and other natural products described in Chapter 10 that are used as preferred IUPAC names or recommended only for general nomenclature.

In order to arrive at a non-ambiguous description of stereoisomers, Cahn, Ingold and Prelog (ref. 30, 31, 32) recommended an order of seniority for the atoms and groups attached to carbon and other atoms, which is commonly called the CIP priority system. The priority is established by the application of 'sequence rules'. As these rules are fundamental to describe both *cis* and *trans* isomers and enantiomers, they are discussed in the first section of this chapter. Their application is then described for stereogenic units, mainly for the most usual compounds, synthetic or natural, encountered in organic chemistry

When different stereodescriptors are recommended to describe *cis* and *trans* isomers, diastereoisomers, and enantiomers, one of them is recommended as a preferred stereodescriptor. This preferred stereodescriptor is used to generate a preferred IUPAC name. Obviously, in general nomenclature, any appropriate descriptor can be used.

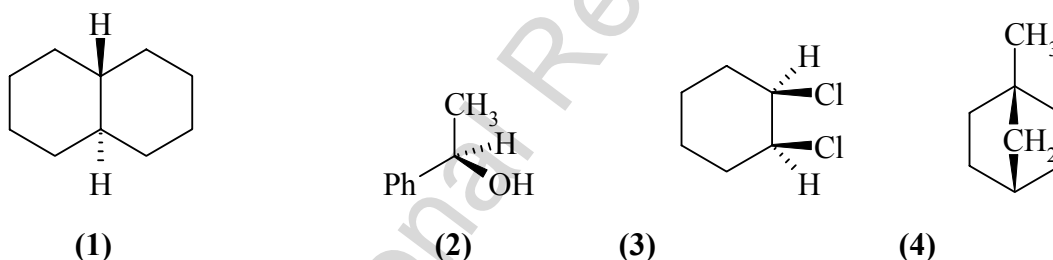
Example:



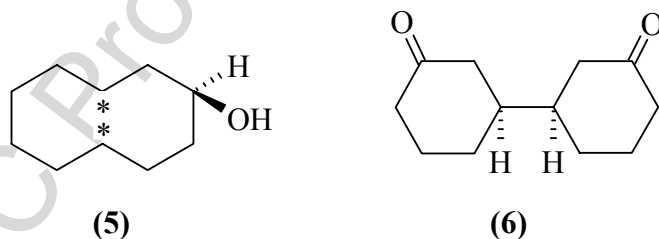
(2*Z*)-but-2-ene (PIN)
cis-but-2-ene

Structural diagrams which depicts tridimensional structures must be prepared with extra care to ensure there is no ambiguity. In general, normal lines depict bonds approximately in the plane of the drawing; bonds to atoms above the plane are shown with a bold wedge \blacktriangle (starting from an atom in the plane of the drawing at the narrow end of the wedge); and bonds to atoms below the plane are shown with a hashed wedge ----- which is used with the understanding that the narrow end of the wedge begins at the atom in the plane of the drawing. This system is used in the recommendations in this book. A guide to graphic representation of tridimensional structures has been published along with the basic terminology of stereochemistry (ref. 33). In that publication, an alternative to the hashed wedge has been proposed which uses short parallel lines; however, it must be noted that this is not a symbol in many chemical structure drawing programs. A broken line ----- has been used instead of hashed wedge but this is better reserved for a partial bond, delocalization, or a hydrogen bond. When the configuration of a bond is unknown this can be shown explicitly by a wavy line ~~~~ . The use of dots or open circles at a center to show configuration is strongly deprecated.

Strict rules for drawing configuration are not possible. In general it is most clear if all rings of an *ortho*-fused ring system (or saturated derivatives) are kept in the plane and bridgehead substituents are shown above or below the plane (1). With an acyclic structure (2) or other substituent on a ring (3) [(including bridges (4)] bonds are shown as above or below the plane. Hydrogen atoms attached to stereochemically designated positions should not be omitted (3).



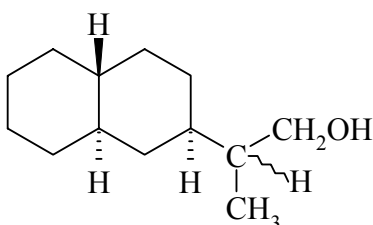
The configuration due to substituents attached to a ring should not be shown at a reentrant angle (marked with an asterisk on (5), although this is suitable for a carbonyl group or *N*-methyl group). Any bond between two stereochemically designated positions should be left plane (6).



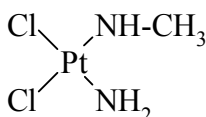
For tetrahedral configuration the following are recommended:



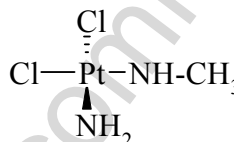
A wavy line can be used to indicate either that the configuration is unknown (7) but only one form is present, or if explained in the text that both isomers are present and will be defined when required. If it is intended not to show any configuration it is best to only use plain lines for all bonds. Note that the planar molecule (8) can also be drawn as (9) or (10).



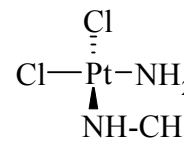
(7)



(8)

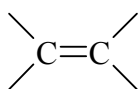


(9)

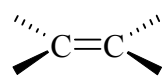


(10)

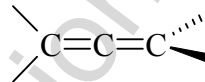
Double bonds should be shown as far as possible with accurate angles (*ca* 120°) when configuration is implied [(11),(12),(13)]. To show the absence of any configurational information a linear representation should be used [see (14),(15),(16)].



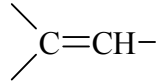
(11)



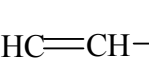
(12)



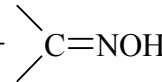
(13)



(14)

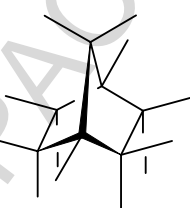


(15)

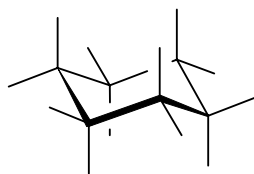


(16)

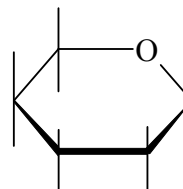
In a perspective drawing it is preferable to indicate which edge of the ring is considered in front by bold or wedge lines as in (17), (18), and (19) and 'breaking' the bond at the back when a bond passes in front, as in (17) and (18). In this type of configurational representation bonds to substituents should usually be left plain.



(17)



(18)



(19)

P-91 Enantiomers and *cis-trans* isomers

- P-91.1 Enantiomers: the CIP priority system
- P-91.2 *cis-trans* Isomers

P-91.1 Enantiomers: the CIP priority system

- P-91.1.1 The CIP priority system
- P-91.1.2 Digraphs
- P-91.1.3 Exploration of a hierarchical digraph
- P-91.1.4 Application of Sequence Rule **1** to tetrahedral systems
- P-91.1.5 Sequence Rule **2**

P-91.1.1 The CIP priority system

This Section describes the CIP priority system which was developed to deal with all compounds with a bonding number up to six for organic compounds, and for all configurations and conformations of these compounds (ref. 30, 31, 32). Its description for specifying configurations and conformations is discussed herein.

Chirality is the property of an object, thus of a molecular entity, of being non-superposable on its mirror image. If the object (molecular entity) is superposable to its mirror image, it is said to be 'achiral'.

The CIP system is based on rules and a strict hierarchical order of decisions until a single stereodescriptor can be used to describe a given configuration.

For tetrahedral stereogenic atoms having four different atoms or groups, the chirality rule is based on the arrangement of these atoms or groups (including chains and rings) in an order of precedence, often referred to as an order of priority. For discussion this order can conveniently be generalized as 'a' > 'b' > 'c' > 'd', where > denotes 'has priority over' or 'has precedence over'. The order of precedence is reached by the application of the sequence rules using specific and hierarchical digraphs as explained below.

In inorganic terminology, the term 'ligand' is defined as 'the atoms or groups joined to the central atom in an inorganic coordination entity' (ref. 14). Thus, for organic compounds, the term ligand is inappropriate to describe the atoms or groups attached to an atom of a stereogenic unit. The expression 'atom or group' will be used. The terms derived from 'ligand' such as ligancy and tetraligancy that are widely used in reference to the CIP system, are replaced by valence and tetravalence.

The chirality rule is expressed by Prelog and Helmchen (ref. 32) as follows: "Among ligands of highest precedence the path of their sequence is followed from their preferred side of the model, that is, the side remote from the group of lowest precedence, and, depending on whether the path turns to right or left, the chirality unit will be assigned the chiral label *R* or *S*."

For 'a' > 'b' > 'c' > 'd':

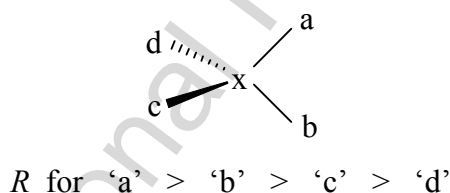


P-91.1.1.1 Stereogenic units

A stereogenic unit (i.e. a unit generating stereoisomerism) is a grouping within a molecular entity that may be considered a focus for stereoisomerism. At least one stereogenic unit must be present in every enantiomer; however, conversely, the presence of stereogenic units does not require the corresponding molecular entity to be chiral. Three basic types of stereogenic units in molecular entities involving atoms having not more than four substituents are considered below:

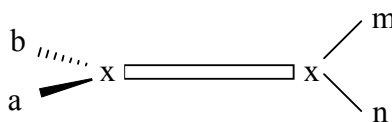
- (a) A grouping of atoms consisting of a central atom (X) and distinguishable atoms or groups ('a', 'b', 'c', 'd'), so that the interchange of any two of the atoms or groups 'a', 'b', 'c', and 'd', leads to a stereoisomer. A chirality center, formerly known as an 'asymmetric atom', is the classical example of a stereogenic unit.

Example:



- (b) A chain of four noncoplanar atoms (or rigid groups) in a stable arrangement, such that an imaginary or real (restricted) rotation (with a change of sign of torsion angle) about the central bond leads to a stereoisomer.

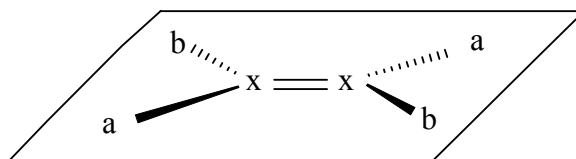
Example:



R_a or *M* for 'a' > 'b' and 'm' > 'n' (m and n = or ≠ 'a' and 'b')

- (c) A grouping of atoms consisting of a double bond with substituents which give rise to *cis-trans* isomerism.

Example:



E for 'a' > 'b'

P-91.1.1.2 The 'Sequence Rules'

The following 'Sequence Rules' are used (ref. 30, 31, 32) to establish the order of precedence of atoms and groups. A more encompassing set of rules, proposed by Mata, Lobo, Marshall, and Johnson (ref. 34), including amendments by Custer (ref. 35), Hirschmann and Hanson (ref. 36), is used in this Chapter. The rules are hierarchical, i.e., each rule must be exhaustively applied in the order given until a decision is reached:

Rule 1 (a) Higher atomic number precedes lower;

(b) A duplicated atom, with its predecessor node having the same label closer to the root, ranks higher than a duplicated atom, with its predecessor node having the same label farther from the root, which ranks higher than any nonduplicated-atom-node (proposed by Custer, ref. 36)

Rule 2 Higher atomic mass number precedes lower;

Rule 3 *seqcis* Stereogenic units precede *seqtrans* stereogenic units and these precede nonstereogenic units (*seqcis* > *seqtrans* > *nonstereogeni*). (Proposed by Mata, Lobo, Marshall, and Johnson, ref. 34);

The domain of application of this rule is restricted to geometrically diastereomorphic planar tetravalent atoms and double bonds. All cases involving geometrically diastereomorphic two-dimensional stereogenic units are considered in Rules 4 and 5. (Proposed by Hirschmann and Hanson, ref. 36).

Rule 4 (a) Chiral stereogenic units precede pseudoasymmetric stereogenic units and these precede nonstereogenic units. (Sub-rule originally proposed by Prelog and Helmchen (ref. 32), but their inclusion as first sub-rule of Rule 4 was proposed by Custer, ref. 35). Geometrically enantiomorphic twodimensional stereogenic units precede two-dimensional nonstereogenic units (Proposed by Mata, Lobo, Marshall and Johnson, ref. 34).

(b) When two ligands have different descriptor pairs, then the one with the first chosen *like* descriptor pairs has priority over the one with a corresponding *unlike* descriptor pair.

(i) *Like* descriptor pairs are: 'RR', 'SS', 'MM', 'PP',
'*seqCis/seqCis*', '*seqTran/sseqTrans*', '*RseqCis*',
'*SseqTrans*', '*MseqCis*', '*PseqTrans*'.

- (ii) Unlike descriptor pairs are '*RS*', '*MP*', '*RP*', '*SM*', '*seqCis/seqTrans*', '*RseqTrans*', '*SseqCis*', '*PseqCis*' and '*MseqTrans*'. (the descriptor pairs '*RRe*', '*SSi*', '*ReRe*', '*SiSi*', '*ReM*', '*SiP*', '*ReSi*', '*Rsi*', '*ReP*' and '*MSi*' are not included in this rule (proposed by Mata, Lobo, Marshall and Johnson, ref. 34).

Methodology for pairing descriptors:

The descriptor assigned to geometrically enantiomorphic double bonds should be associated in the digraph with the first node corresponding to the atoms involved in the double bond (proposed by Mata, Lobo, Marshall and Johnson, ref. 34).

For each atom or group the descriptor chosen at first (highest ranked descriptor) is paired with all the remaining descriptors. The following characteristics determine the hierarchical rank of the pairs of descriptors:

- (i) higher rank of the second descriptor in the pair;
 - (ii) lower rank of the least common ancestor in the graph (proposed by Custer, ref. 35).
- (c) '*r*' Precedes '*s*' and '*p*' precedes '*m*' (proposed by Mata, Lobo, Marshall and Johnson, ref. 34).

Re-inclusion of this subrule in Rule 4 was proposed by Custer (ref. 35).

Rule 5 An atom or group with descriptor '*R*', '*M*' and '*seqCis*' has priority over its enantiomorph '*S*', '*P*' or '*seqTrans*', '*seqCis*' and '*seqTrans*' (proposed by Hirschmann and Hanson, ref. 36)

These rules are based on the hierarchical order of atoms or groups properties, material and topological properties for rules 1 and 2, geometrical properties for rules 3 and 4, and topographical properties for rule 5. The first four properties are reflection-invariant, the fifth is reflection-variant.

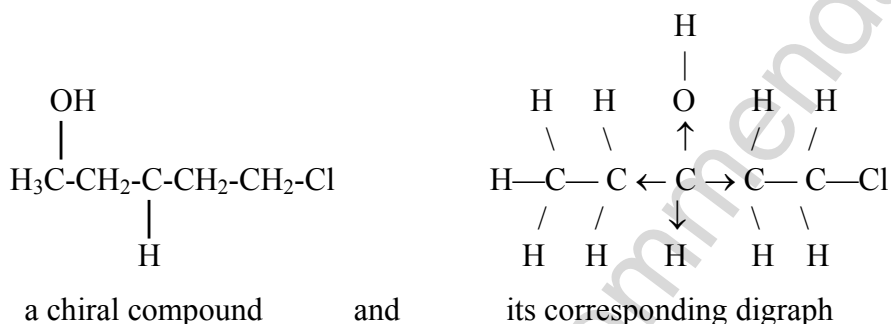
Atoms and groups of atoms are monovalent or divalent as exemplified by 'diyl' groups; they can be acyclic or cyclic.

The five 'Sequence Rules' are applied as follows:

- (a) each rule is applied exhaustively to all atoms or groups being compared;
- (b) each rule is applied in accordance with a hierarchical digraph (see P-91.2)
- (c) the atom or group that is found to have precedence (priority) at the first occurrence of a difference in a digraph retains this precedence (priority) regardless of differences that occur later in the exploration of the digraph;
- (d) precedence (priority) of an atom in a group established by a rule does not change on application of a subsequent rule.

P-91.1.2 Digraphs

In order to establish the order of precedence of atoms or groups in a stereogenic unit, the atoms of the stereogenic unit are rearranged in a hierarchical diagram, called a 'digraph' or a 'tree-graph', representing the connectivity (topology) and make-up of atoms; a digraph originates from the core of the stereogenic unit and is developed by indicating the various branches (see section 3, ref. 32) representing atoms or groups of atoms, monovalent or divalent, acyclic or cyclic. A simple example for a stereogenic center follows.



P-91.1.3 Exploration of a hierarchical digraph

Digraphs are constructed to show the ranking of atoms according to the topological distance i.e., number of bonds, from the core of the stereogenic unit (i.e., center) and their evaluation by the sequence rules (see section 3.3, ref. 34).

- (a) Atoms lie in spheres and atoms of equal distance from the core of the stereogenic unit are in the same sphere; spheres are identified as **I**, **II**, **III**, and **IV**, as shown in **Fig. 1**. The first sphere is occupied by the 'proximal atoms', 'p' and 'p''. Those in the sphere **II** are numbered 1,2,3 and 1',2',3'. Those in sphere **III** are numbered 11, 12, 13, 21, 22, 23,... 11',12',13'... and so on for each further sphere. Indicated branches may not be present in all molecules.
- (b) Atoms in the n^{th} sphere have precedence over those in the $(n + 1)^{\text{th}}$ sphere. (Ranking Rule **1**).
- (c) The ranking of each atom in the n^{th} sphere depends in the first place on the ranking of atoms of the same branch in $(n - 1)^{\text{th}}$ sphere, and then by the application of the Sequence Rules to it; the smaller the number, the higher the relative ranking. (Ranking Rule **2**).
- (d) Those atoms in the n^{th} sphere which are of equal rank to those in the $(n - 1)^{\text{th}}$ sphere in the same branch are ranked by means of the sequence rules, first by the exhaustive application of Sequence Rule **1**; if no decision is reached, Sequence Rule **2** is exhaustively applied, and so on.

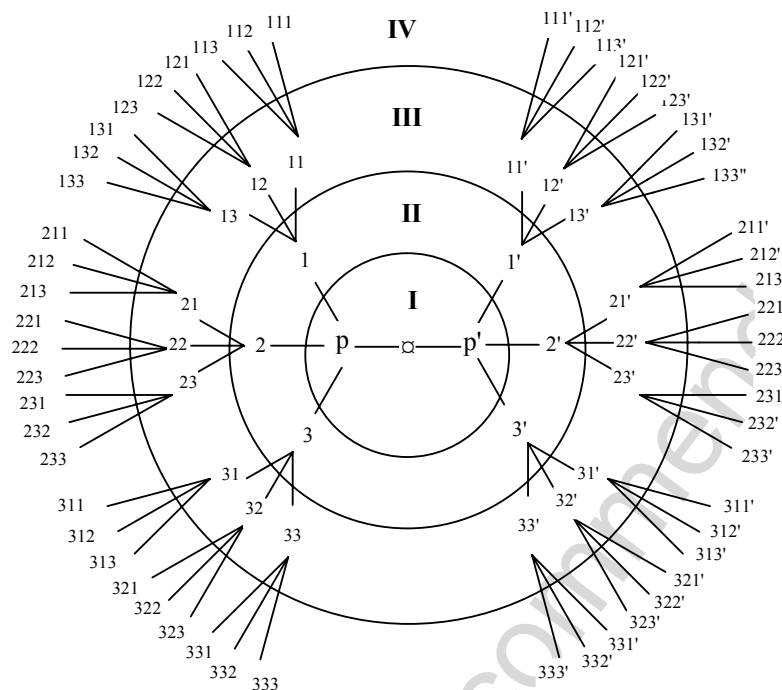


Fig. 1 Ranking order of two ligands

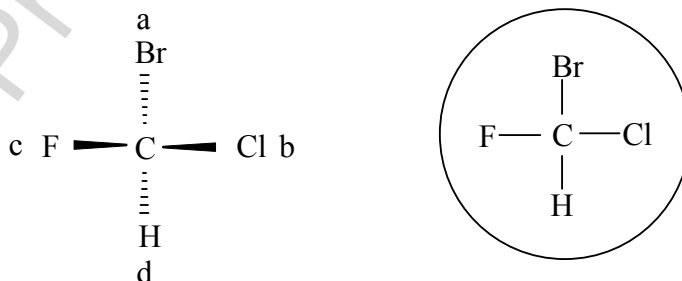
P-91.1.4 Application of Sequence Rule 1 to tetravalent systems

P-91.1.4.1 Sequence Rule 1 is expressed as follows: atoms or groups are arranged in order of decreasing atomic number.

Atoms or groups 'a', 'b', 'c', and 'd' are ranked stepwise, by a procedure called the 'ranking procedure' that always starts at the atom to be specified and proceeds further away until a decision is reached. The comparison of atoms starts at sphere I and proceeds to sphere II if a decision is not reached, and so on.

P-91.1.4.1.1 Analysis of sphere I

In the compound HCB_rClF, below, all atoms are included in sphere I.



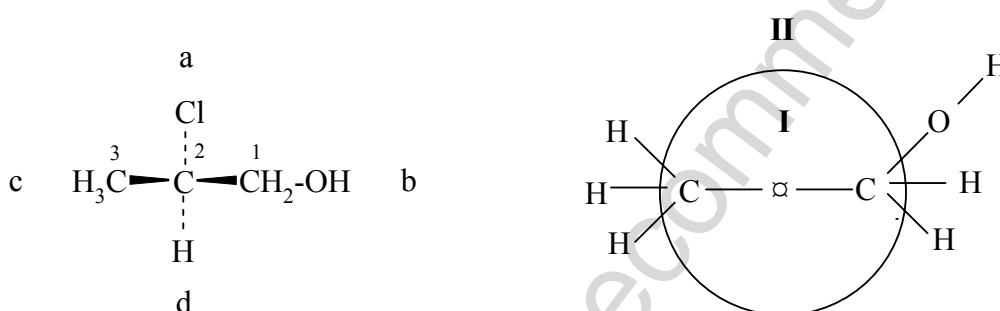
The order 'a' > 'b' > 'c' > 'd' is, in accordance with Sequence Rule 1, i.e., Br > Cl > F > H.

P-91.4.1.2 Analysis of spheres I and II

When atoms attached to the stereogenic unit are identical, precedence is established by the atoms in turn that are directly attached to the identical atoms. When the molecule contains several atoms and branches, it is convenient to number it, either by using the numbering system recommended in nomenclature or by applying an arbitrary system to properly identify all atoms appearing in the digraph.

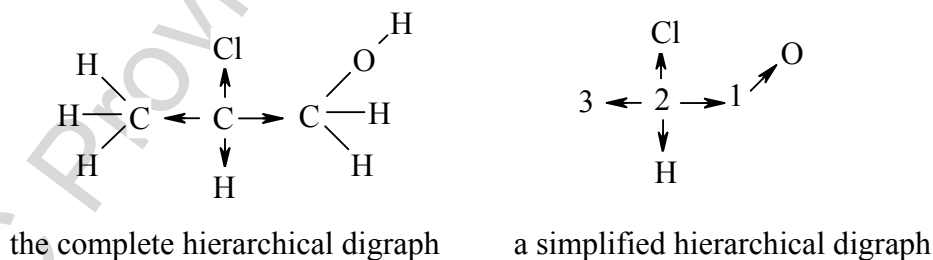
Example 1:

In the compound $\text{H}_3\text{C}-\text{CHCl}-\text{CH}_2\text{OH}$, below, the order of seniority for 'a' > 'b' > 'c' > d is $\text{Cl} > \text{C}$ and $\text{C} > \text{H}$. No decision is attained in sphere I, as the two proximate atoms are identical.

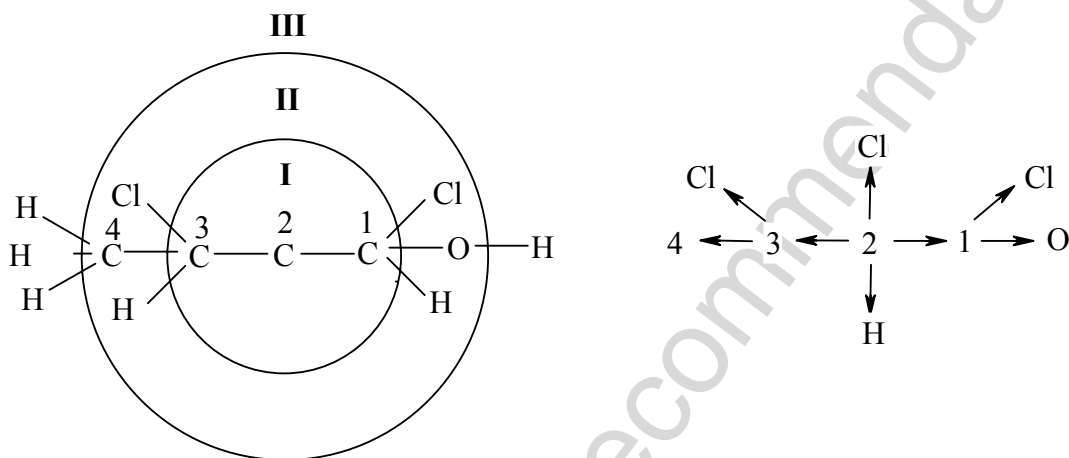
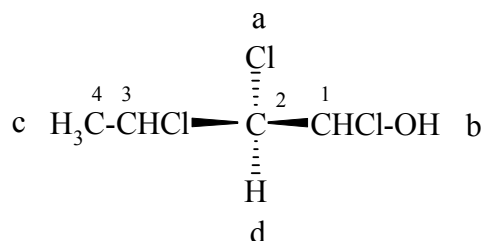


In sphere II, however, the atoms attached to the two carbon atoms are (O,H,H) and (H,H,H), respectively, and, as $\text{O} > \text{H}$, the order of precedence is 'b' > 'c' and hence the group $-\text{CH}_2\text{OH}$ is 'b' and the group $-\text{CH}_3$ is 'c'.

Different types of digraphs may be used, the so called complete hierarchical digraph and the simplified hierarchical digraph based on the numbering of the structure. For the compound 2-chloropropan-1-ol, below, the complete hierarchical digraph and the simplified hierarchical digraph are shown:



Example 2:

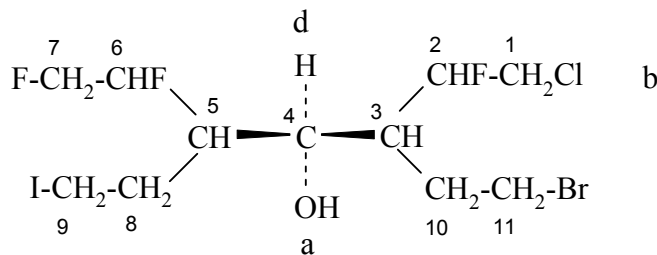


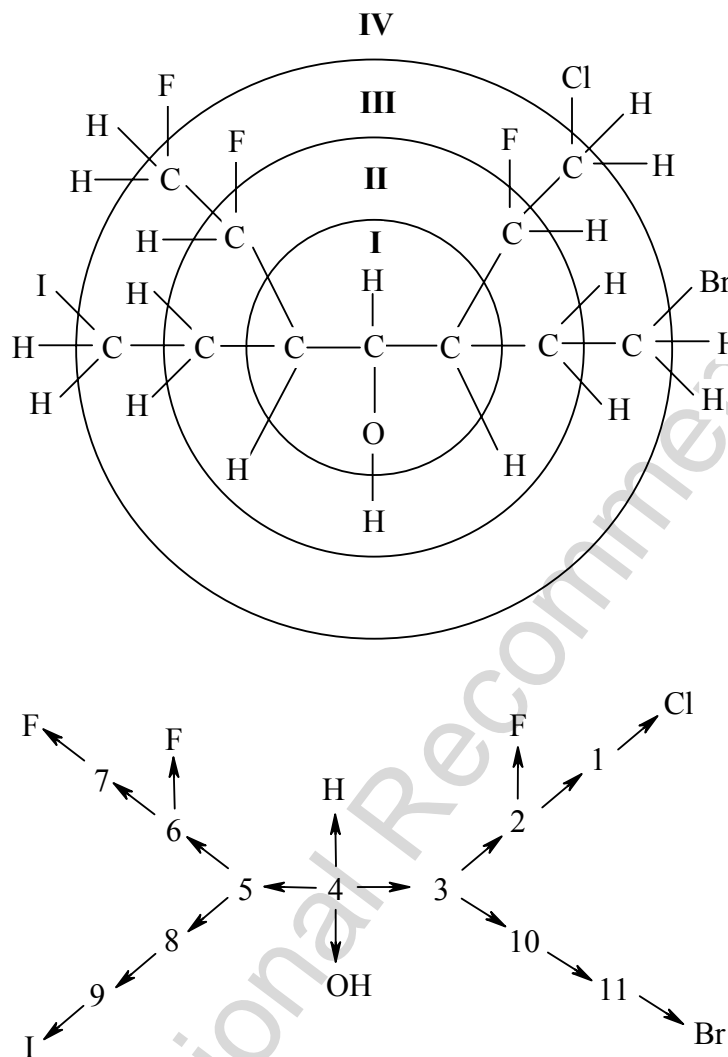
In this example, Sequence Rule 1 establishes the seniority order $\text{Cl} > \text{C} > \text{C} > \text{H}$ in sphere I; but no decision between 'b' and 'c' can be reached. However, in sphere II, the atoms attached to the carbon atoms 1 and 3 are (Cl,O,H) and (Cl,C,H), respectively. The comparison of the two senior atoms in each set, Cl atoms, does not permit a choice to be made; however, comparison of the two second atoms in the set O and C, respectively, establishes the order $\text{O} > \text{C}$ and thus the group $-\text{CHCl}-\text{OH}$ is 'b' and the group $-\text{CHCl}-\text{CH}_3$ is 'c'.

P-91.1.4.1.3 Analysis of spheres I, II, III and IV

When choices remain after evaluating the second level, the exploration procedure is continued farther away from the stereogenic center.

Example:





The first level of the exploration, sphere **I**, leads to $O > C$ and $C > H$, but no decision can be made between the carbon atoms. And, in sphere **II**, still no decision can be made, because of the two identical sets of (C,C,H) atoms attached to carbon atoms. In sphere **III**, the two branches on the left hand side are ranked $(F,C,H) > (C,H,H)$; on the right hand side, the two branches are ranked $(F,C,H) > (C,H,H)$. However, still no decision can be made, but the two branches can be ranked giving precedence to the branches denoted by (F,C,H) over (C,H,H). Then, in sphere **IV**, the two branches having precedence are examined and a decision is reached, because (Cl,H,H) has precedence over (F,H,H) . Accordingly, the branch on the right hand side is assigned the priority 'b' and the branch on the left gets priority 'c'. The fact that, in the branches of lower precedence in sphere **III**, the iodine and Br atoms have priority over Cl and F are not taken into consideration, because a decision has already been reached.

P-91.1.4.1.4 Higher levels

After the fourth level, exploration is continued in the same manner until a decision can be made.

P-91.1.4.2 Duplicate atoms and phantom atoms

There is no difficulty in the expression of the connectivity between the various atoms used in a digraph of atoms or groups when they are monovalent. A special interpretation is necessary to treat multiple bonds, saturated and mancude rings and ring systems, and lone pairs of electrons in order to maintain the tetravalency indispensable to the application of the sequence rules.

P-91.1.4.2.1 Treatment of double and triple bonds

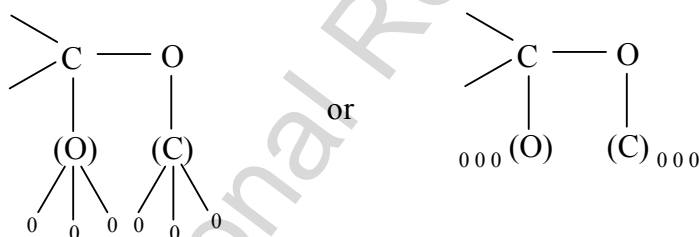
P-91.1.4.2.2 Treatment of saturated rings and ring systems

P-91.1.4.2.3 Treatment of mancude rings and ring systems

P-91.1.4.2.4 Treatment of tetrahedral systems including a pair of electrons

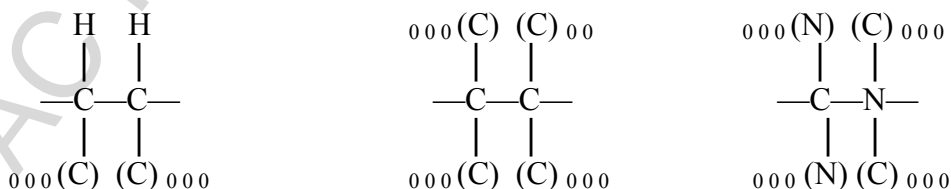
P-91.1.4.2.1 Treatment of double and triple bonds

When double and triple bonds have to be considered, as in the groups $>C=O$ and $-C\equiv N$, the multiple bonds are split into two and three single bonds respectively. A $>C=O$ group is treated as

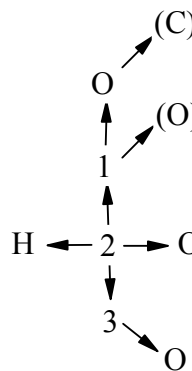
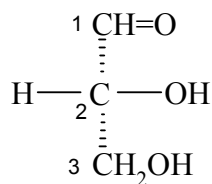


where the (O) and (C) are duplicate representations of the atoms at the other end of the double bond. Each real atom, except for hydrogen, and each duplicated atom is converted to single bond tetravalency by adding 'phantom atoms', i.e. imaginary atoms having an atomic number of zero. Duplicate atoms are denoted in parentheses; 'phantom atoms' are denoted by the cipher zero, which often is shown as a subscript.

Similarly, $-CH=CH-$, $-C\equiv C-$, and $-C\equiv N$ are treated as follows, respectively:



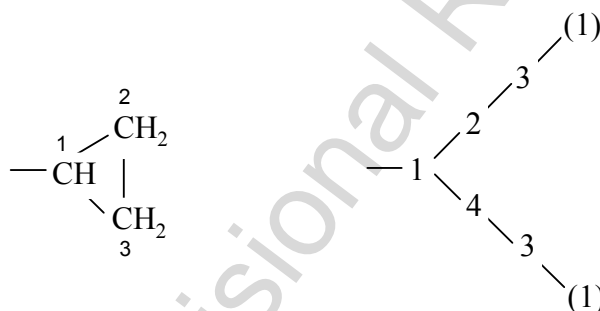
Example:



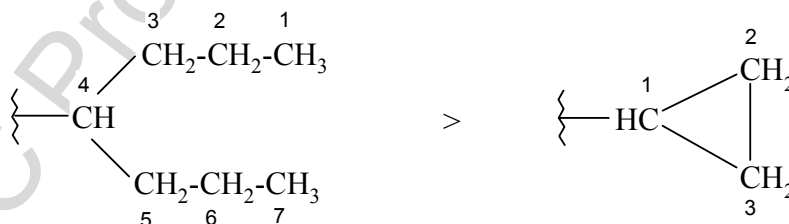
The priority order is $O > C$ and $C > H$ in accordance with Sequence Rule 1. The priority order is (O,O,H) for the $-\text{CH=O}$ group and (O,H,H) for the $-\text{CH}_2\text{OH}$ group; thus, $-\text{CH=O} > -\text{CH}_2\text{OH}$.

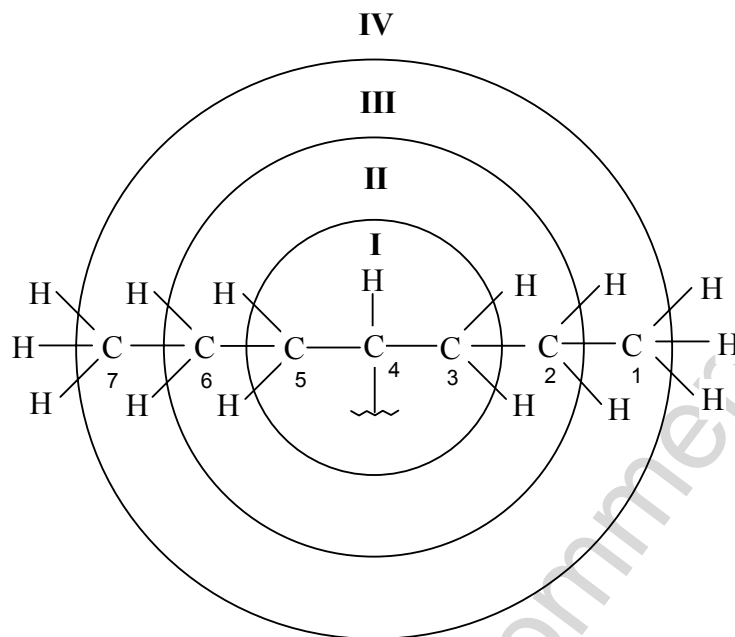
P-91.1.4.2.2 Treatment of saturated rings and ring systems

Saturated rings are opened and treated as branched chains. In order to arrive at a decision, the ranking operation is pursued until an atom already involved in the exploration is reached. This atom is considered as a 'duplicate atom' to which 'phantom atoms' are attached. In the examples, the symbol ' $>$ ' means 'has precedence over' in Sequence Rule terminology.

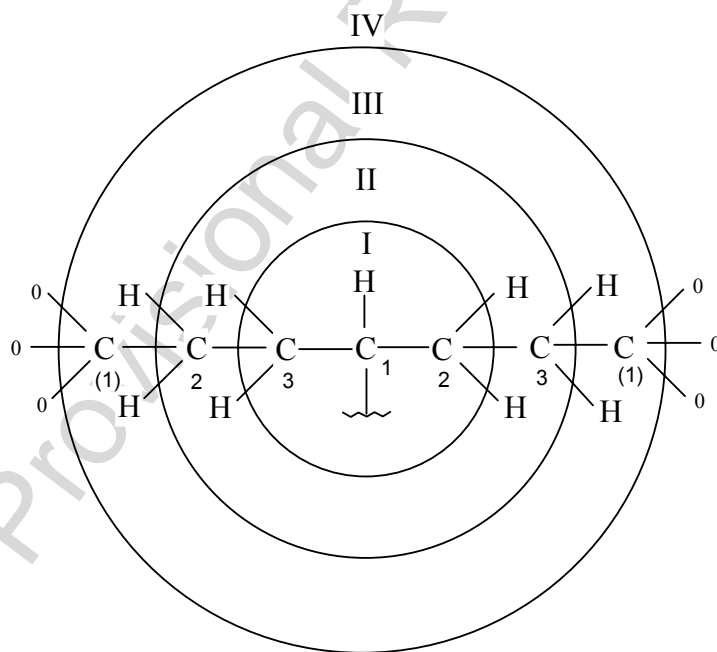


Example 1:





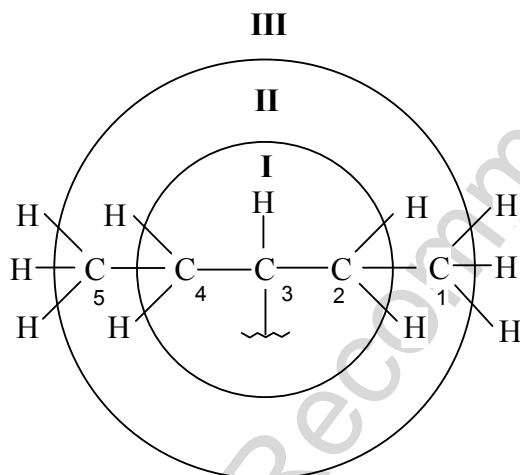
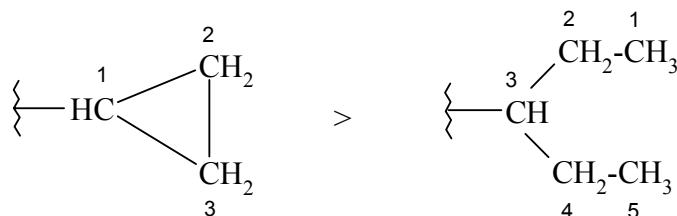
Digraph of heptan-4-yl showing the hydrogen atoms in sphere IV



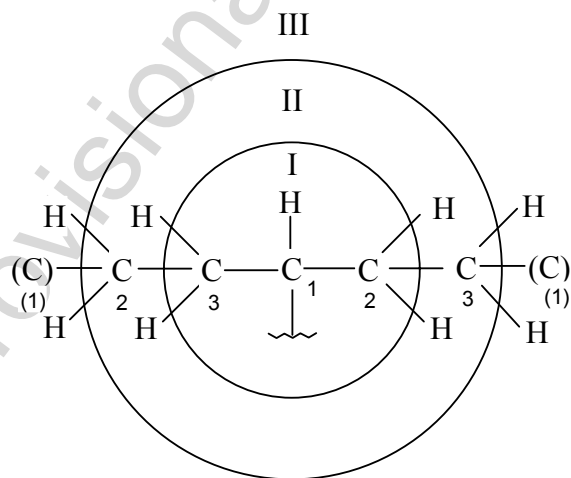
Digraph of cyclopropyl showing phantom atoms in sphere IV

Since real hydrogen atoms have priority over phantom atoms, heptan-4-yl has Sequence Rule precedence over cyclopropyl.

Example 2:



Digraph of pentan-3-yl showing the hydrogen atoms in sphere III

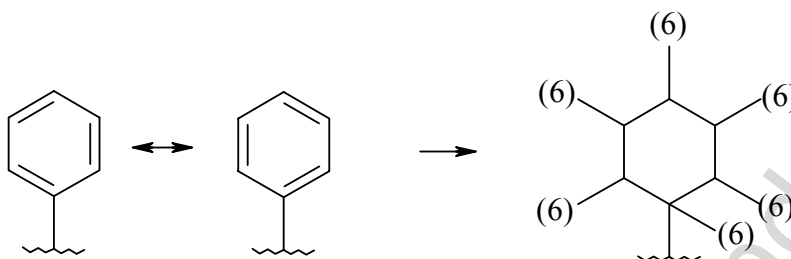


Digraph of cyclopropyl showing duplicate carbon atoms in sphere III

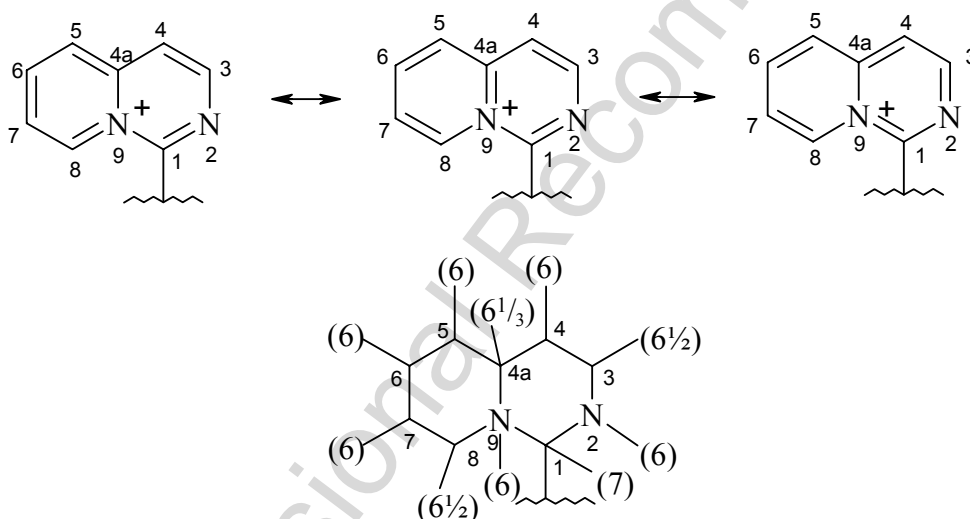
P-91.1.4.2.3 Treatment of mancude rings and ring systems

Mancude rings, i.e., rings or ring systems having the maximum number of noncumulative double bonds, are treated as Kekulé structures. For mancude hydrocarbons, it is immaterial which

Kekulé structure is used because 'splitting' the double bonds give the same result in all cases. The atomic number 6 is always present, as exemplified for a phenyl group:



For mancude heterocycles, each duplicate atom is given an atomic number that is the mean of what it would have if the double bonds were located at each of the possible positions. A complete case is illustrated.

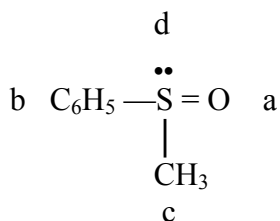


Explanation: C-1 is doubly bonded to one or the other of their nitrogen atoms and never to carbon, so its added duplicate atom has an atomic number '7' (that of nitrogen). C-3 is doubly bonded either to C-4 (atomic number 6) and to N-2 (atomic number 7); so its added duplicate atom has an atomic number of '6^{1/2}'; as it is for C-8. But C-4a may be doubly bonded to C-4, C-5 and N-9; so its added duplicate atom has an atomic number of '6^{1/3}'.

P-91.1.4.2.4 Treatment of tetrahedral systems having a pair of electrons

A lone pair of electrons on an atom such as nitrogen or sulfur has the fictitious atomic number of zero. It is thus ranked lower than a hydrogen atom.

Example:

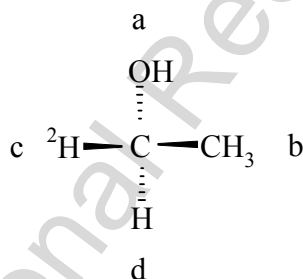


Explanation: The ranking order 'a' > 'b' > 'c' > 'd' is O > -C₆H₅ > -CH₃ > lone pair of electrons (atomic number = zero). The 'double bond' S=O is not duplicated; it is part of the tetrahedral structure that includes the nonbonded electron pair.

P-91.1.5 Sequence Rule 2

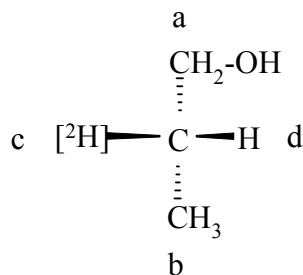
When isotopes are present in a chiral center, Sequence Rule 1 is first applied ignoring isotopic differences between otherwise identical atoms or groups; no decision can be reached. Isotopes are then taken into consideration; they are arranged in decreasing order of their atomic mass, i.e. ³H > ²H > ¹H (or H).

Example 1:



The ranking order, 'a' > 'b' > 'c' > 'd', after application of Sequence Rule 1 followed by Sequence rule 2, is O > C > ²H > H

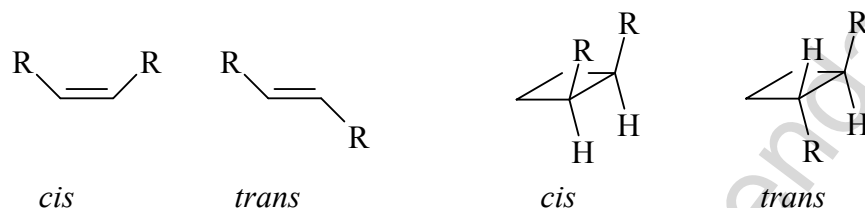
Example 2:



The ranking order 'a' > 'b' > 'c' > 'd', after application of Sequence Rules 1 followed by Sequence Rule 2, is CH₂-OH > CH₃ < [²H] > H

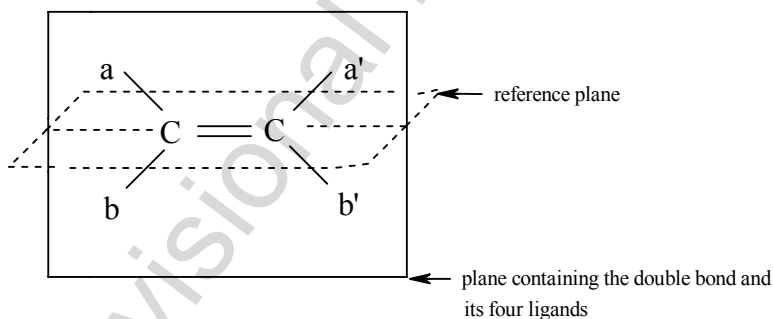
P-91.2 *cis/trans*-Isomers

cis/trans-Stereoisomerism is the relationship between isomers which differ in the position of atoms or groups relative to a reference plane: in the *cis*-isomer the atoms or groups are on the same side of the reference plane, in the *trans*-isomer they are on opposite sides. This type of isomerism is encountered in double bonds and in cycloalkanes and their hetero analogues.

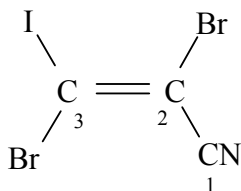


P-91.2.1 ‘*E*’ and ‘*Z*’ descriptors.

The descriptors ‘*E*’ and ‘*Z*’ are used to describe *cis/trans*-isomers at double bonds. The sequence rule atom or group having precedence attached to one of a doubly bonded pair of atoms are compared with the sequence rule atom or group having precedence attached to the other atom; if the atoms or groups having precedence are on the same side of the reference plane, the italic capital letter ‘*Z*’ is used as a stereodescriptor; if the atoms or groups having precedence are on opposite sides, the italic capital letter ‘*E*’ is used. These stereodescriptors have been coined from German, ‘*Z*’ is derived from ‘zusammen’ (together) and ‘*E*’ from ‘entgegen’ (opposite).



Example:



(*Z*)-2,3-dibromo-3-iodoprop-2-enitrile (PIN)

In this compound, application of Sequence Rule 1 described in P-91.1.1.2 gives precedence to I over Br in position 3; similarly, in position 2, Br precedes the C of the CN group. Thus the configuration of the double bond is ‘*Z*’, the atoms I in position 3 and Br in position 2 being compared

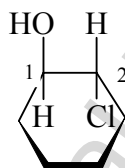
P-91.2.2 *cis/trans*-Isomerism in rings

The stereodescriptors '*cis*' and '*trans*' are used to show the relationship (relative configuration) between two atoms or groups attached to separate atoms that are contained in a ring. The two atoms or groups are said to be located '*cis*' to each other if they lie on the same side of a pseudo plane. If they are on opposite sides, their relative position is described as '*trans*'. The pseudo plane is the mean plane of the ring(s) (the ring being in a conformation, real or assumed, without reentrant angles at the two substituted atoms)

The structures below look like *cis/trans*-isomers, but are actually different conformations of the same *cis*-stereoisomer. In the conformation on the left hand side, the stereogenic center at C-1 is located on a reentrant angle.



Example:



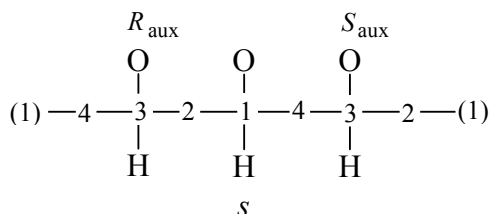
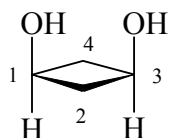
(1*R*,2*R*)-2-chlorocyclohexan-1-ol (absolute configuration) (PIN)
trans-2-chlorocyclohexan-1-ol (relative configuration)

In this example, the compound is chiral and the hydroxy group and the Cl atom are *trans*. The absolute configuration is expressed by the stereodescriptors '*R*' and '*S*' (see P-92.1.1). The relative configuration may be described by using the stereodescriptor '*trans*'; in this case the compound may be the isomer shown or its enantiomer.

P-91.3 Auxiliary stereodescriptors

Auxiliary stereodescriptors have been recommended by Prelog and Helmchen (Section 6.2.1, ref. 32) to permit the assignment of stereodescriptors to stereogenic units that could not be described by using the recommended methodology for determining '*R*' and '*S*' configuration (see P-92.1.1.2). These descriptors are temporary descriptors that do not appear in the final stereodescriptor. It is recommended that the subscript 'aux' be added in digraphs to clearly indicate their temporary status and function.

Example:



(1*s*,3*s*)-cyclobutane-1,3-diol (PIN)
cis-cyclobutane-1,3-diol (see P-91.2)

Explanation: In order to specify the configuration of the achiral cyclic diol, the configuration of the pseudoasymmetric centers at C-1 and C-3 cannot be specified directly. In the digraph of the cyclic system the configuration at C-3 can be specified as '*R*' in the left branch, and as '*S*' in the right branch, thus permitting the use of Sequence Rule 5, '*R*' precedes '*S*', to determine the configuration '*s*' at C-1; by the same method, the configuration '*s*' is determined for C-3. For use of auxiliary descriptors, see P-92.1.1.2, P-92.1.4, P-92.1.6.2.1, and examples in P-93.

P-92 Definition and use of configurational stereodescriptors

P-92.0 Introduction

P-92.1 CIP Stereodescriptors

P-92.2 Non-CIP stereodescriptors

P-92.0 Introduction

The steric structure of a compound is denoted by an affix or affixes to the name that does not prescribe the configuration. Such affixes do not change the name and the numbering of the compound, except in certain cases where stereochemical relations are used to decide between alternative names and numbering (see for example P-92.5.4 and P-92.7.3).

The CIP stereodescriptors are described in this section, with the methodology used to generate them. Two or three simple examples are given. In Section 93, examples are described and the use of non-CIP stereodescriptors are discussed.

P-92.1.1 Absolute configuration. Stereodescriptors '*R*' and '*S*'

P-92.1.2 Relative configuration. Stereodescriptors '*rel*', '*R**', and '*S**'

P-92.1.3 Racemates and meso compounds. Stereodescriptors '*rac*', '*RS*', and '*SR*'

P-92.1.4 Pseudo-asymmetric carbon atom. Stereodescriptors '*r*' and '*s*'

- P-92.1.5 Helicity, axial and planar chirality. Stereodescriptors '*M*', '*P*', '*R_a*', '*S_a*', '*R_p*', and '*S_p*'
- P-92.1.6 Pseudo-asymmetric axes. Stereodescriptors '*r_a*', '*s_a*', '*m*', and '*p*'
- P-92.1.7 *cis/trans*-Isomerism. Stereodescriptors '*E*' and '*Z*'
- P-92.1.8 *cis/trans*-Isomerism. '*r*', '*c*', and '*t*' Stereodescriptors
- P-92.1.9 Nontetrahedral configurations. Stereodescriptors '*TPY-3*', '*TS-3*', '*SS-4*', '*TBPY-3*', '*TBPY-4*', '*YBPY-5*', '*TPY-5*', '*OC-6*', '*A*', '*C*'

P-92.1.1 Absolute configuration. Stereodescriptors '*R*' and '*S*'

Chiral compounds in which the absolute configuration is known are described by the stereodescriptors '*R*' and '*S*' assigned by the sequence rule procedure (ref. 30,31,32). For carbon (and other atoms) to which four different atoms or groups are attached in the system, Cabcd may be depicted as follows, where '*a*' > '*b*' > '*c*' > '*d*'.



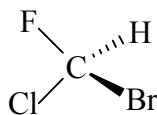
When the model is viewed from the carbon atom along the axis C → '*d*', the path from '*a*' to '*b*' to '*c*' traces a clockwise direction, and the system has the '*R*' configuration. If passing from '*a*' to '*b*' to '*c*' traces an anticlockwise direction, the configuration is '*S*'.

The sequence rules (1) and (2) described in P-91.1.4 and P-91.1.5, respectively, are used to establish the seniority '*a*' > '*b*' > '*c*' > '*d*', when four different atoms or groups are present.

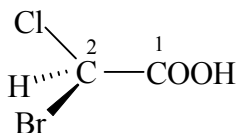
P-92.1.1.1 Name formation

In names, a single stereodescriptor, '*R*' or '*S*', related to the parent structure is cited at the front of the name of the compound, preceded by the appropriate locants and enclosed in parentheses. In preferred IUPAC names, locants that denote chiral centers are repeated before the stereodescriptors '*R*' and '*S*'; when no locant is used in the name of the compound, none is necessary before the stereodescriptor.

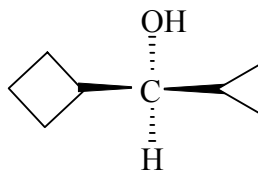
Examples:



(*R*)-bromochlorofluoromethane (PIN)



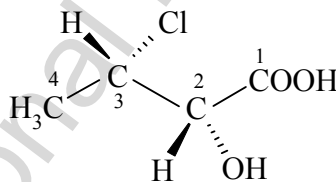
(2*R*)-2-bromo-2-chloroacetic acid (PIN)



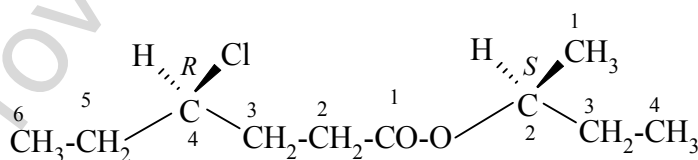
(*S*)-cyclobutyl(cyclopropyl)methanol (PIN)
(α *S*)- α -cyclopropylcyclobutanemethanol

When a molecule contains more than one chiral centre, the above mentioned procedure is applied to each chiral center, and the configuration of the parent structure is expressed as a set of '*R/S*' symbols. In names of compounds, the symbols '*R*' and '*S*', with locants if needed, are written in parentheses and separated by a comma, followed by a hyphen, at the front of the complete name or appropriate substituent.

Examples:



(2*S*,3*S*)-3-chloro-2-hydroxybutanoic acid (PIN)

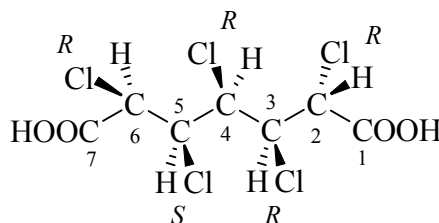


(2*S*)-butan-2-yl (4*R*)-4-chlorohexanoate (PIN)

P-92.1.1.2 Compounds with polychiral centers denoted by '*R*' and '*S*' stereodescriptors

When the use of Sequence Rules 1 and 2 does not permit the determination of the configuration of all chirality centers of a molecule, Sequence Rules 3, 4 and 5 are applied as described by the following examples.

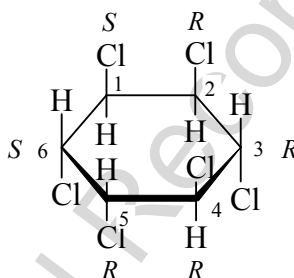
Example 1:



(2*R*,3*R*,4*R*,5*S*,6*R*)-2,3,4,5,6-pentachloroheptanedioic acid (PIN)

In this example, the configuration at C-4 is determined by comparing the two pairs of configurations denoted by 'RR' on one side (C-2 and C-3) and 'SR' on the other side (C-5 and C-6). Since like descriptor pairs precede unlike descriptor pairs [(sequence rule (4))], the order 'a > b > c > d' corresponds to OH > RR > SR > H; thus, the configuration at C-4 is 'R'

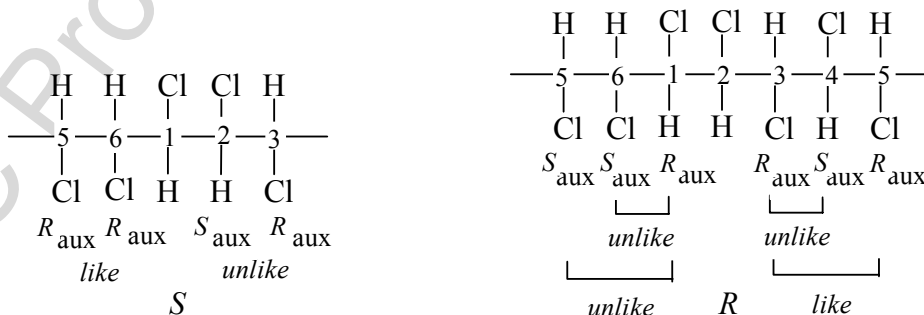
Example 2:



(1*S*,2*R*,3*R*,4*R*,5*R*,6*S*)-1,2,3,4,5,6-hexachlorocyclohexane (PIN)

(not 1*L*-*chiro*-1,2,3,4,5,6-hexachlorocyclohexane; the use of such configurational prefixes is not recommended for preferred IUPAC names)

(not 1,2,3,4,5,6-hexachloro-1,2,3,4,5,6-hexachloro-1*L*-*chiro*-inositol; replacement of -OH groups in inositols by monovalent atoms or groups is limited to three, see I-7.1, ref. 44)

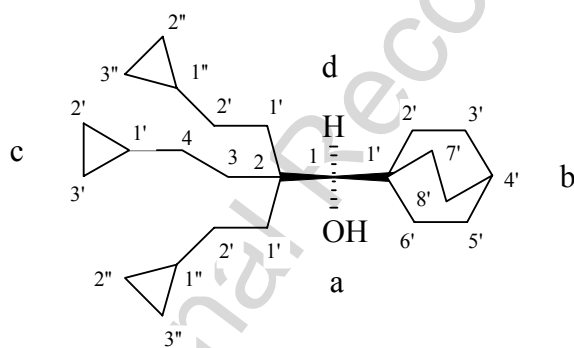


Explanation: *cis/trans*-Pairs of chlorine atoms are present in hexachlorocyclohexanes. For example, in the above compound, starting from C-1, atoms at C-2 and C-3 are in a 'trans' arrangement and atoms at C-5 and

C-6 are in a 'cis' arrangement. This difference is used to determine the chirality at C-1, by applying sequence rule (4) that gives precedence to *like* pairs of descriptors over *unlike* pairs of descriptors. For C-1, the priority order 'a' > 'b' > 'c' > 'd' is Cl > C-6 > C-2 > H; this order generates a 'S' configuration. The determination of the configuration at C-2 is not possible using the pairs C-3/C-4 and C-6/C-5 which are both described as *unlike* pairs of descriptors. A difference, however, is found when the pairs C-2/C-4 and C-6/C-4 are determined and compared: C-2 and C-4 are described as *like*, C-6 and C-4 are described as *unlike*, leading to the configuration 'R' for C-2. The configuration of the six chirality centers are determined in the same way.

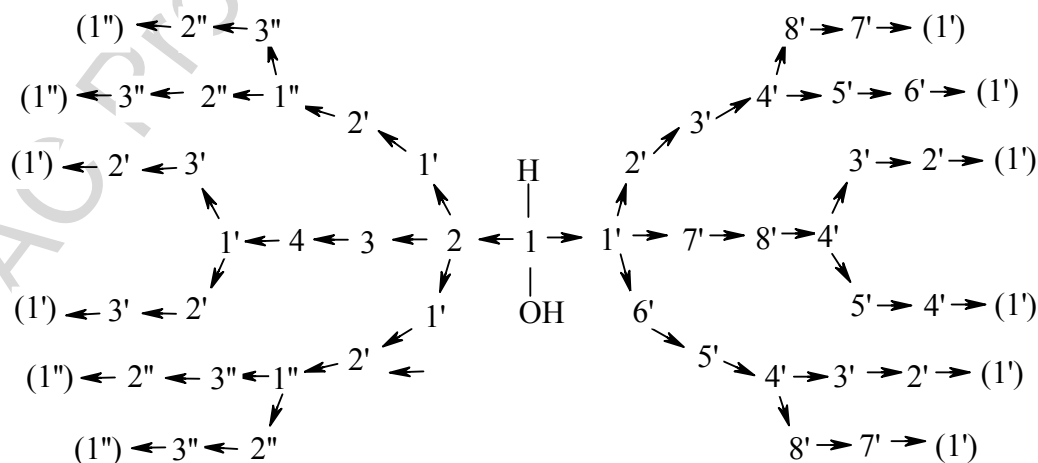
P-92.1.1.3 Sub-rule 1b. Priority due to duplicate atoms

Custer (ref. 35) proposed an amendment to Sequence Rule **1a** to establish the priority between two cyclic substituents which give the same exploratory pathway. The sub-rule is expressed as 'a duplicate atom corresponding to an atom closer to the start of the exploration pathway precedes one further away'. The following example illustrates the sub-rule:



1-(bicyclo[2.2.2]octan-1-yl)-1-[1,5-dicyclopropyl-3-(2-cyclopropylethyl)]pentan-3-yl]methan-1-ol (PIN)

(numbering shown corresponds to the construction of digraph below)

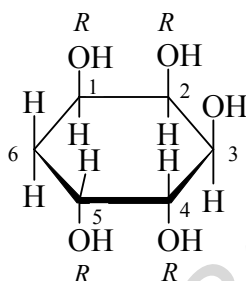


Explanation: The duplicate atoms on the right correspond to the carbon at the first level (C-1 of the bicycle[2.2.2]octan-1-yl) whereas those on the left correspond to atoms at the fourth level (C-1 of the cyclopropyl groups). As nearer duplicate atoms take precedence, the substituent on the right is assigned the priority 'b' and the other the priority 'c'. The first level of the exploration, sphere I, leads to the ranking O > H.

P-92.1.1.4 Nonstereogenic centers

In chiral compounds some centers may be nonstereogenic. No stereodescriptors are assigned to these centers.

Example:

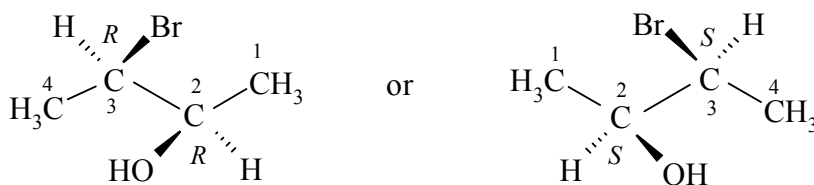


(1*R*,2*R*,4*R*,5*R*)-cyclohexane-1,2,3,4,5-pentol (PIN)
(the exchange of the hydrogen atom and the -OH group
in position 3 generates the same enantiomer)
(not 6-deoxy-*allo*-inositol, see P-104.2.2)

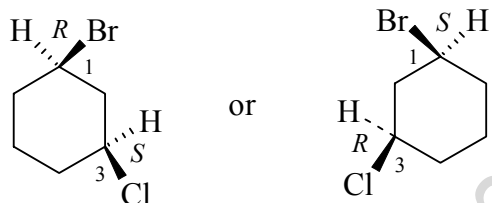
P-92.1.2 Relative configuration. The stereodescriptors '*rel*', and '*R**' and '*S**'

Chirality centers, of which the relative but not the absolute configuration is known, may be labeled '*rel*' (for relative) (not to be confused with *r* for reference, see P-92.6.4) followed, in parentheses, by the stereodescriptors '*R*' and '*S*', each preceded by the appropriate locant (see E-4.10, ref. 1). The stereodescriptors may also be '*R**' and '*S**' (spoken R star, S star), preceded when necessary by appropriate locants (see E-4.10, ref. 1). These stereodescriptors '*R*', '*R**', '*S*', '*S**' are assigned by the sequence rule procedure, arbitrarily assuming that the stereogenic center first cited (which usually has the lowest locant) has the chirality descriptor '*R*' or '*R**'. The method using the stereodescriptor '*rel*' is preferred when preferred IUPAC names are to be specified. It is important to note that the descriptor '*rel*' applies to all stereogenic centers when more than one such center is present in a compound.

Examples:



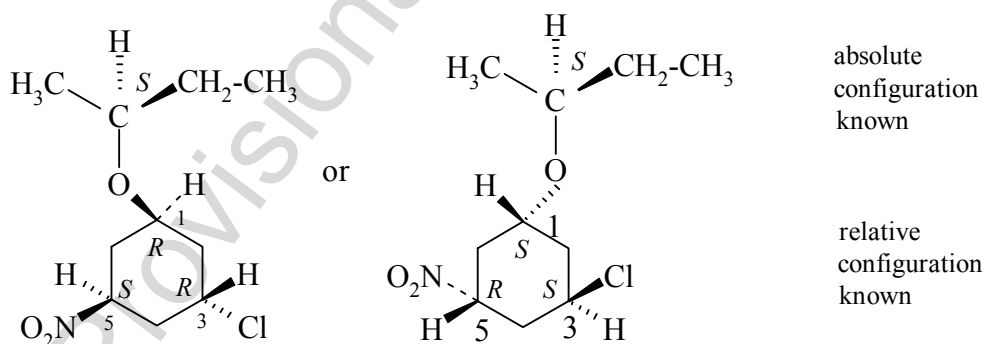
rel-(2*R*,3*R*)-3-bromobutan-2-ol (PIN)
(2*R**,3*R**)-3-bromobutan-2-ol



rel-(1*R*,3*S*)-1-bromo-3-chlorocyclohexane (PIN)
(1*R**,3*S**)-1-bromo-3-chlorocyclohexane

P-92.4.2 In compounds containing chirality centers with known absolute configurations and a sterically unrelated set of chiral centers with known relative configuration, the '*R*' and '*S*' descriptors must be used to designate the latter (see E-4.10, ref. 1). The prefix '*rel*' cannot be used as it does apply to the entire molecule.

Example:



(1*R**,3*R**,5*S**)-1-[(2*S*)-butan-2-yloxy]-3-chloro-5-nitrocyclohexane (PIN)

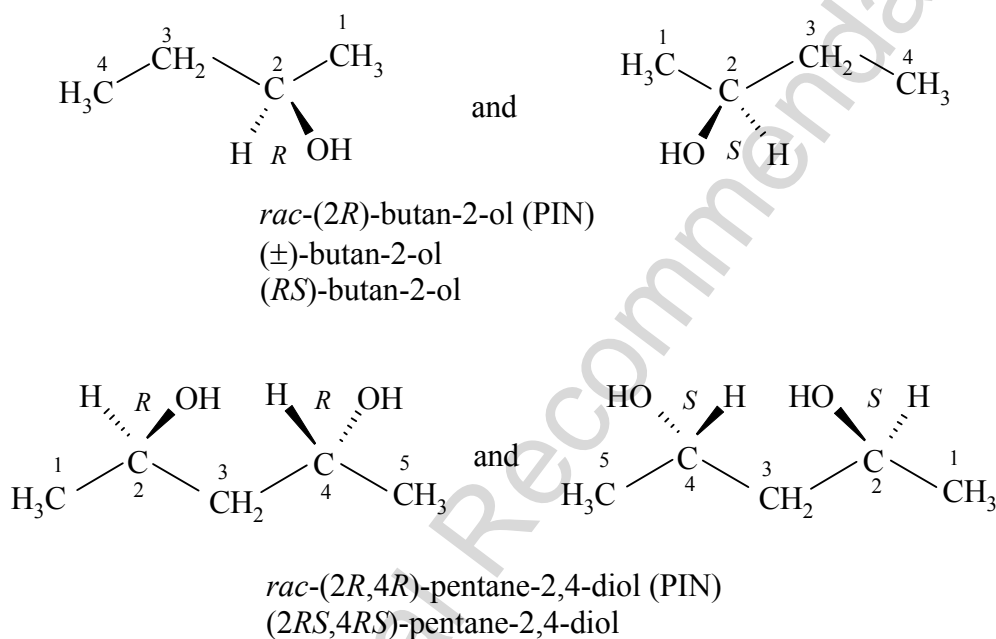
P-92.1.3 Racemates and meso compounds. The stereodescriptors '*rac*', '*RS*' and '*SR*'

A racemate is an equimolar mixture of a pair of enantiomers. It does not exhibit optical activity in solution.

Different methods are used to characterize the name of a racemate or of a racemic compound. The prefixes '(±)' or '*rac*' (or '*racem*') or the stereodescriptors '*RS*' or '*SR*' may all be used in general nomenclature. The descriptor '*rac*' is used in preferred IUPAC names.

Racemates containing a single stereogenic center are labeled 'RS'. If there is more than one center, the first (corresponding to the lowest locant assigned to stereodescriptors) is labeled 'RS' and the others are 'RS' or 'SR' according to whether they are 'R' or 'S' when the first is 'R'. The method used in preferred IUPAC names is to describe the descriptor having the lowest locant by 'R' and the others accordingly; the prefix 'rac' is placed in front of the set of descriptors and locants.

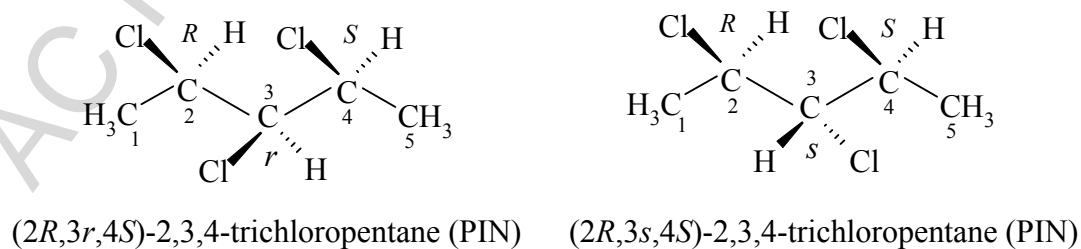
Examples:



P-92.1.4 Pseudo-asymmetric centers. The stereodescriptors 'r' and 's'

P-92.1.4.1 An atom that is a tetrahedrally substituted atom and bonded to four different entities, two and only two of which have opposite configurations, is stereogenic. The descriptors 'r' and 's' are used to denote such centers; they are assigned in accordance with Sequence Rule 5, taking into consideration that 'R' has precedence over 'S' in the order of priority. The stereodescriptors 'r' and 's' are reflexion invariant (see 2.5.3, ref. 30).

Example 1:



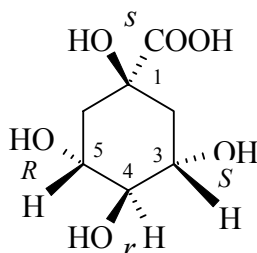
Guide to name construction:

Step 1: configuration 'R' or 'S' is assigned to stereogenic centers C-2 and C-4;

Step 2: configuration at C-3 is assigned by applying sequence rule 5, '*R*' precedes '*S*'.

In the above set of compounds, the exchange of the Cl and H atoms at C-3 of the compound described on the left generates the compound on the right, and '*3r*' becomes '*3s*'

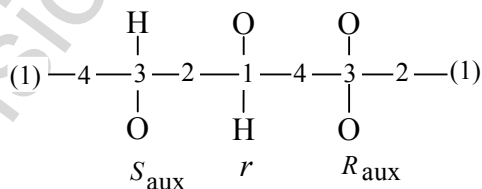
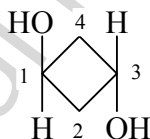
Example 2:



(1*s*,3*S*,4*r*,5*R*)-1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid (PIN)

P-92.1.4.2 The use of auxiliary stereodescriptors '*R*_{aux}' and '*S*_{aux}' leads to the specification of the configuration of pseudoasymmetric centers. Achiral cyclic diols, for example, are named by this method.

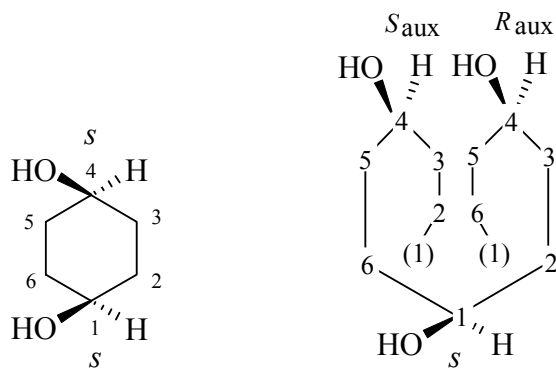
Example 1:



(1*r*,3*r*)-cyclobutane-1,3-diol (PIN)

Explanation: the digraph puts into evidence the opposite configuration at C-3 in the two branches. Sequence rule (5), '*R*' precedes '*S*', generates the stereodescriptor '*r*' for C-1 and, similarly, for C-3.

Example 2:



(1*s*,4*s*)-cyclohexane-1,4-diol (PIN)

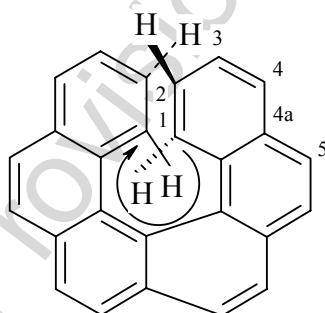
Explanation: the digraph permits to assign the 's' configuration to C-1 (shown in the digraph) and C-4.

P-92.1.5 Helicity, axial and planar chirality. The stereodescriptors '*M*', '*P*', '*R_a*', '*S_a*', '*R_p*' and '*S_p*'

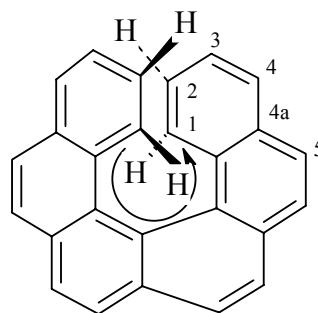
P-92.1.5.1 Helicity: The stereodescriptors '*M*' and '*P*'

Helicity is the chirality of a helical, propeller, or screw-shaped molecular entity (see subsection 2.6, ref. 31). A left-handed helix is described as '*M*' (or minus) and a right-handed helix as '*P*' (or plus), as expressed by the rotation angle θ (see torsion angle, P-94.2).

The chirality of hexahelicenes is denoted by the stereodescriptors '*P*' and '*M*'. When the upper right ring is near the observer, and the upper left ring away from the observer, the path from front to rear along the periphery of the molecule gives a clockwise course denoted by '(+)' or '*P*'. The anticlockwise course is denoted by '(-)' or '*M*'.



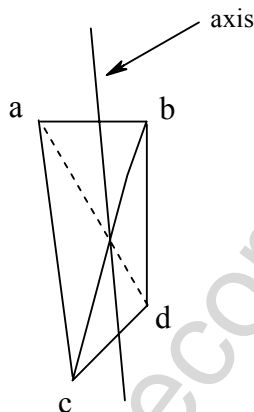
(*P*)-hexahelicene (PIN)



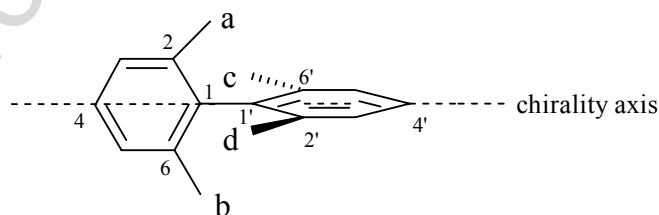
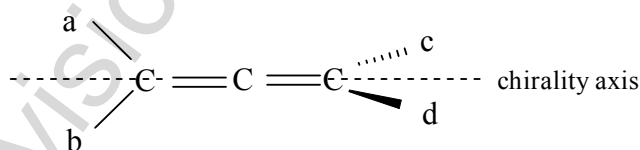
(*M*)-hexahelicene (PIN)

P-92.1.5.2 Axial chirality: The stereodescriptors ' R_a ' or ' P ' and ' S_a ' or ' M '

Structures with axial chirality are regarded as elongated tetrahedra and viewed along the axis; it is immaterial from which side it is viewed (see subsection 2.6, ref. 31). Axial chirality is used to refer to stereoisomerism resulting from the nonplanar arrangement of four groups in pairs about a chirality axis. A chirality axis is the axis about which a set of atoms or groups is held so that it results in a spatial arrangement which is not superposable on its mirror image. For instance, in an allene ' $abC=C=Ccd$ ', the chiral axis is defined by the ' $C=C=C$ ' bonds, and in a 2,2',6,6'-tetrasubstituted biphenyl the atoms 1,1',4,4' lie on the chirality axis.



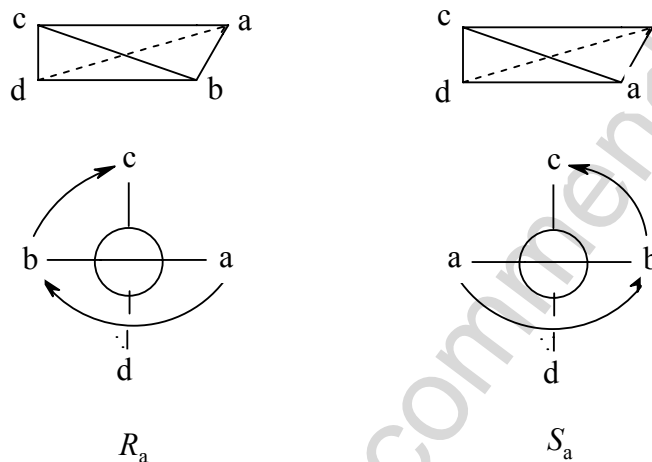
In chiral compounds owing their chirality to a stereogenic center, it is necessary to have four different atoms or groups ('a', 'b', 'c', and 'd'). With an elongated tetrahedron, this requirement is no longer necessary because of reduced symmetry. The only condition is that 'a' be different from 'b' and 'c' be different from 'd'; thus compounds with two pairs of substituents 'a' and 'b' are chiral if 'a' is different than 'b'.



Descriptors ' R_a ' and ' S_a ' and ' M ' and ' P ' are assigned in accordance with two different methods.

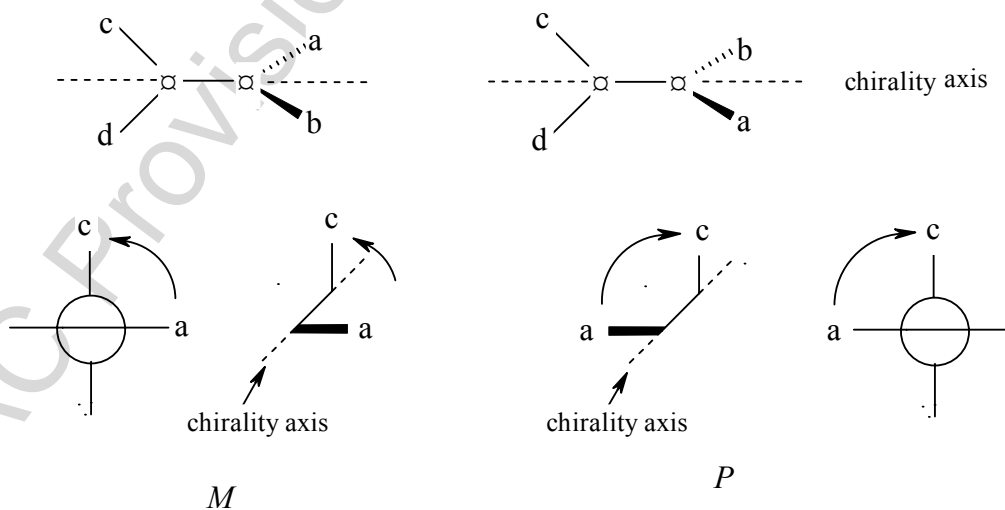
P-92.1.5.3 The descriptors ' R_a ' / ' S_a '

Substituents (atoms or groups) are arranged in the elongated tetrahedral system. Two higher-ranking substituents are chosen, one in each pair, using the sequence rule. For the pairs ' a ' > ' b ' and ' c ' > ' d ', the chirality is described by ' R_a ' if the path going from ' a ' to ' b ' to ' c ' is clockwise, while looking toward ' d '. The symbol is ' S_a ' if this path is anticlockwise.

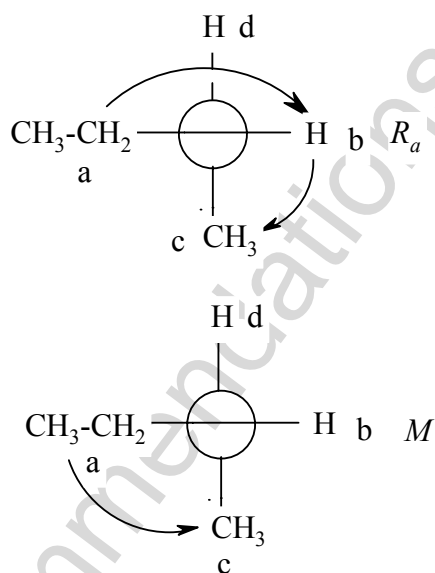
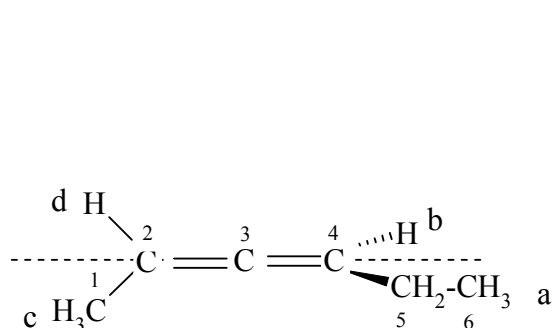


P-92.1.5.4 The descriptors ' M ' and ' P '

Looking along the chirality axis the atoms or groups are arranged in pairs. When proceeding from the nearer atom or group having priority in the pair to the further away atom or group having priority in the pair, the chirality is described by the symbols ' M ' if the path is anticlockwise; the symbol is ' P ' if the path is clockwise. Stereodescriptors ' R_a ' and ' S_a ' are used in preferred IUPAC names.

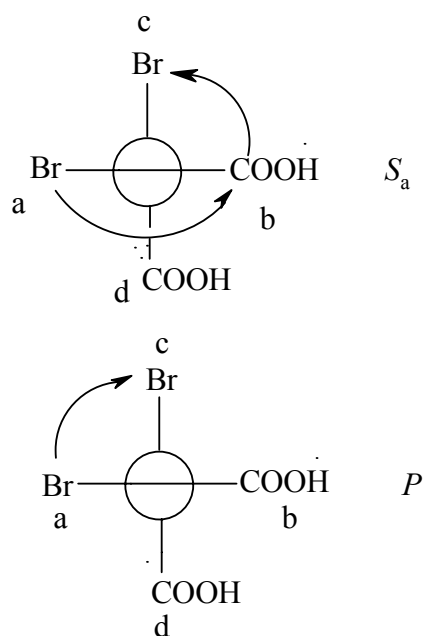
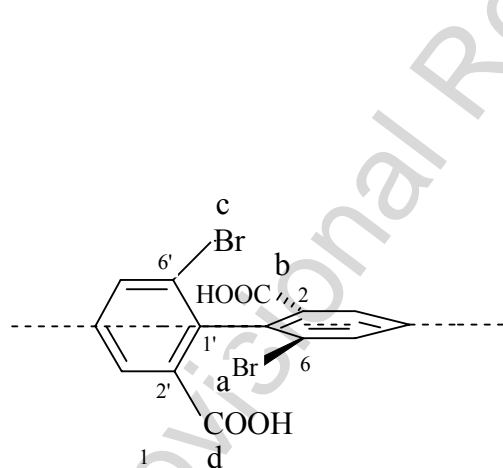


Example 1:



(*R_a*)-hexa-2,3-diene (PIN)
(*M*)-hexa-2,3-diene

Example 2:



(*S_a*)-6,6'-dibromobiphenyl-2,2'-dicarboxylic acid (PIN)
(*P*)-6,6'-dibromobiphenyl-2,2'-dicarboxylic acid

P-92.1.5.4 The stereodescriptors '*R_p*' and '*S_p*'

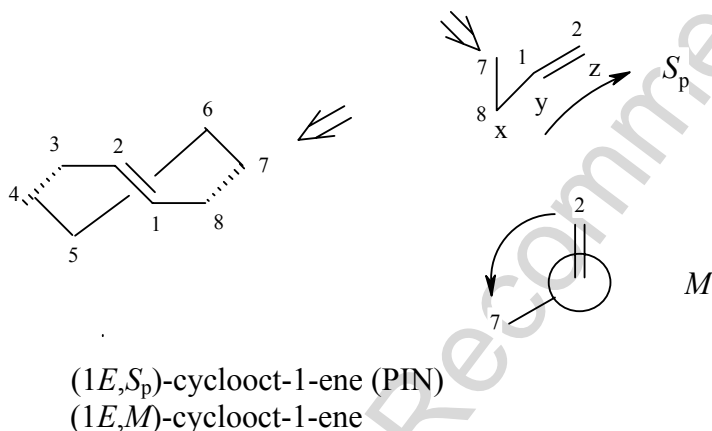
Planar chirality is a term used to refer to stereoisomerism resulting from the arrangement of out of plane groups with respect to a plane (chirality plane) (see subsection 2.6, ref. 31). It is exemplified by the atropisomerism of (*E*)-cyclooctene (chiral plane = double bond and attached

atoms) or a monosubstituted cyclophane (chiral plane = substituted ring). The configuration is specified by the stereodescriptors ' R_p ' and ' S_p ' (or ' P ' and ' M ').

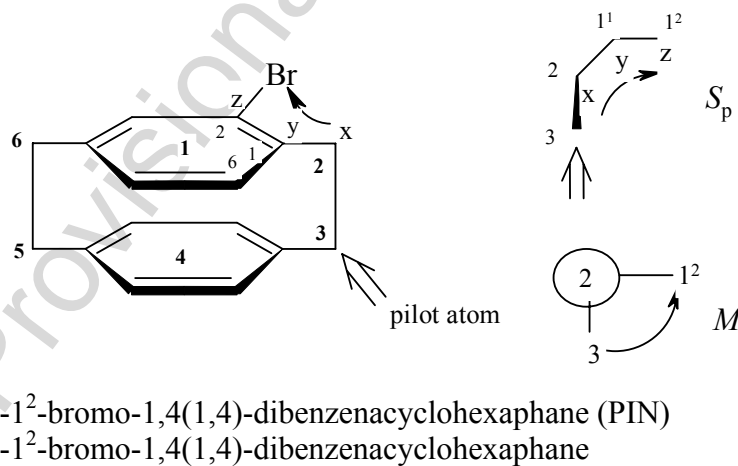
Three atoms are used to define the direction of rotation, clockwise or anticlockwise ('x', 'y', and 'z'). A pilot atom, next to 'x', is chosen at an observation site (\Rightarrow) to determine the direction of rotation. A clockwise path is described by the stereodescriptors ' P ' (helicity descriptor) or ' R_p ' (CIP descriptor). The opposite path is described by ' M ' (helicity descriptor) or ' S_p ' (CIP descriptor).

Stereodescriptors ' R_p ' and ' S_p ' are used in preferred IUPAC names.

Example 1:



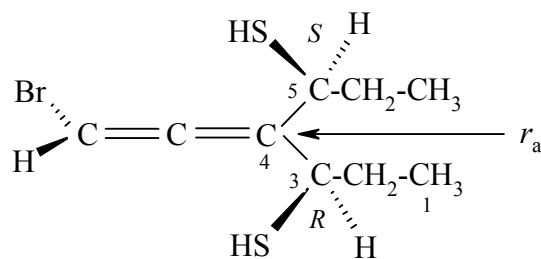
Example 2:



P-92.1.6 Pseudoasymmetric axes. The stereodescriptors ' r_a ' and ' s_a ', ' m ' and ' p '

The descriptors ' r_a ' or ' m ', and ' s_a ' or ' p ', are used to denote a stereogenic unit that is exhibiting axial chirality due to the presence of two enantiomeric substituents groups; they are assigned in accordance with the sequence rule 5, taking into consideration that ' R ' has precedence over ' S ' in the order of priority. The stereodescriptors ' r_a ', ' s_a ', ' m ' and ' p ' are reflexion invariant (see 2.5.3, ref. 30).

Example:



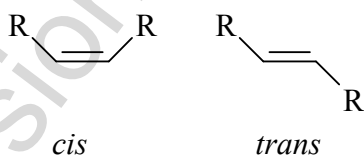
(3*R*,4*r_a*,5*S*)-4-(2-bromoethenylidene)heptane-3,5-dithiol (PIN)
 (3*R*,4*m*,5*S*)-4-(2-bromoethenylidene)heptane-3,5-dithiol
 (3*R*,5*S*)-4-[(*m*)-(2-bromoethenylidene)]heptane-3,5-dithiol
 (3*R*,5*S*)-4-[(*r_a*)-(2-bromoethenylidene)]heptane-3,5-dithiol

P-92.1.7 Stereodescriptors '*E*', '*Z*', *cis/trans*-isomerism.

P-92.1.7.1 Definitions

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 or are contained in a ring. The two atoms or groups are said to be located '*cis*' to each other if they lie on the same side of a plane. If they are on opposite sides, their relative position is described as '*trans*'. The appropriate reference plane of a double bond is perpendicular to that of the relevant σ -bonds and passes through the double bond.

Examples:



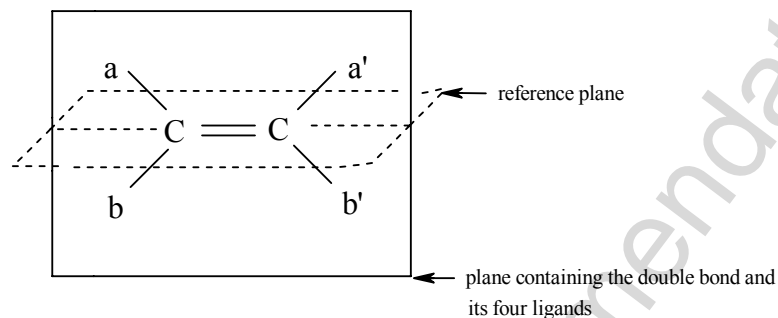
The terms '*cis*' and '*trans*' are also used as stereodescriptors to describe the configuration of a compound (see P-92.2.1.1).

P-92.1.7.2 *cis/trans*-Isomerism. The stereodescriptors '*E*' and '*Z*'

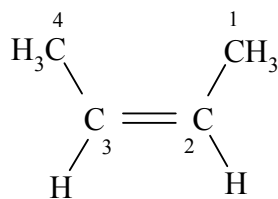
The '*E*' and '*Z*' descriptors are assigned as follows to describe the configuration of a double bond. The sequence rule atom or group having precedence attached to one of a doubly bonded pair of atoms is compared with the sequence rule atom or group having precedence attached to the other atom; if the atoms or groups having precedence are on the same side of the reference plane, the italic capital letter '*Z*' is used as a stereodescriptor; if the atoms or groups having precedence are on opposite sides, the italic capital letter '*E*' is used. These stereodescriptors have been coined from the German language, '*Z*' is derived from '*zusammen*' (together) and '*E*' from '*entgegen*' (opposite). Placed in parentheses, they are cited at the front of a name. When the position of the double bond is denoted by a locant, this locant is also placed at the front of the

stereodescriptor. When no locant is used to describe the double bond, no locant is placed at the front of the stereodescriptor.

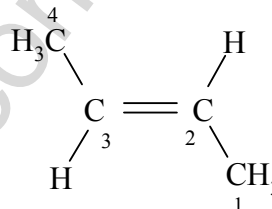
The '*E*' and '*Z*' descriptors are preferred to '*cis*' and '*trans*' in IUPAC names (see P-92.2.1.1)



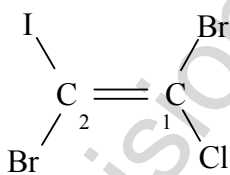
Examples:



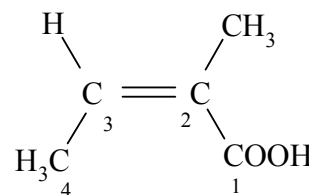
(*Z*)-but-2-ene (PIN)



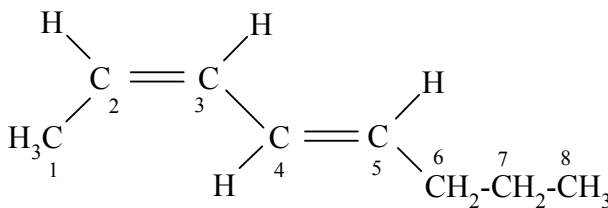
(*E*)-but-2-ene (PIN)



(*Z*)-1,2-dibromo-1-chloro-2-iodoethene (PIN)



(*Z*)-2-methylbut-2-enoic acid (PIN)

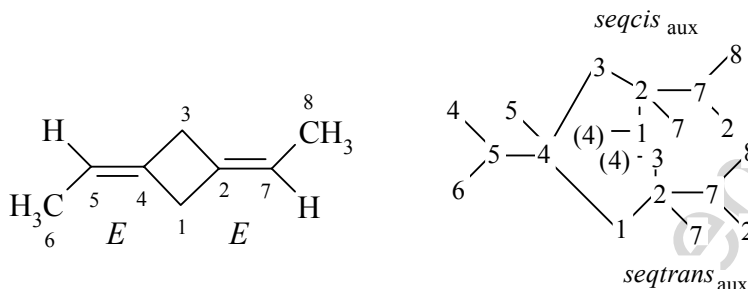


(*2Z,4E*)-octa-2,4-diene (PIN)

P-92.1.7.2.1 Use of auxiliary stereodescriptors

The use of auxiliary stereodescriptors leads to the assignment of 'Z' and 'E' stereodescriptors to sets of double bonds undistinguishable by direct application of sequence rule (1).

Example:



2,4-di[(*E*)-ethylidene]cyclobutane (PIN)
(*E*)-2,4-diethylidenecyclobutane

Explanation: In the digraph, when considering the two branches at C-4, one contains a *seqcis*_{aux} double bond (path 3-2-7-8), the other branch contains a *seqtrans*_{aux} double bond (path 1-2-7-8). As *seqcis*_{aux} precedes *seqtrans*_{aux}, C-3 precedes C-1, the double bond at C-4 is *seqtrans*, or *E* that is the stereodescriptor used in the name of the compound. Similarly, the double bond at C-2 is *E*.

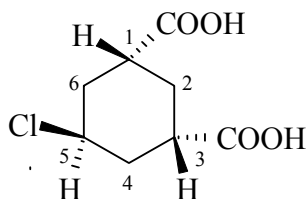
In names, the stereodescriptor *E* is used to describe each double bond; it is placed before the name of the substituent group having this configuration. This method is preferred to the use of the stereodescriptor *E*, to describe the whole molecule, considered as an extended double bond.

P-92.1.8 *cis/trans*-Isomerism. The stereodescriptors '*r*', '*c*', and '*t*'

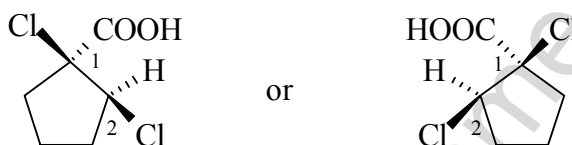
When one substituent and one hydrogen atom are attached to each of more than two positions of a monocycle, or when two different substituents are attached at the same position of a monocycle, then the lowest-numbered substituent named as a suffix is selected as a reference group. If none of the substituents is named as a suffix, then that substituent of the pair of substituents having the lowest locant, and which has precedence in the sequence rule, is chosen as the reference group; it is denoted as '*r*'. The relationship of substituents, relative to the reference group, is cited as '*c*' (for *cis*) or '*t*' (for *trans*), as appropriate. When alternative numberings of a ring are possible, that numbering is chosen which gives a '*cis*' attachment at the first point of difference.

The notation consisting of adding '*r*' (for reference substituent) followed by a hyphen and the locant of the lowest numbered of these substituents and '*c*' (for *cis*) and '*t*' (for *trans*) (as appropriate) followed by a hyphen and the locant for another substituent, as used in Section E of the 1979 edition of Nomenclature of Organic Chemistry (ref. 1) and in the Guide to IUPAC Nomenclature of Organic Compounds (ref. 2), is no longer recommended.

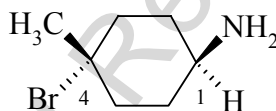
Examples:



5*t*-chlorocyclohexane-1*r*,3*c*-dicarboxylic acid
(1*R*,3*S*,5*r*)-5-chlorocyclohexane-1,3-dicarboxylic acid (PIN)
(not *t*-5-chlorocyclohexane-*r*-1,*c*-3-dicarboxylic acid)



1,2-dichlorocyclopentane-1*r*-carboxylic acid
rel-(1*S*,2*S*)-1,2-dichlorocyclopentane-1-carboxylic acid (PIN)
(not 1,*t*-2-dichlorocyclopentane-*r*-1-carboxylic acid)



4*t*-bromo-4-methylcyclohexan-1*r*-amine
(1*s*,4*s*)-4-bromo-4-methylcyclohexan-1-amine (PIN)

P-92.1.9 P-92.1.7 Nontetrahedral configurations. Stereodescriptors ‘*TPY*-3’, ‘*TS*-3’, ‘*SS*-4’, ‘*TBPY*-3’, ‘*TBPY*-4’, ‘*TBPY*-5’, ‘*TPY*-5’, ‘*OC*-6, *A,C*’

P-92.1.9.1 When an atom is attached to 3, 4, 5, or 6 atoms or groups a number of geometrical configurations are possible. In general there will be some distortion from the idealized geometry of the regular solid due to differences between the atoms involved. Thus with five attached ligands they may be arranged as a trigonal bipyramid or square pyramid and with six as an octahedron. The notation described below for these systems is based on inorganic coordination nomenclature (ref. 14, Red Book I). Details of the geometry of systems with a coordination greater than six will be found in reference 14.

The stereodescriptors are composed of three parts.

- (1) A symbol indicating overall geometry called a ‘polyhedral symbol’;
- (2) A symbol called a ‘configuration index’;
- (3) A symbol indicating the chirality associated with the central atom called a ‘chirality symbol’.

The three parts are enclosed in parentheses and separated from each other by hyphens to form the descriptor, which is cited in front of the name separated by a hyphen.

P-92.1.9.2 Polyhedral symbol

The polyhedral symbol takes the form of an abbreviation of the name of the closest idealized geometry (italic upper case letters) and a number indicating how many atoms or groups (ligands in coordination nomenclature) are attached (see Rule I-10.5.2, ref. 14). Table 8.1 describes the most frequently encountered polyhedrons related to structures of organic compounds. The configuration of molecules containing a tetrahedral center has been discussed in Sections P-91 and P-92.1 to P-92.6

Table 8.1 List of polyhedral symbols

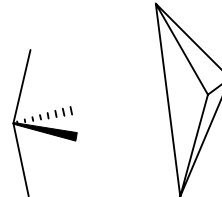
Idealized geometry	Attached atoms or groups	Polyhedral symbol
trigonal pyramid	3	<i>TPY-3</i>
T-shape	3	<i>TS-3</i> (ref. 37)
see-saw	4	<i>SS-4</i> (ref. 37)
trigonal bipyramid	5	<i>TBPY-5</i>
square pyramid	5	<i>SPY-5</i>
octahedron	6	<i>OC-6</i>



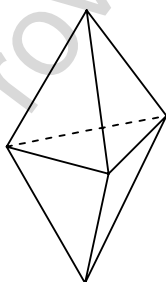
TPY-3



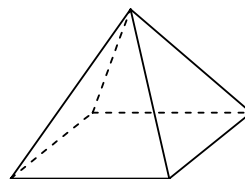
TS-3



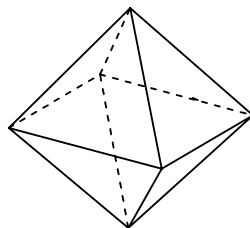
SS-4



TBPY-5



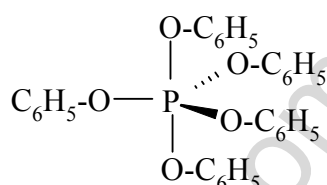
SPY-5



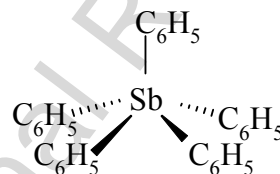
OC-6

The abbreviation and number are separated by a hyphen and enclosed in parentheses in front of the name of the compound, if no further information is required.

Examples:



(*TBPY-5*)-pentaphenoxy- λ^5 -phosphane

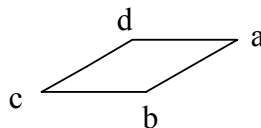


(*SPY-5*)-pentaphenyl- λ^5 -stibane

P-92.1.9.3 Configuration index and priority rules

The configuration index is a series of numbers to identify where each atom or group is located (see Rule I-10-5.3, ref. 14). It is based on the CIP priority order of the atoms attached. The atom or atoms with highest priority are given priority number one (**1**); the next priority number two (**2**), and so on. In addition to the standard CIP sequence rules 1 and 2, two additional rules are needed:

- (a) *trans*-maximum difference of priority (see I-10.5.3.3, ref. 14). Between atoms with the same priority number, high priority is assigned to the atom which is *trans* (opposite) to the atom having the lowest priority number; in the following planar structure, 'a' and 'c' (and 'b' and 'd') are '*trans*':

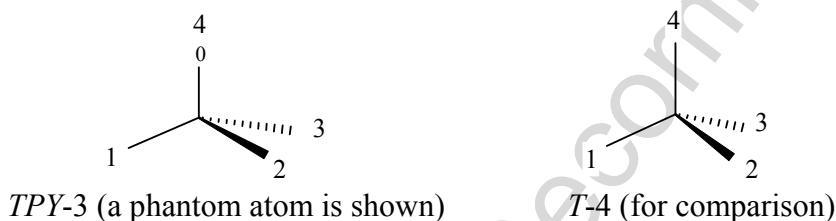


- (b) Priming convention (see I-10-6.3.2, ref. 14). When there are two (or three) identical rings present, the priority numbers of one of them is primed (and the third double primed).
- (c) Unprimed priority numbers are preferred to primed. In coordination nomenclature rings are di- and polydentates ligands.

Each idealized geometry has its own rules for assignment of the configuration index.

P-92.1.9.3.1 Trigonal pyramid

The configuration of molecules containing a trigonal pyramidal center (*TPY-3*) is described in a similar way to that of tetrahedral centers (*T-4*) described above in P-91 and P-92.1 through P-92.6. The tetrahedral configuration is achieved by adding a phantom atom (0) to the central atom perpendicular to the base of the pyramid. No configuration index is used with the '*TPY-3*' symbol. Priority numbers are '1' > '2' > '3' > '4'.



Sulfoxides, when the central atom and substituents only are considered, constitutes a trigonal system. The polyhedral symbol is placed at the front of the name.

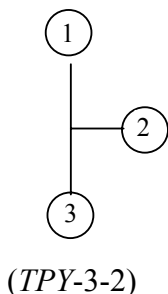
Example:



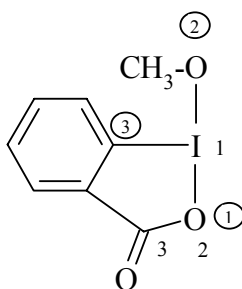
(*T-4*)-methylsulfinylmethane (PIN)
(*TPY-3*)-methylsulfinylmethane

P-92.1.9.3.2 T-shape systems

The configuration index of the T-shape configuration follows the polyhedral symbol and consist of a single digit, the priority number of the atom or substituent group on the stem of the 'T' (as opposed to the cross piece of the 'T').



Example:

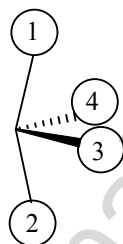


(*TPY-3-3*)-1-methoxy-1 λ^3 ,2-benziodoxol-3(1*H*)-one

(*TBPY-3*)- 1-methoxy-1 λ^3 ,2-benziodoxol-3(1*H*)-one (PIN, see P-92.1.7.3.4.2)

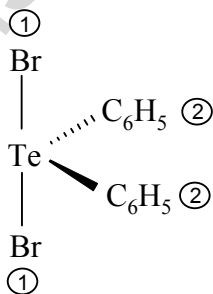
P-92.1.9.3.3 See-saw systems

The configurational index of a see-saw system is composed of the priority number indicating the two atoms or groups separated by the largest angle.



SS-4-12

Example:

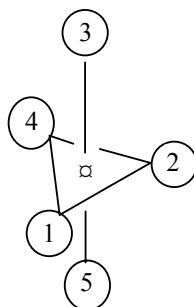


(*SS-4-11*)-dibromodiphenyl- λ^5 -tellurane

(*TBPY-4*-dibromodiphenyl- λ^5 -tellurane (PIN, see P-92.1.7.3.4.2)

P-92.1.9.3.4 Trigonal bipyramid

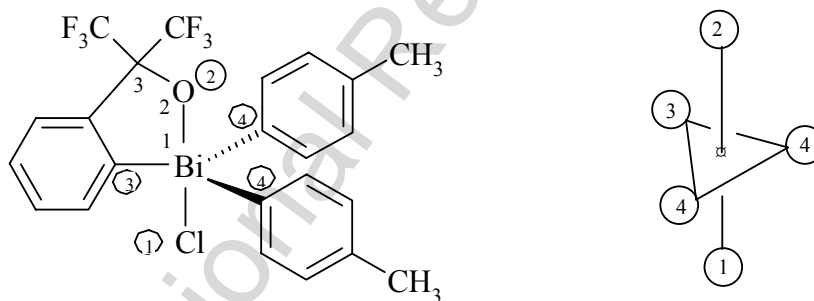
P-92.1.9.3.4.1 The configuration index of a trigonal bipyramid (see Rule I-5.4.4) is composed of the priority number of the two apical atoms (lower number first if different). They represent the reference axis of the system. Priority numbers are: '1' > '2' > '3' > '4' > '5'.



TBPY-5-35

The polyhedral symbol and configuration index, separated by a hyphen, are enclosed in parentheses in front of the name of the compound, if no further information is required.

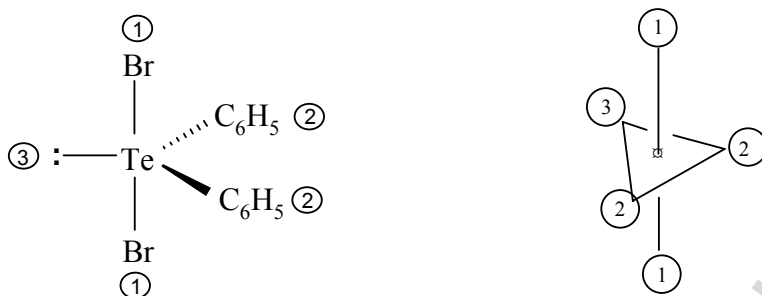
Example:



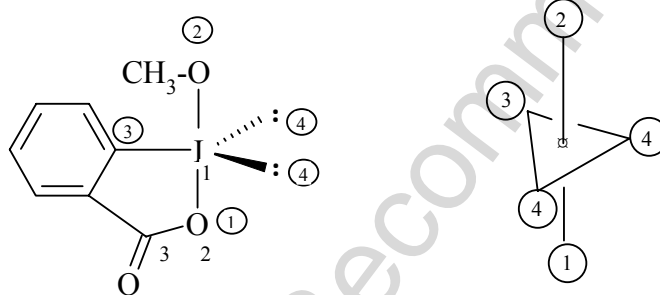
(TBPY-5-12)-1-chloro-1,1-bis(4-methylphenyl)-3,3-bis(trifluoromethyl)-1,3-dihydro-2,1λ⁵-benzoxabismole (PIN)

P-92.1.9.3.4.2 The trigonal bipyramid system can be extended to central atoms substituted by four atoms or groups and one lone pair of electrons, and by three atoms or groups and two lone pairs of electrons; the use of a lone pair of electrons as a component in tetrahedral configuration is discussed in P-91.4.2.4 and illustrated in P-93.1.1.4.5. When one lone pair is present, the polyhedral symbol is *(TBPY-4)*; the symbol is *(TBPY-3)* when two lone pairs of electrons are present. The configuration index is determined in the usual way, taking into account that a lone pair of electrons has the atomic number zero, as indicated in P-91.4.2.4. In preferred IUPAC names, the symbol *(TBPY-4)* is preferred to the see-saw system; similarly the symbol *(TBPY-3)* is preferred to the T-shape system.

Examples:



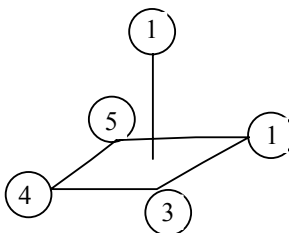
(*TBPY*-4-11)-dibromodiphenyl- λ^5 -tellurane (PIN)
(*SS*-4-11)-dibromodiphenyl- λ^5 -tellurane (see P-92.1.7.3.3)



(*TBPY*-3-12)-1-methoxy-1 λ^3 ,2-benziodoxol-3(1*H*)-one (PIN)
(*TPY*-3-3)-1-methoxy-1 λ^3 ,2-benziodoxol-3(1*H*)-one (see P-92.1.7.3.2)

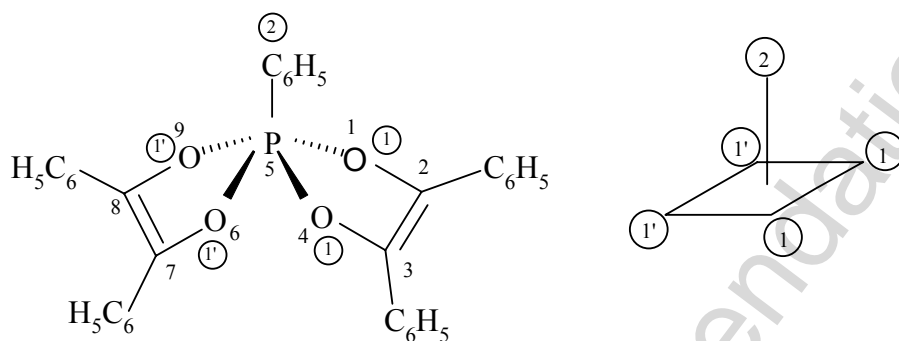
P-92.1.9.3.5 Square pyramid

The configuration index of a square pyramid (see Rule I-10.5.4.3, ref. 14) is given by two numbers. The first is the priority number of the apical atom and the second is the priority number of the atom *trans* (opposite) with reference to the atom having the highest priority (lowest priority number) in the base of the pyramid. If necessary, the rule of the ‘*trans*-maximum difference of priority numbers’ is applied (see Rule I-10.5.3.2, ref. 14). The reference axis corresponds to the bond to the apical ligand. The polyhedral symbol and configuration index, separated by a hyphen, are enclosed in parentheses and cited in front of the name of the compound, if no further information is required. For the ranking order ‘1’ > ‘2’ > ‘3’ > ‘4’ > ‘5’, the following configuration is denoted by the configuration index ‘24’.

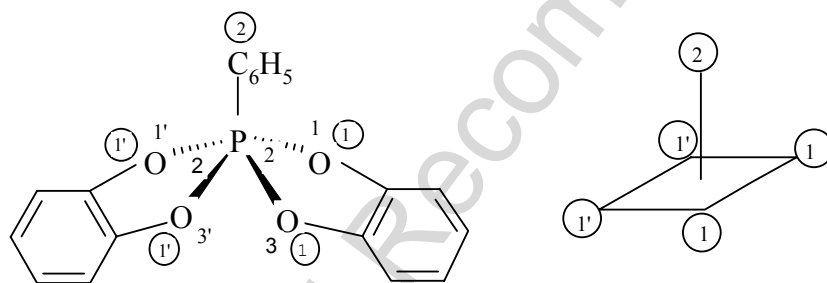


SPY-5-24

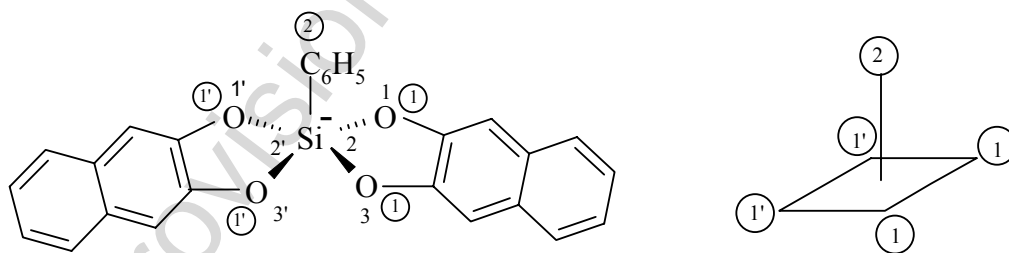
Examples:



(*SPY-5-21'*)-2,3,5,7,8-pentaphenyl-1,4,6,9-tetraoxa-5 λ^5 -phosphaspiro[4.4]nona-2,7-diene (PIN)



(*SPY-5-21'*)-2-phenyl-2 λ^5 ,2'-spirobi[1,3,2-benzodioxaphosphole] (PIN)

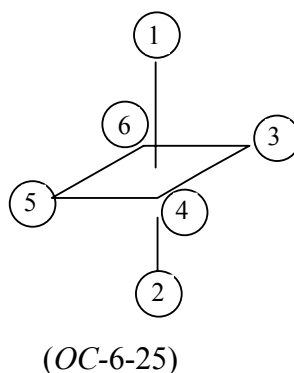


(*SPY-5-21'*)-2-phenyl-2,2'-spirobi[naphtho[2,3-*d*][1,3,2]dioxasilol]-2-uide (PIN)

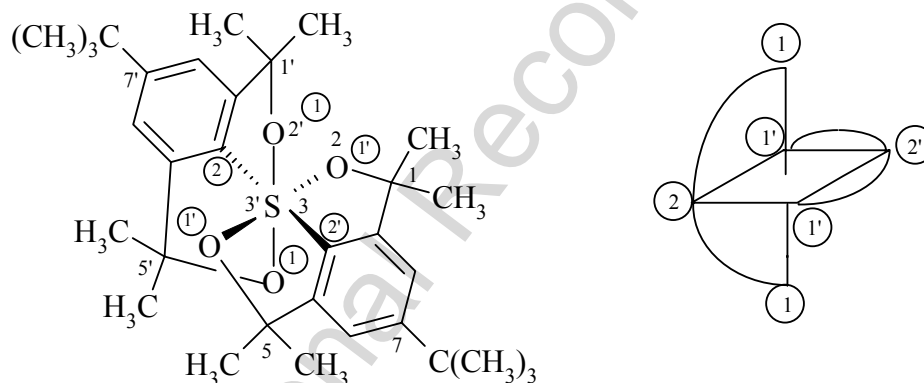
P-92.1.9.3.6 Octahedron

The configuration index of an octahedron (see Rule I-10.5.4.2, ref. 14) is given by two numbers. The first is the priority number of the atom 'trans' (opposite) the atom of highest priority (lowest priority number). This defines the reference axis. The second number is the priority number of the atom 'trans' (opposite) the atom of highest priority (lowest priority number) in the plane perpendicular to the reference axis. If necessary, the principle of the 'trans maximum difference' of priority numbers' is applied (see Rule I-10.5.3.2, ref. 14). The polyhedral symbol and configuration index, separated by a hyphen, are enclosed in parentheses

and cited in front of the name of the compound, if no further information is needed. For the order of priority '1' > '2' > '3' > '4' > '5' > '6', the configuration index is '25', as illustrated below.



Examples:



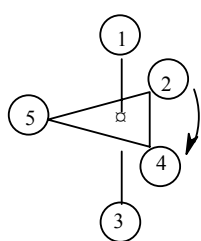
(OC-6-11')-7,7'-di-*tert*-butyl-1,1,1',1',5,5,5',5'-octamethyl-1*H*,1'*H*,5*H*,5'*H*-3λ⁶,3'-spirobi[[1,2]oxathiole[4,3,2-*hi*][2,1]benzoxathiole] (PIN)

P-92.1.9.4 Chirality

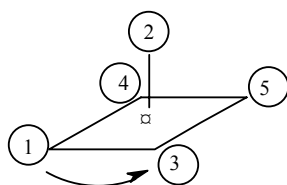
The chirality symbols '*A/C*' are used to indicate the absolute configuration of compounds described by a polyhedral symbol and a configuration index, with the exception of the trigonal pyramidal configuration that is described by '*R/S*' stereodescriptors.

P-92.1.9.4.1 The chirality symbols '*A*' and '*C*'

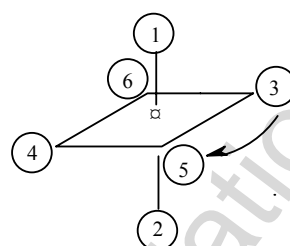
P-92.1.9.4.1.1 The atoms in the plane perpendicular to the reference axis are viewed from the side with the atom or group of highest priority (lowest priority number) on the reference axis. If the direction from the atom in this plane with highest priority (lowest priority number) to the atom with the next higher priority is clockwise the chirality symbol is '*C*', if anticlockwise '*A*'. The term 'anticlockwise' is also called 'counterclockwise'. The polyhedral symbol, configuration index and chirality symbol, each separated by a hyphen, are enclosed in parentheses and cited in front of the name of the compound (see Rule I-10.7.3. ref. 14). For the order of priority '1' > '2' > '3' > '4' > '5' > '6', the symbols are illustrated below:



TBPY-5-13-C

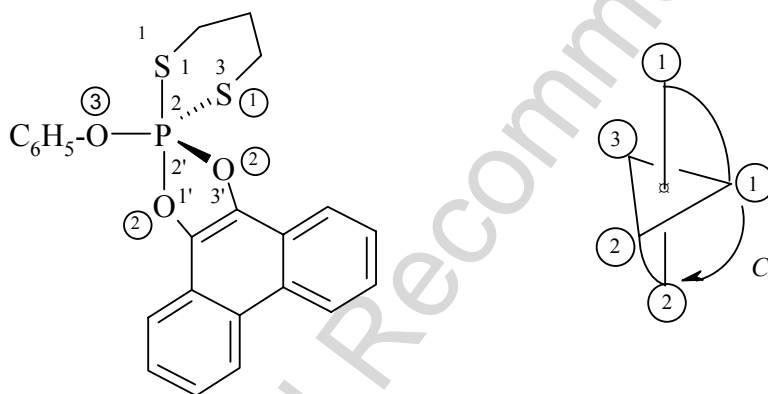


SPY-5-25-A

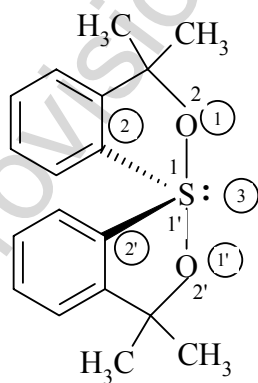


OC-6-24-C

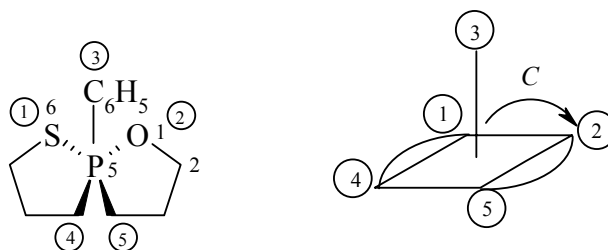
Examples:



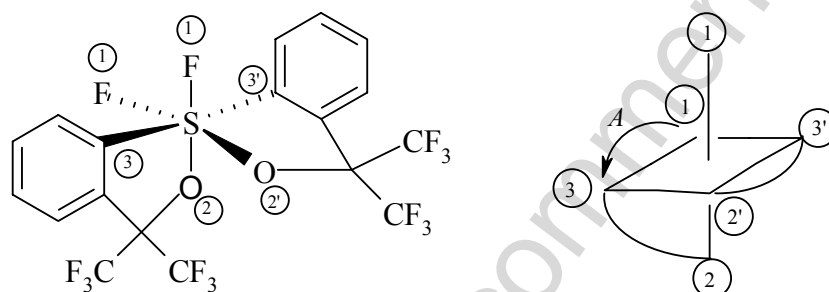
*(TBPY-5-12-C)-2-phenoxy-2λ⁵-spiro[1,3,2-dithiaphosphinane-2,2'-phenanthro[9,10-*d*][1,3,2]dithiaphosphole]* (PIN)



*(TBPY-4-11'-A)-3,3,3',3'-tetramethyl-3*H*,3'*H*-1λ⁴-spirobi[2,1-benzoxathiole]* (PIN)



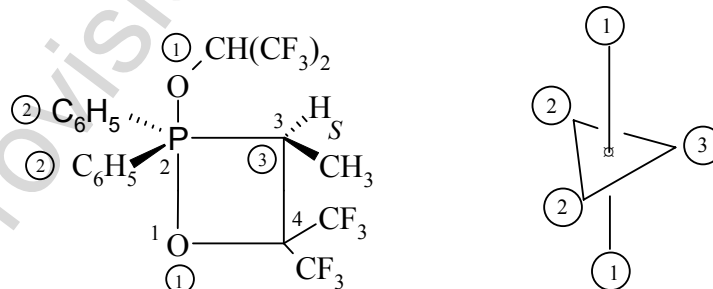
(*SPY-5-34-C*)-5-phenyl-1-oxa-6-thia-5 λ^5 -phosphaspiro[4.4]nonane (PIN)



(*OC-6-22'-A*)-1,1-difluoro-3,3,3',3'-tetrakis(trifluoromethyl)-3*H*,3'*H*-1 λ^6 -spiro-bi[2,1-benzoxathiole] (PIN)

P-92.1.9.4.1.2 When necessary, the locant of the chiral center is included in front of the polyhedral descriptor, and other chiral centers are specified in accordance with the increasing value of locants as indicated in P-92.3.2.2; parentheses are put around the complete descriptor denoting the overall geometry of the molecule.

Examples:



[2(*TBPY-5-12*),3*S*]-2-[(1,1,1,3,3,3-hexafluoropropan-2-yl)oxy]-3-methyl-2,2-diphenyl-4,4-bis(trifluoromethyl)-1,2 λ^5 -oxaphosphetane (PIN)

P-92.1.9.4.2 The chirality symbols '*R/S*'.

The stereodescriptors '*R/S*' (as defined in P.92.3) are used to indicate the absolute configuration of a trigonal pyramidal system discussed in P-92.7.3.1. They are added after the '*TPY-3*' symbol. A phantom atom of low priority, and not a pair of electrons, is used to create the tetrahedral configuration permitting the use of '*R/S*' stereodescriptors in the manner

described for tetrahedral configurations. Names associated with the tetrahedral configuration including a lone pair of electrons in place of an atom or substituent group are preferred to those expressing a trigonal pyramidal configuration including a phantom atom.

Example:



(*S*)-(methylsulfinyl)ethane (PIN)
(*TPY-3-S*)-(methylsulfinyl)ethane

P-92.2 Non-CIP stereodescriptors

P-92.2.0 Introduction

CIP stereodescriptors are preferred stereodescriptors in association with preferred IUPAC names constructed in accordance with the principles, rules and conventions described in Chapters 1 to 8 of this book. Stereodescriptors used before the CIP system was established are still recommended for general nomenclature and are mandatory in the field of Natural Products as indicated in Chapter 10.

P-92.2.1 Stereodescriptors used in preferred IUPAC names: '*cis*', '*trans*'; '*r*', '*c*', '*t*'; '*endo*', '*exo*', '*syn*', '*anti*'.

P-92.2.2 Stereodescriptors no longer recommended in systematic IUPAC nomenclature but used in the nomenclature of natural products (see Chapter 10): '*D*' and '*L*'; '*erythro*', '*threo*'. '*meso*'; '*α*', '*β*', and '*ξ*'; '*cis*', '*trans*', '*all-trans*'. '*ambo*'.

P-92.2.1 Stereodescriptors used in preferred IUPAC names: '*cis*', '*trans*', '*endo*', '*exo*', '*syn*', '*anti*'

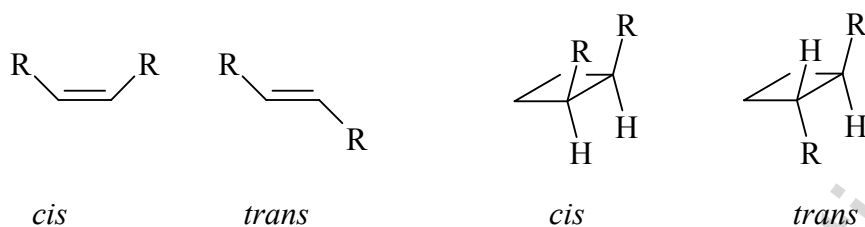
P-92.2.1.1 The stereodescriptors '*cis*', '*trans*', and '*r*', '*c*', '*t*'

P-92.2.1.2 The stereodescriptors '*endo*', '*exo*', '*syn*' and '*anti*'

P-92.2.1.1 Stereodescriptors '*cis*' and '*trans*'

The stereodescriptors '*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 or are contained in a ring. The two atoms or groups are said to be located '*cis*' to each other if they lie on the same side of a plane. If they are on opposite sides, their relative position is described as '*trans*'. The appropriate reference plane of a double bond is perpendicular to that of the relevant σ -bonds and passes through the double bond. For a ring (the ring being in a conformation, real or assumed, without reentrant angles at the two substituted atoms) it is the mean plane of the ring(s).

Examples:



The structures below look like *cis/trans*-isomers, but are actually different conformations of the same *cis* stereoisomer. In the conformation on the left hand side, the stereogenic center at C-1 is located on a reentrant angle.

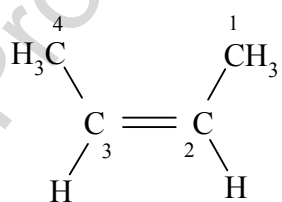


The stereodescriptors '*cis/trans*' are placed in front of the names, followed by a hyphen. Locants are placed in front of these descriptors when more than one double bond are present; locants and stereodescriptors are cited in parentheses. When alternative numberings are possible, that numbering is chosen which gives a '*cis*' attachment at the first point of difference.

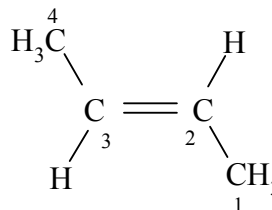
P-92.2.1.1.1 Application to double bonds

The '*cis*' and '*trans*' descriptors are recommended only in general nomenclature to describe the configuration of a double bond that are substituted once on each carbon atom. The '*cis*' and '*trans*' descriptors are placed at the front of the name when one double bond is present; when double bonds have to be identified by locants, these locants are reproduced at the front of the stereodescriptor, followed by a hyphen; parentheses are used to nest the entire stereodescriptor. Double bonds that are more substituted must be named by using the stereodescriptors '*E*' and '*Z*' described in P-92.1.6.2. For all double bonds, stereodescriptors '*E*' and '*Z*' are preferred to '*cis*' and '*trans*'.

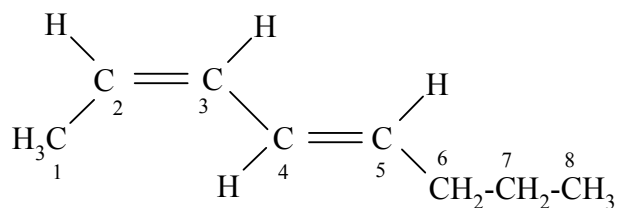
Examples:



cis-but-1-ene
(*Z*)-but-1-ene (PIN)



trans-but-2-ene
(*E*)-but-2-ene (PIN)

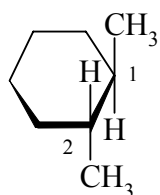


(2-*cis*,4-*trans*)-octa-2,4-diene
(2*Z*,4*E*)-octa-2,4-diene (PIN)

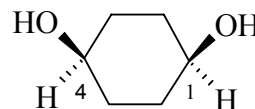
P-92.2.1.1.2 Application to substituted cyclic compounds.

P-92.2.1.1.2.1 When one substituent and one hydrogen atom are attached at each of two positions of a monocycle, the steric relations (the relative configuration) of the two substituents is expressed as '*cis*' or '*trans*', followed by a hyphen and placed before the name of the compound. No locants are required before the stereodescriptors. In names, '*cis*' isomers are cited before '*trans*' isomers, when a choice is possible. CIP stereodescriptors must be used to describe relative configuration in preferred IUPAC names, as shown in P-91.3 and P-92.1.2..

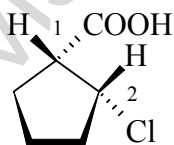
Examples:



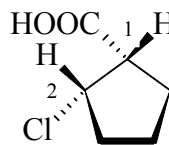
trans-1,2-dimethylcyclohexane
rel-(1*R*,2*R*)-1,2-dimethylcyclohexane (PIN,
see P-92.1.2)



cis-cyclohexane-1,4-diol
(1*s*,4*s*)-cyclohexane-1,4-diol (PIN,
see P-91.3)



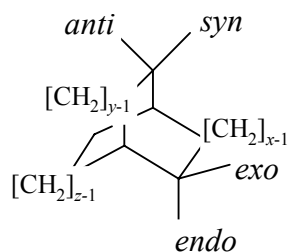
or



cis-2-chlorocyclopentane-1-carboxylic acid
rel-(1*R*,2*R*)-2-chlorocyclopentane-1-carboxylic acid (PIN)

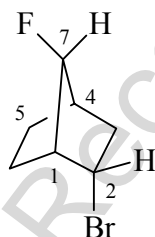
P-92.2.1.2 The stereodescriptors '*endo*', '*exo*', '*syn*', '*anti*' (relative configuration)

The stereodescriptors '*endo*', '*exo*', '*syn*', '*anti*' are used to indicate the relative orientation of groups attached to nonbridgehead atoms in bicyclo[x.y.z]alkanes, where '*x*' ≥ '*y*' > '*z*' > 0, and with the additional provision that '*x* + *y*' must be smaller than 7.

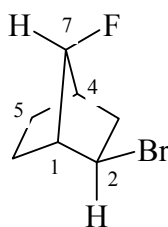


If the group is orientated toward the highest numbered bridge ('z bridge, e.g. C-7 in example below) it is given the description '*exo*'; if it is orientated away from the highest numbered bridge it is given the description '*endo*'. If the group is attached to the highest numbered bridge and is orientated toward the lowest numbered bridge ('x bridge, e.g. C-2 in example below) it is given the description '*syn*'; if the group is orientated away from the lowest numbered bridge it is given the description '*anti*'. The descriptors are always preceded by an appropriate locant.

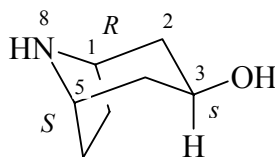
Examples:



(2-*endo*,7-*anti*)-2-bromo-7-fluorobicyclo[2.2.1]heptane
(2*S*,7*R*)-2-bromo-7-fluorobicyclo[2.2.1]heptane (PIN)



(2-*exo*,7-*syn*)-2-bromo-7-fluorobicyclo[2.2.1]heptane
(2*R*,7*S*)-2-bromo-7-fluorobicyclo[2.2.1]heptane (PIN)



(3-*exo*)-8-azabicyclo[3.2.1]octan-3-ol
(1*R*,3*s*,5*S*)-8-azabicyclo[3.2.1]octan-3-ol (PIN)

P-92.2.2 Descriptors no longer recommended in systematic IUPAC nomenclature but still used in the nomenclature of natural products described in Chapter 10: ‘D and L’; ‘*erythro*’, ‘*threo*’, ‘*meso*’; ‘ α ’, ‘ β ’, and ‘ ξ ’; ‘*cis*’, ‘*trans*’, ‘*all-trans*’; *ambo*.

P-92.2.2.1 The descriptors ‘D’ and ‘L’

The descriptors ‘D’ and ‘L’ are used to describe the configuration of amino acids and peptides (ref. 23 and P-103), carbohydrates (ref. 22 and P-102), and cyclitols (ref. 42 and P-104).

P-92.2.2.2 The descriptors ‘*erythro*’ and ‘*threo*’

The descriptors ‘*erythro*’ and ‘*threo*’ are used in the nomenclature of carbohydrates, along with descriptors such as ‘*arabino*’ and ‘*gluco*’ (see ref. 22 and P-102).

P-92.2.2.3 The stereodescriptors ‘ α ’, ‘ β ’, and ‘ ξ ’

The stereodescriptors ‘ α ’, ‘ β ’, and ‘ ξ ’ are used in the nomenclature of natural products described to describe the absolute configuration of alkaloids, terpenes and terpenoids, steroids, and other compounds as described in P-101.

P-92.2.2.4 The stereodescriptors ‘*cis*’, ‘*trans*’ and ‘*all-E*’ and ‘*all-trans*’ are used in the nomenclature of carotenoids and similar compounds (see ref. 40 and 48)

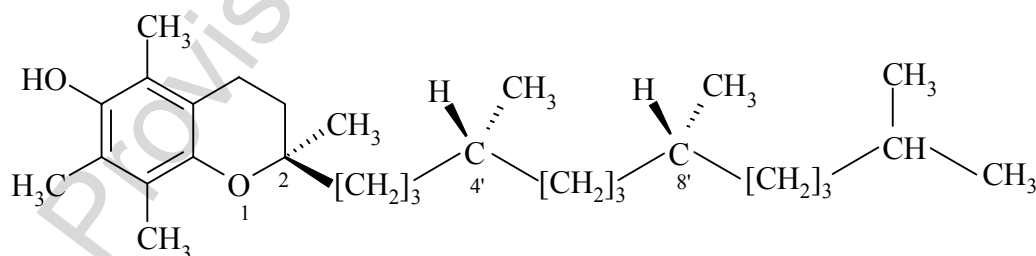
P-92.2.2.5 The descriptor ‘*meso*’

The descriptor ‘*meso*’ is used in the nomenclature of carbohydrates to designate compounds such as alditols and aldaric acids that are symmetrical and thus optically inactive (ref. 22 and P-102).

P-92.2.2.6 The stereodescriptor ‘*ambo*’

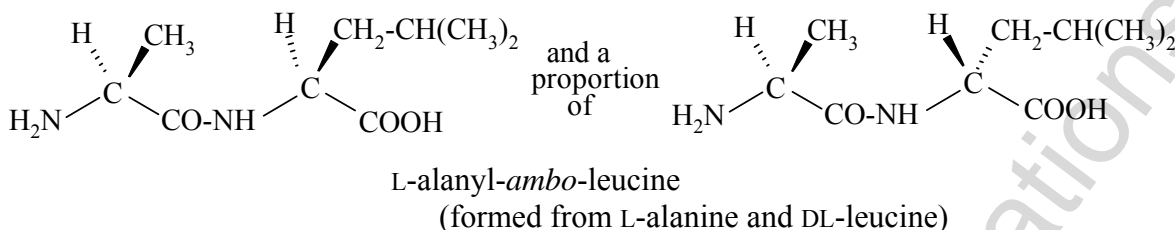
Formation of diastereoisomers by reaction at a nonstereogenic center of a chiral molecule or the reaction of a chiral compound with a racemic compound will not normally give a 50-50 mixture. To indicate this, the prefix ‘*ambo*’ is used.

Examples:



plus a proportion of the epimer at C-2

2-ambo-(2*R*,4'*R*,8'*R*)- α -tocopherol.



P-93 Applications to specific parent structures

P-93.0 Introduction

P-93.1 Specification of configuration of acyclic compounds

P-93.2 Specification of configuration of cyclic compounds

P-93.3 Specification of configuration of assemblies of rings and chains

P-93.0 Introduction

Different systems are used to describe the configuration of acyclic and cyclic compounds. This Section describes these various systems and the selection of preferred descriptors to denote the tridimensional structure in preferred names. In Sections P-91 and P-92, the various stereodescriptors were described in accordance with different types of configuration. In this Section, they are applied on the basis of the parent structures, i.e., acyclic or cyclic. It is important to remember that stereodescriptors represent the entire molecule.

P-93.1 Specification of configuration of acyclic compounds

P-93.1.1 Specification of configuration due to chirality centers

P-93.1.2 Specification of configuration of allenes and similar compounds

P-93.1.3 Specification of configuration due to double bonds

P-93.1.4 Specification of configuration in cumulenes having an odd number of double bonds

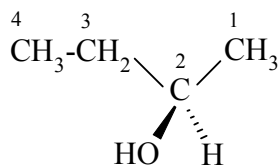
P-93.1.5 Specification of chiral unsaturated compounds

P-93.1.1 Specification of configuration due to chirality centers

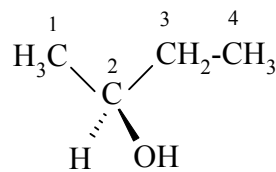
P-93.1.1.1 The presence of one center of chirality is denoted by the stereodescriptors '*R*' and '*S*', as described in P-92.1. These stereodescriptors, preceded by '*rel*' are preferred to '*R**' and '*S**' to indicate the relative configuration. The stereodescriptor '*rac*', is preferred to '*RS*' and '*SR*' to describe racemates.

Stereodescriptors are preceded by a locant when the chirality center needs to be described by a locant. When no locant is required in the name of the chiral compound, no locant is necessary before the stereodescriptor.

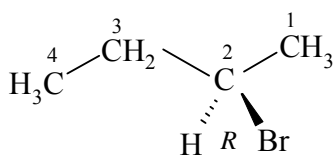
Examples:



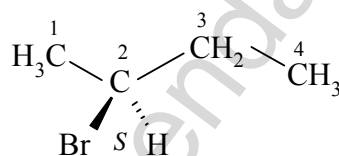
(2*R*)-butan-2-ol (PIN)



(2*S*)-butan-2-ol (PIN)

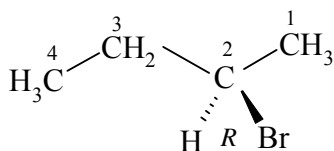


or

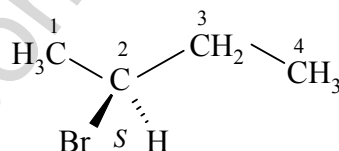


rel-(2*R*)-butan-2-ol (PIN)

(2*R*^{*})-butane-2-ol



+



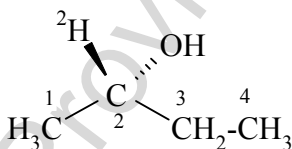
rac-(2*R*)-2-bromobutane (PIN)

(*RS*)-2-bromobutane

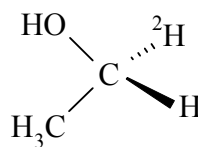
(±)-2-bromobutane

Sequences rules (1) and (2) are successively applied to specify the configuration of isotopically modified compounds. When inserted into the name at the same place as isotopic descriptors, the stereochemical affixes are cited first.

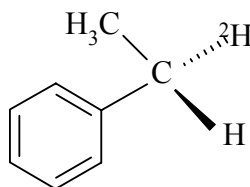
Examples:



(2*S*)-(2-²H)-butan-2-ol (PIN)



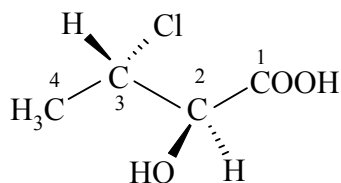
(1*S*)-(1-²H₁)ethan-1-ol (PIN)



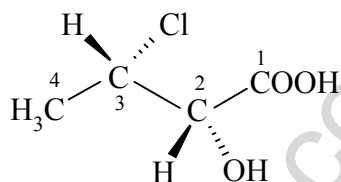
[(1*S*)-(1-²H₁)ethyl]benzene (PIN)

P-93.1.1.1.2 When, in a parent structure, two or more stereodescriptors, 'R and/or 'S' are required to describe a single tridimensional (3D) structure, they are placed in front of the name and cited according to the ascending order of their corresponding locants, regardless of the kind of descriptor.

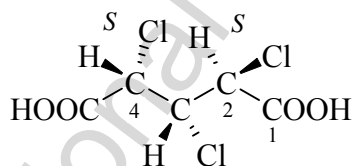
Examples:



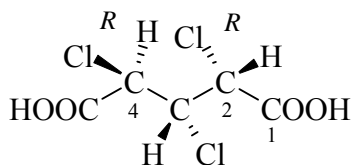
(2*R*,3*S*)-3-chloro-2-hydroxybutanoic acid (PIN)



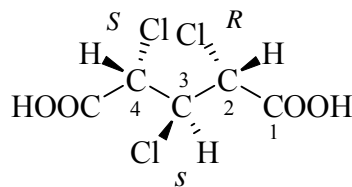
(2*S*,3*S*)-3-chloro-2-hydroxybutanoic acid (PIN)



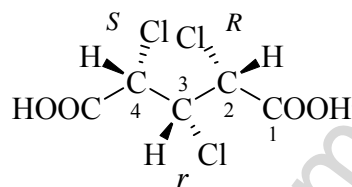
(2*S*,4*S*)-2,3,4-trichloropentanedioic acid (PIN)



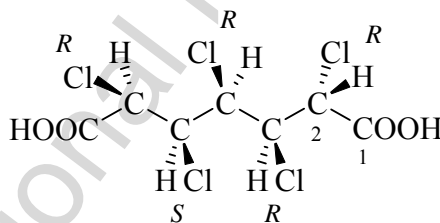
(2*R*,4*R*)-2,3,4-trichloropentanedioic acid (PIN)



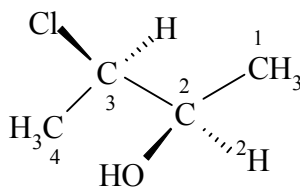
(2*R*,3*s*,4*S*)-2,3,4-triisopentanedioic acid (PIN)
(Chirality center '*R*' receives the lowest locant [see P-14.4(k)];
application of sequence rule 5 generates the
stereodescriptor '*s*' at C-3)



(2*R*,3*r*,4*S*)-2,3,4-trichloropentanedioic acid (PIN)
(Chirality center '*R*' receives the lowest locant [see P-14.4(k)];
application of sequence rule 5 generates
stereodescriptor '*r*' at C-3)



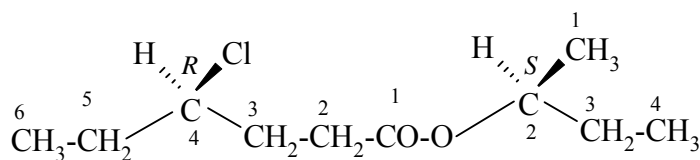
(2*R*,3*R*,4*R*,5*S*,6*R*)-2,3,4,5,6-pentachloroheptanedioic acid (PIN)
(application of Sequence rule 4 generates stereodescriptor '*R*' at C-4)



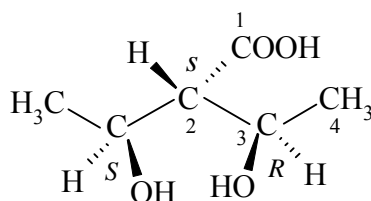
(2*R*,3*R*)-2-chloro-(3-²H₁)-butan-2-ol (PIN)

P-93.1.1.1.3 Stereodescriptors, if any, denoting the absolute configuration of a component cited as a prefix or in functional class names, are cited immediately before each respective component.

Examples:



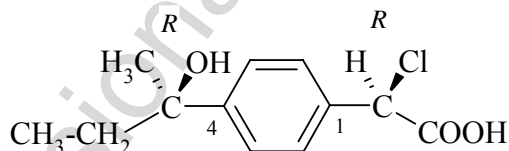
(2*S*)-butan-2-yl (4*R*)-4-chlorohexanoate (PIN)



(2*s*,3*R*)-3-hydroxy-2-[(1*S*)-1-hydroxyethyl]butanoic acid (PIN)

Guide to name construction:

- Step 1: configurations '*R*' and '*S*' are assigned to the hydroxylated stereogenic centers;
- Step 2: configuration '*s*' is assigned to the pseudo-asymmetric carbon atom;
- Step 3: the principal chain has the maximum of stereogenic centers having the '*R*' configuration [see P-44.4.5.3(a)];
- Step 4: the name is constructed by citing the stereodescriptors at the front of the principal chain and of the substituent.



(2*R*)-2-chloro-2-{4-[(2*R*)-2-hydroxybutan-2-yl]phenyl}acetic acid (PIN)

P-93.1.1.1.4 Tetrahedral configuration of elements other than carbon

- P-93.1.1.1.4.0 Introduction
- P-93.1.1.1.4.1 Ammonium and phosphonium salts
- P-93.1.1.1.4.2 Amine oxides and phosphanones
- P-93.1.1.1.4.3 λ^3 -Phosphanes
- P-93.1.1.1.4.4 Phosphates, phosphonates and related compounds
- P-93.1.1.1.4.5 Sulfoxides and related compounds
- P-93.1.1.1.4.6 Sulfates, sulfonates and related compounds

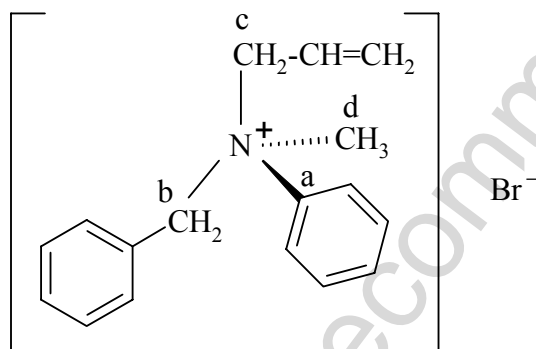
P-93.1.1.1.4.0 Introduction

The absolute configuration of any atom with four atoms or groups tetrahedrally arranged is described by '*R*' and '*S*' stereodescriptors. The assignment of these descriptors is the same as for carbon centered compounds.

P-93.1.1.1.4.1 Azanium (ammonium) and phosphanium (phosphonium) compounds

The four different atoms or groups are considered in priority order '*a*' > '*b*' > '*c*' > '*d*' in the manner described in P-91.4. Stereodescriptors are cited as indicated in P-92.3.2.

Examples:

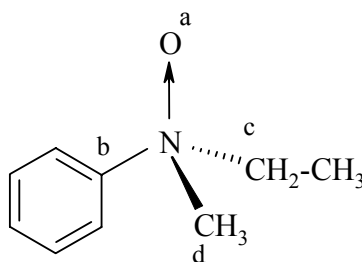


(*R*)-*N*-benzyl-*N*-methyl-*N*-(prop-2-en-1-yl)anilinium bromide (PIN)
(*R*)-benzyl(methyl)phenyl(prop-2-en-1-yl)azanium bromide
(*R*)-benzyl(methyl)phenyl(prop-2-en-1-yl)ammonium bromide

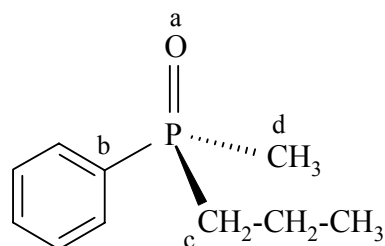
P-93.1.1.1.4.2 Amine oxides and phosphane oxides

With chiral amine oxides and phosphane oxides the oxygen atom is treated as the fourth atom. The nature of the bonding to this oxygen atom is not relevant.

Examples:



(*R*)-*N*-ethyl-*N*-methylaniline oxide (PIN)
[(*R*)-*N*-ethyl-*N*-methylaniliniumyl]oxidanide
(see P-74.2.1.2)

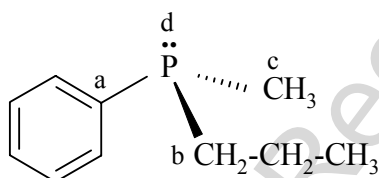


(*S*)-methyl(phenyl)propyl- λ^5 -phosphanone
(*S*)-methyl(phenyl)propylphosphane oxide (PIN)

P-93.1.1.1.3 Phosphanes

A tetrahedral configuration is assumed for chiral λ^3 -phosphanes. The lone pair of electrons is considered as the group of lowest precedence in the order 'a' > 'b' > 'c' > 'd' (see P-91.4.2.4).

Examples:

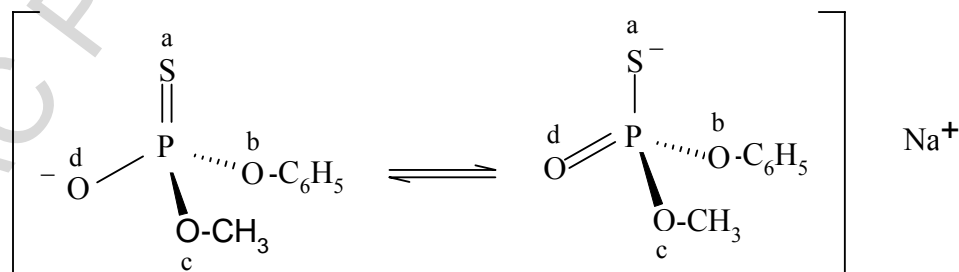


(*R*)-methyl(phenyl)propylphosphane (PIN)

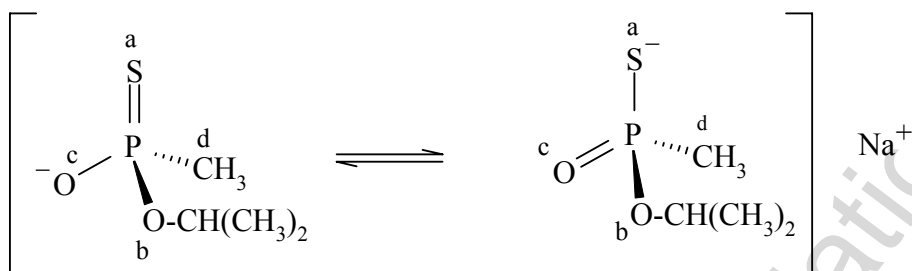
P-93.1.1.1.4 Phosphates, phosphonates and related compounds

The P=O bond, as conventionally written in phosphates, phosphonates and related compounds, is considered as a single bond, as there are already four atoms or groups in the tetrahedral configuration. Similarly, the formal arrangement of charges is not considered when determining the configuration of a chiral molecule. As the stereodescriptors '*R*' and '*S*' describe the entire structure, either a salt or an ester, the full name is placed in parentheses to denote the global configuration.

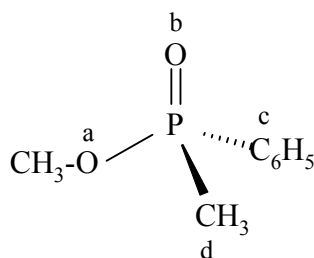
Examples:



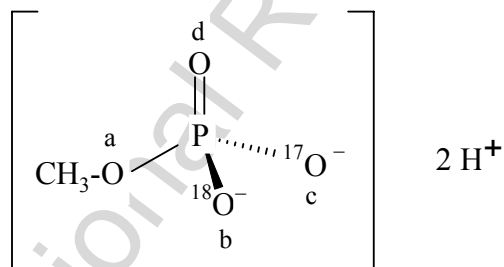
sodium (*R*)-(*O*-methyl *O*-phenyl phosphorothioate) (PIN)



sodium (*R*)-(*O*-propan-2-yl methylphosphonothioate) (PIN)
sodium (*R*)-[*O*-(1-methylethyl) methylphosphonothioate] (PIN)



(*S*)-[methyl methyl(phenyl)phosphinate] (PIN)

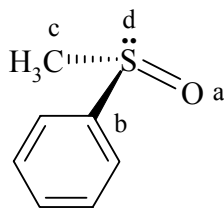


dihydrogen (*R*)-(*O*-methyl [¹⁷O, ¹⁸O]phosphate) (PIN)

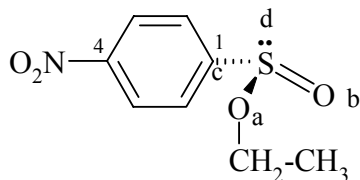
P-93.1.1.1.4.5 Sulfoxides and related compounds

The geometry of the sulfoxide group is tetrahedral when the lone pair of electrons is treated as if it were an atom. This lone pair of electrons has lowest priority. Chiral examples of other related sulfur compounds with three atoms attached to the sulfur atom are treated in the same way.

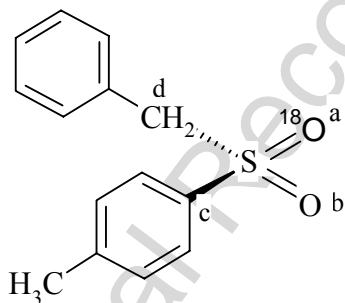
Examples:



(*S*)-methanesulfinylbenzene (PIN)



(*R*)-(ethyl 4-nitrobenzene-1-sulfinate) (PIN)

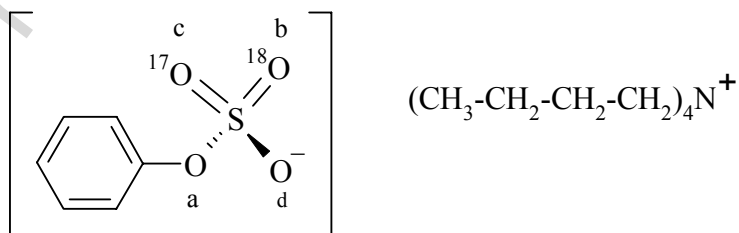


1-methyl-4-[(*R*)-phenyl(¹⁸O₁)methanesulfonyl]benzene (PIN)

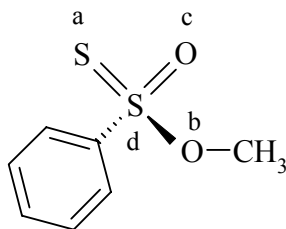
P-93.1.1.1.4.6 Sulfates, sulfonates and related compounds

Sulfates, sulfonates and related anions are treated in the same way as phosphate anions (see P-93.1.1.1.4.4).

Examples:



N,N,N-tributylbutanaminium (*S*)-[*O*-phenyl (¹⁷O, ¹⁸O)sulfate] (PIN)
tetraethylammonium (*S*)-[*O*-phenyl (¹⁷O, ¹⁸O)sulfate]
tetraethylazanium (*S*)-[*O*-phenyl (¹⁷O, ¹⁸O)sulfate]

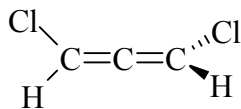


(*S*)-(O-methyl benzenesulfonylthioate) (PIN)

P-93.1.2 Allenes and cumulenes having an even number of double bonds

When appropriately substituted, allenes are chiral compounds having an axis of chirality. Chirality is thus described by the stereodescriptors ' R_a ' and ' S_a ' or ' M ' and ' P ', as described in P-92.1.5.1). Stereodescriptors ' R_a ' and ' S_a ' are preferred to ' M ' and ' P '.

Examples:

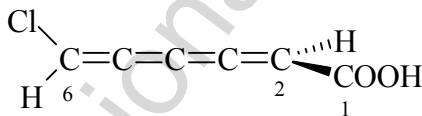


(R_a)-1,3-dichloropropa-1,2-diene (PIN)

(M)-1,3-dichloropropa-1,2-diene

(R_a)-1,3-dichloroallene

(M)-1,3-dichloroallene



(S_a)-6-chlorohexa-2,3,4,5-tetraenoic acid (PIN)

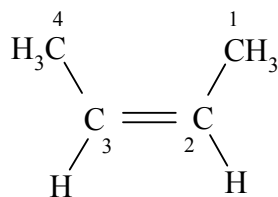
(P)-6-chlorohexa-2,3,4,5-tetraenoic acid

P-93.1.3 Specification of configuration due to double bonds

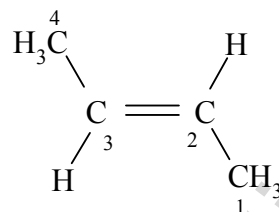
P-93.1.3.1 Description of the configuration of one double bond

The stereodescriptors ' E ' and ' Z ' are preferred to ' cis ' and ' $trans$ ' to describe one or more C=C double bonds. Stereodescriptors ' cis ' and ' $trans$ ' are used in general nomenclature only to describe double bonds having two hydrogen atoms, one on each carbon atom. Locants corresponding to those needed to describe a double bond are repeated before the stereodescriptors ' E ' and ' Z ', but not before ' cis ' and ' $trans$ '

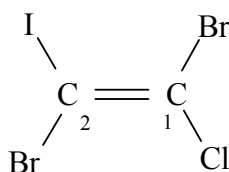
Examples:



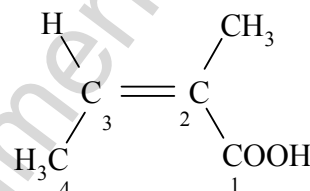
(2*Z*)-but-2-ene (PIN)
cis-but-2-ene



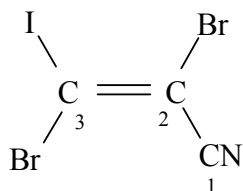
(2*E*)-but-2-ene (PIN)
trans-but-2-ene



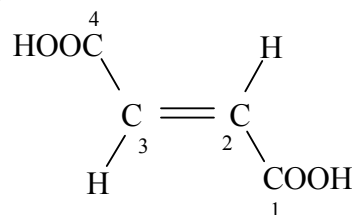
(1*Z*)-1,2-dibromo-1-chloro-2-iodoethene (PIN)



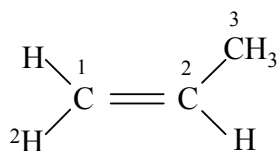
(2*Z*)-2-methylbut-2-enoic acid (PIN)



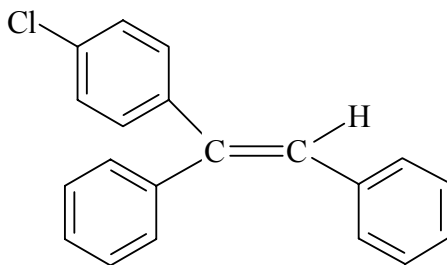
(2*E*)-2,3-dibromoprop-2-enenitrile (PIN.)
(2*E*)-2,3-dibromoacrylonitrile



(2*E*)-but-2-enedioic acid (PIN)
fumaric acid (the stereochemistry
is implied in the retained name)



(1*E*)-(1-²H₁)prop-1-ene (PIN)
cis-(1-²H₁)prop-1-ene



(*E*)-1,1'-[1-(4-chlorophenyl)ethene-1,2-diyl]dibenzene (PIN)

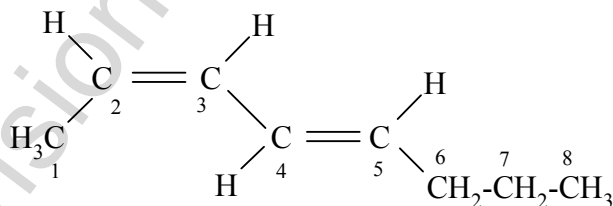
P-93.1.3.2 Compounds containing more than one double bond

The stereodescriptors '*E/Z*' related to the parent are cited, preceded by the appropriate locant if more than one double bond is present, before the complete name of the compound, or before the name of the appropriate component. Chain locants are used when double bonds are 'exo' to the chain (see fourth example below). If more than one descriptor is used, the descriptors are cited in ascending order of their respective locants.

When alternative numberings of a chain or rings or ring systems are possible, that numbering is chosen which gives a '*cis*' attachment at the first point of difference. Attention must be given to the fact that a '*cis*' attachment is denoted by the stereodescriptor '*Z*'.

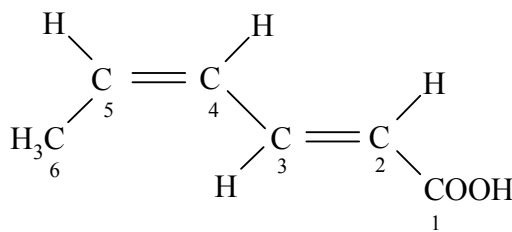
Stereodescriptors '*cis*' and '*trans*' may be used to describe double bonds having two hydrogen atoms, one on each carbon atom, but stereodescriptors '*E*' and '*Z*' are used in preferred IUPAC names. The stereodescriptors '*cis*' and '*trans*', placed in parentheses, are cited at the front of the name, preceded by the appropriate locant followed by a hyphen.

Examples:



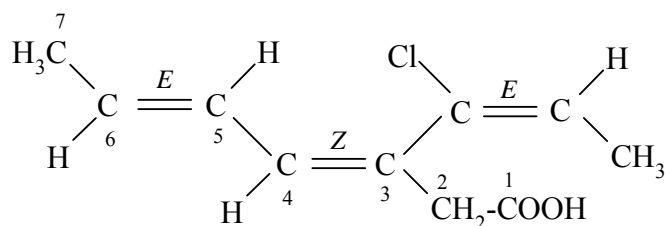
(*2Z,4E*)-octa-2,4-diene (PIN)

(*2-cis,4-trans*)-octa-2,4-diene

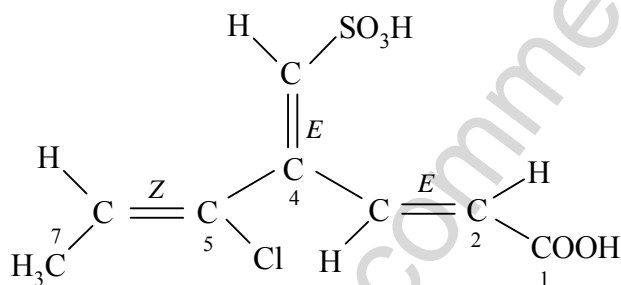


(*2E,4Z*)-hexa-2,4-dienoic acid (PIN)

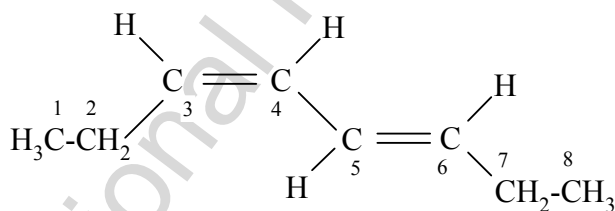
(*2-trans,4-cis*)-hexa-2,4-dienoic acid



(3*Z*,5*E*)-3-[(1*E*)-1-chloroprop-1-en-1-yl]hepta-3,5-dienoic acid (PIN)
(3-*cis*,5-*trans*)-3-[(1*E*)-1-chloroprop-1-en-1-yl]hepta-3,5-dienoic acid



(2*E*,4*E*,5*Z*)-5-chloro-4-(sulfomethylidene)hepta-2,5-dienoic acid (PIN)



(3*Z*,5*E*)-octa-3,5-diene (PIN)

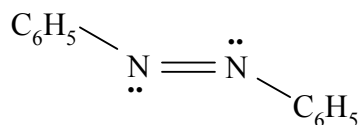
(3-*cis*,5-*trans*)-octa-3,5-diene

[the double bond with the *cis* configuration
receives the lowest locants (see P-44.4.5.1)]

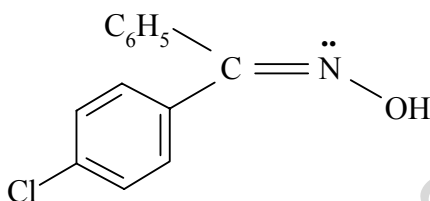
P-93.1.3.3 Descriptors 'E' and 'Z' to denote double bonds linked to heteroatoms

The stereodescriptors 'E' and 'Z' are also used to indicate the configuration of double bonds involving atoms other than carbon. A lone pair of electrons, when present, is considered to have the atomic number '0' (zero). The descriptors '*syn*' and '*anti*', and '*cis*' and '*trans*', are no longer recommended for these situations. No locant is required before the stereodescriptor when none is present in a name.

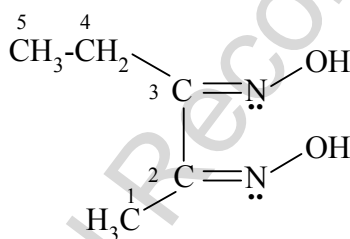
Examples:



(*E*)-diphenyldiazene
(not *trans*-diphenyldiazene)



(*Z*)-(4-chloro- α -phenylbenzylidene)hydroxylamine (PIN)
(*Z*)-(4-chlorophenyl)phenylmethanone oxime



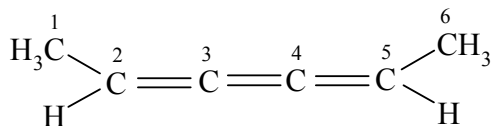
(*2Z,3E*)-pentane-2,3-diylidenebis(hydroxylamine) (PIN)
(*2Z,3E*)-pentane-2,3-dione dioxime

P-93.1.3.4 Cumulenes having odd number of double bonds

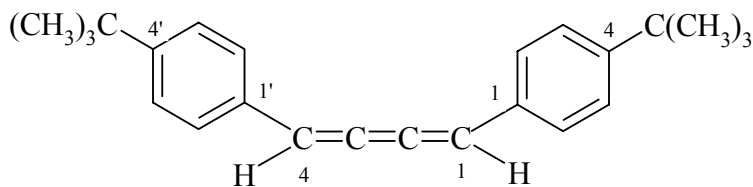
Cumulenes having an odd number of double bonds are planar molecules, like double bonds. The preferred stereodescriptors are '*E*' and '*Z*'. Stereodescriptors '*cis*' and '*trans*' may be used in general nomenclature.

The stereodescriptor '*E*' or '*Z*', describing the cumulene system, is preceded by composite locants indicating the starting point and the end point of the cumulated double bond system

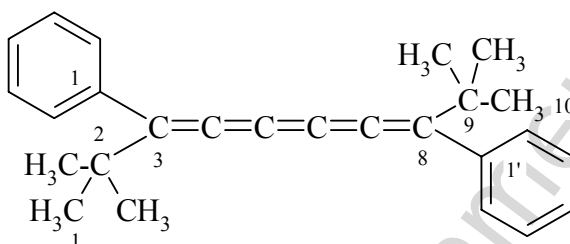
Examples:



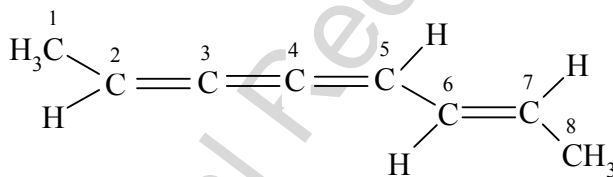
[2(5)*Z*]-hexa-2,3,4-triene
cis-hexa-2,3,4-triene



[1(4)*Z*]-1,1'-buta-1,2,3-triene-1,4-diylbis(4-*tert*-butylbenzene) (PIN)
(*cis*)-1,1'-buta-1,2,3-triene-1,4-diylbis(4-*tert*-butylbenzene)



[3(8)*E*]-1,1'-(2,2,9,9-tetramethyldeca-3,4,5,6,7-pentaene-3,8-diyl)dibenzene (PIN)
[3(8)*E*]-2,2,9,9-tetramethyl-3,8-diphenyl-deca-3,4,5,6,7-pentaene

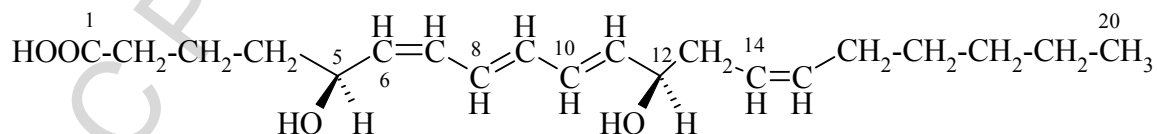


[2(5)*E*,6*E*]-octa-2,3,4,6-tetraene (PIN)
[2[5]-*trans*,6-*trans*]-octa-2,3,4,6-tetraene

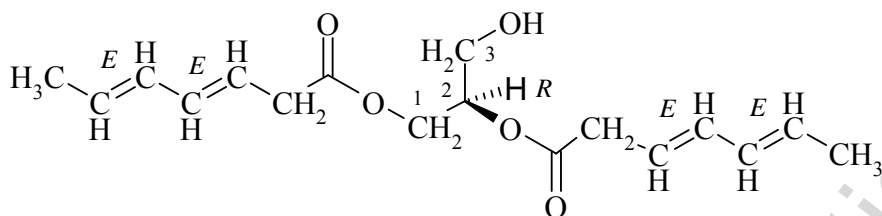
P-93.1.3.5 Specification of configuration in chiral unsaturated compounds

When chiral compounds contain C=C double bond(s), stereodescriptors are assigned as describe above. Stereodescriptors are cited at the front of the name or of any substituent group or appropriate portion of the name, in ascending order of the locants.

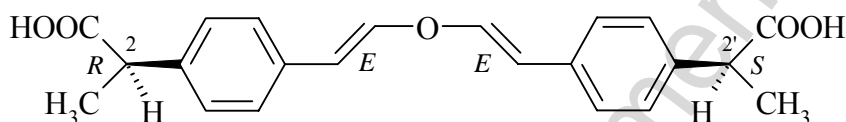
Examples:



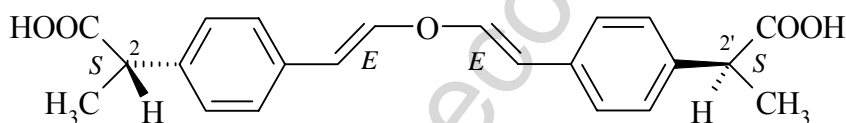
(5*S*,6*Z*,8*E*,10*E*,12*R*,14*Z*)-5,12-dihydroxyicosa-6,8,10,14-tetraenoic acid (PIN)
(5*S*,6-*cis*,8-*trans*,10-*trans*,12*R*,14-*cis*)-5,12-dihydroxyicosa-6,8,10,14-tetraenoic acid



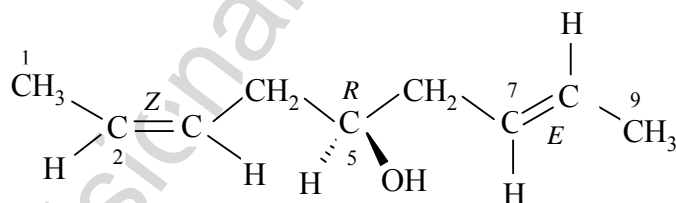
(2*R*)-3-hydroxypropane-1,2-diyl di(3*E*,5*E*)-hepta-3,5-dienoate (PIN)
(2*R*)-3-hydroxypropane-1,2-diyl di(3-*trans*,5-*trans*)-hepta-3,5-dienoate



(2*R*,2'*S*)-2,2'-{oxybis[(1*E*)-ethene-2,1-diyl-4,1-phenylene]}dipropanoic acid

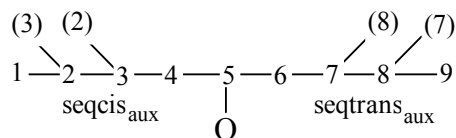


(2*S*,2'*S*)-2,2'-{oxybis[(1*E*)-ethene-2,1-diyl-4,1-phenylene]}dipropanoic acid



(2*Z*,5*R*,7*E*)-nona-2,7-dien-5-ol

Guide to name construction in accordance with the digraph:



- Step 1: configurations '*seqcis*_{aux}' and '*seqtrans*_{aux}' are assigned to the double bonds, respectively '*Z*' and '*E*';
- Step 2: the configuration '*R*' at C-5 is determined in accordance with Sequence Rule 3, *seqcis* precedes *seqtrans*;
- Step 3: the chain is numbered to allocate low locant to the '*Z*' double bond;

Step 4: the name is constructed by citing stereodescriptors and their locants at the front of the name, in the ascending order of locants.

P-93.2 Cyclic compounds

- P-93.2.1 Monocyclic compounds
- P-93.2.2 von Baeyer compounds
- P-93.2.3 Spiro compounds
- P-93.2.4 Fused and bridged fused compounds
- P-93.2.5 Cyclophanes
- P-93.2.6 Fullerenes
- P-93.2.7 Ring assemblies

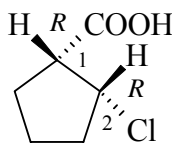
P-93.2.1 Monocyclic compounds

P-93.2.1.1 Chiral compounds

For chiral compounds, absolute configuration is described by using the stereodescriptors '*R*' and '*S*'. To describe the relative configuration the stereodescriptors '*R*' and '*S*' preceded by the term '*rel*' are preferred to '*R**' and '*S**', and also to '*cis*' and '*trans*' and '*r*', '*c*', and '*t*'. To describe the configuration of racemates, the stereodescriptors *R* and *S* preceded by the term *rac* are preferred to '*RS*' and '*SR*'. When relative configuration or racemates are described, the stereodescriptor '*R*' or '*R**' is cited for the chirality center having the lowest locant. It is to be noted that the prefixes '*rel*' or '*rac*' indicate the configuration of the entire molecule.

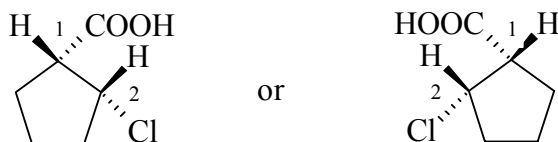
Example 1:

Absolute configuration:



(1*R*,2*R*)-2-chlorocyclopentane-1-carboxylic acid (PIN)

Relative configuration:



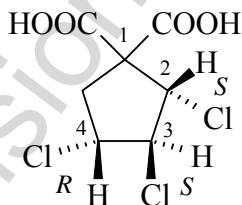
rel-(1*R*,2*R*)-2-chlorocyclopentane-1-carboxylic acid (PIN)
(1*R*^{*},2*R*^{*})-2-chlorocyclopentane-1-carboxylic acid
cis-2-chlorocyclopentane-1-carboxylic acid
[not *rel*-(1*S*,2*S*)-2-chlorocyclopentane-1-carboxylic acid]
[not (1*S*^{*},2*S*^{*})-2-chlorocyclopentane-1-carboxylic acid]



rac-(1*R*,2*R*)-2-chlorocyclopentane-1-carboxylic acid (PIN)
(1*RS*,2*RS*)-2-chlorocyclopentane-1-carboxylic acid

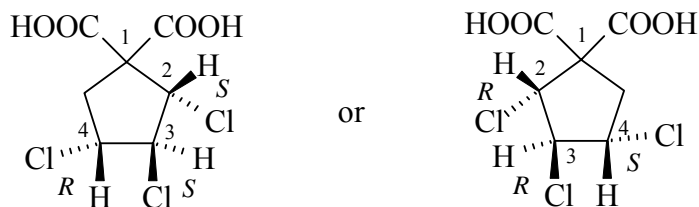
Example 2:

Absolute configuration:



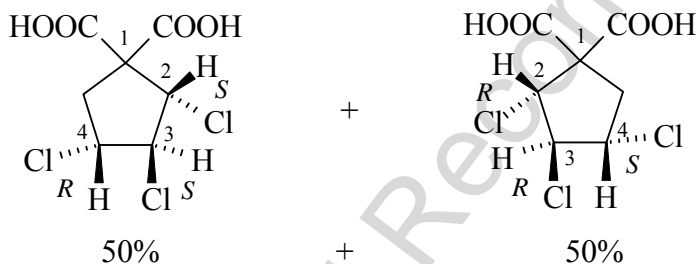
(2*S*,3*S*,4*R*)-2,3,4-trichlorocyclopentane-1,1-dicarboxylic acid (PIN)

Relative configuration:

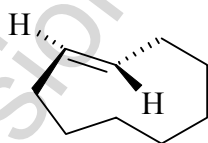


rel-(2*R*,3*R*,4*S*)-2,3,4-trichlorocyclopentane-1,1-dicarboxylic acid (PIN)
(2*R**,3*R**,4*S**)-2,3,4-trichlorocyclopentane-1,1-dicarboxylic acid
[not *rel*-(2*S*,3*S*,4*R*)-2,3,4-trichlorocyclopentane-1,1-dicarboxylic acid]
[not (2*S**,3*S**,4*R**)-2,3,4-trichlorocyclopentane-1,1-dicarboxylic acid]
2-r,3-c,4-t-trichlorocyclopentane-1,1-dicarboxylic acid

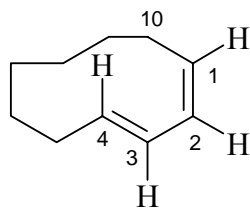
Racemate:



rac-(2*R*,3*R*,4*S*)-2,3,4-trichlorocyclopentane-1,1-dicarboxylic acid (PIN)
(2*RS*,3*RS*,4*SR*)-2,3,4-trichlorocyclopentane-1,1-dicarboxylic acid



(1*E*)-cyclononene (PIN)



(1*Z*,3*E*)-cyclodeca-1,3-diene (PIN)
(1-*cis*,3-*trans*)-cyclodeca-1,3-diene
[lowest locants are assigned to *Z* double bond (see P-44.4.5.1)]

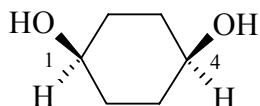
P-92.2.1.2 Achiral compounds

The configuration of achiral compounds is expressed in two ways:

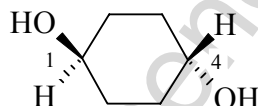
- (a) by using CIP stereodescriptors;
- (b) by using 'cis', 'trans' or 'r', 'c', 't' stereodescriptors.

Preferred IUPAC names are those using CIP stereodescriptors.

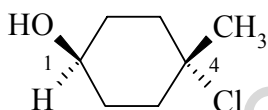
Examples:



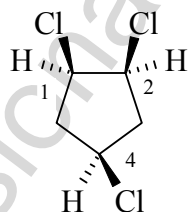
(1*s*,4*s*)-cyclohexane-1,4-diol (PIN)
cis-cyclohexane-1,4-diol



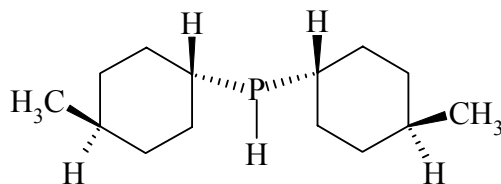
(1*r*,4*r*)-cyclohexane-1,4-diol (PIN)
trans-cyclohexane-1,4-diol



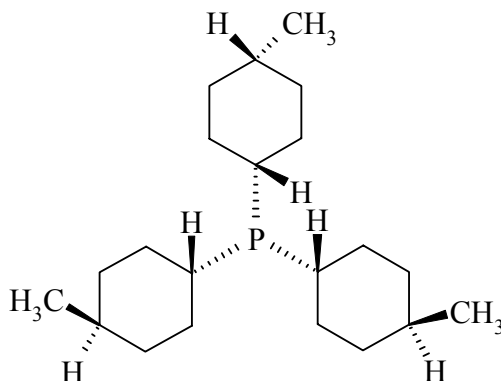
(1*r*,4*r*)-4-chloro-4-methylcyclohexan-1-ol (PIN)
4-*t*-chloro-4-methylcyclohexan-1*r*-ol



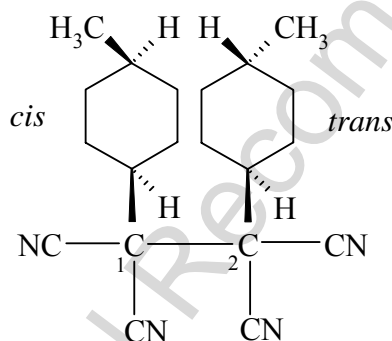
(1*R*,2*S*,4*r*)-1,2,4-trichlorocyclopentane (PIN)
1*r*,2*c*,4*c*-trichlorocyclopentane



bis[(1*r*,4*r*)-4-methylcyclohexyl]phosphane (PIN)
bis(*trans*-4-methylcyclohexyl)phosphane



[(1*s*,4*s*)-4-methylcyclohexyl]bis[(1*r*,4*r*)-4-methylcyclohexyl]phosphane (PIN)
(*cis*-4-methylcyclohexyl)bis(*trans*-4-methylcyclohexyl)phosphane

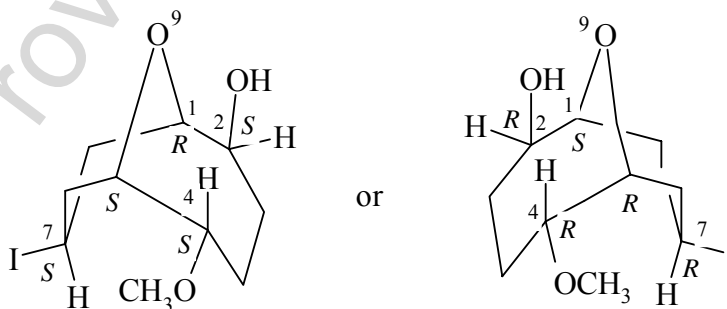


1-[(1*s*,4*s*)-4-methylcyclohexyl]-2-[(1*r*,4*r*)-4-methylcyclohexyl]ethane-1,1,2,2-tetracarbonitrile

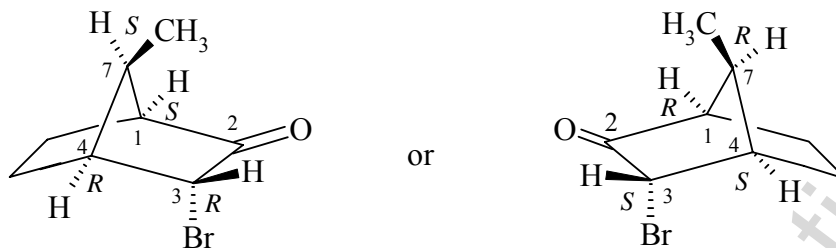
P-93.2.2 von Baeyer compounds

P-93.2.2.1 Chiral compounds

Examples:



rel-(1*R*,2*S*,4*S*,5*S*,7*S*)-7-iodo-4-methoxy-9-oxabicyclo[4.3.1]decan-2-ol (PIN)
(1*R**,2*S**,4*S**,5*S**,7*S**)-7-iodo-4-methoxy-9-oxabicyclo[4.3.1]decan-2-ol
(2-*exo*,4-*endo*,7-*exo*)-7-iodo-4-methoxy-9-oxabicyclo[4.3.1]decan-2-ol



rel-(1*R*,3*S*,4*S*,7*R*)-3-bromo-7-methylbicyclo[2.2.1]octan-2-one (PIN)
(1*R**,3*S**,4*S**,7*R**)-3-bromo-7-methylbicyclo[2.2.1]octan-2-one
(3-*endo*,7-*syn*)-3-bromo-7-methylbicyclo[2.2.1]octan-2-one

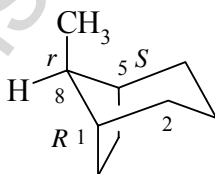


rac-(1*R*,2*S*,4*S*,5*R*)-3,6,8-trioxatricyclo[3.2.1.0^{2,4}]octane (PIN)
(1*RS*,2*SR*,4*SR*,5*RS*)-3,6,8-trioxatricyclo[3.2.1.0^{2,4}]octane

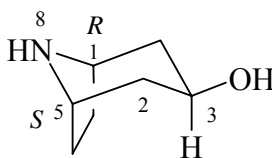
P-93.2.2.2 Achiral compounds

Pseudoasymmetric centers in achiral von Baeyer compounds are described by *r* and *s* stereodescriptors. The descriptors '*endo*', '*exo*', '*anti*' and '*syn*' may be used in general nomenclature to describe the relative configuration (see P-(2.2.1.2)). CIP stereodescriptors are used in preferred IUPAC names.

Examples:



(1*R*,5*R*,8*r*)-8-methylbicyclo[3.2.1]octane (PIN)
syn-8-methylbicyclo[3.2.1]octane



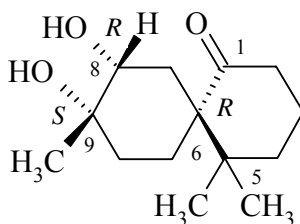
(1*R*,3*s*,5*S*)-8-azabicyclo[3.2.1]octan-3-ol (PIN)
(3-*exo*)-8-azabicyclo[3.2.1]octan-3-ol

P-93.2.3 Spiro compounds

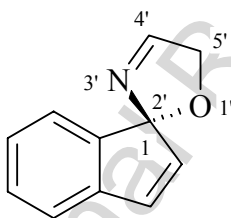
P-93.2.3.1 Chiral spiro atoms of the type Cabcd, where 'a' > 'b' > 'c' > 'd'

The stereodescriptors *R* and *S* are used when the spiro atom is surrounded by four atoms arranged as 'a' > 'b' > 'c' > 'd'. These stereodescriptors are preferred to '*cis*' and '*trans*' that can be used to describe the relative configuration of rings in dispiro compounds. The configuration of any chirality centers located on the spiro skeleton is described by stereodescriptors '*R*' and '*S*' by using the usual method.

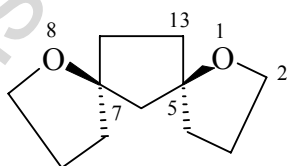
Examples:



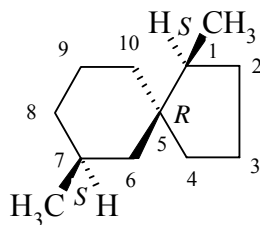
(*6R,8R,9S*)-8,9-dihydroxy-5,5,9-trimethylspiro[5.5]undecan-1-one (PIN)



(*R*)-5*H*-spiro[indene-1,2-(1,3)oxazole] (PIN)

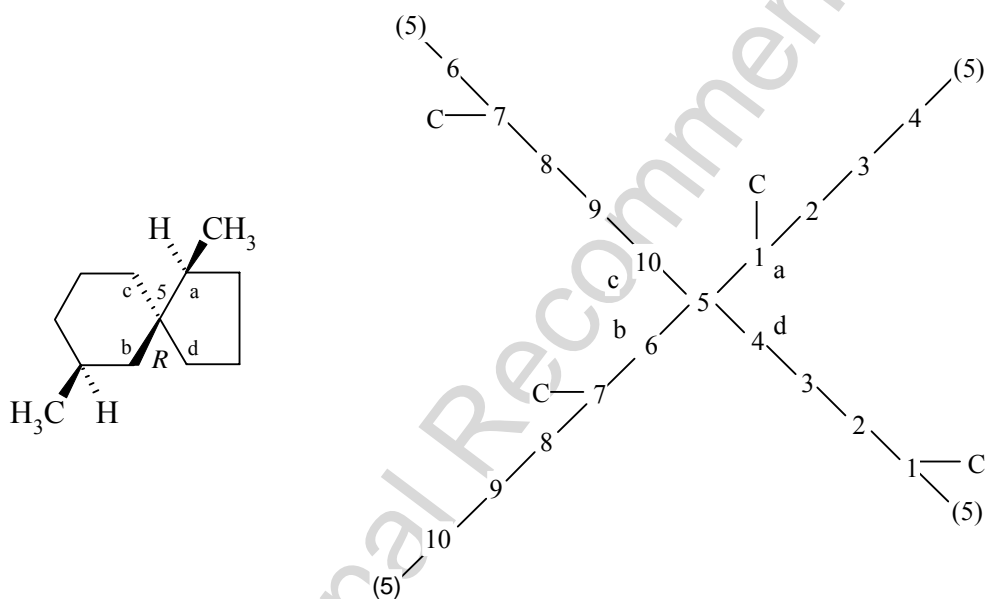


(*5R,7S*)-1,8-dioxadispiro[4.1.4.2]tridecane (PIN)
cis-1,8-dioxadispiro[4.1.4⁷.2⁵]tridecane (see P-92.1.5.2)



(1*S*,5*R*,7*S*)-1,7-dimethylspiro[4.5]decane

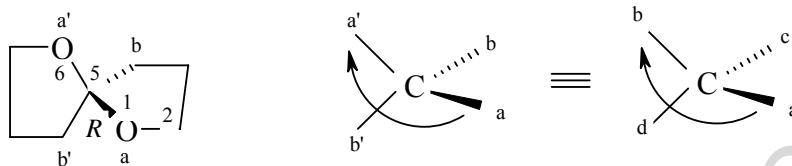
Construction of the digraph



P-93.2.3.2 Chiral spiro atoms of the type Cab, where 'a' > 'b'

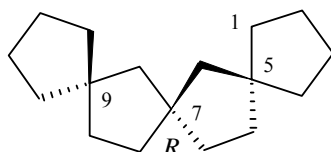
When a choice has to be made between two pairs of atoms or groups, as in the spiro compound below, an atom or group attached to the stereogenic center is chosen as reference, for example the oxygen atom in position 1 (see section 2.5, ref. 31). In the order of precedence 'a' > 'a'' > 'b' > 'b'', equivalent to 'a' > 'b' > 'c' > 'd', it is specified as 'a'. The oxygen atom in position 6 is chosen as 'a''. Among the remaining atoms or groups, two $-\text{CH}_2-$ groups, precedence is given to the atom or group that is in the same ring as atom or group 'a'; thus, the $-\text{CH}_2-$ group in position 4 is 'b' and the other $-\text{CH}_2-$ group is 'b''. Chirality is thus denoted by '*R*'.

Example 1:



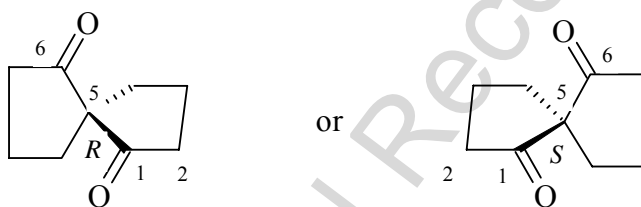
(5*R*)-1,6-dioxaspiro[4.4]nonane (PIN)

Example 2:



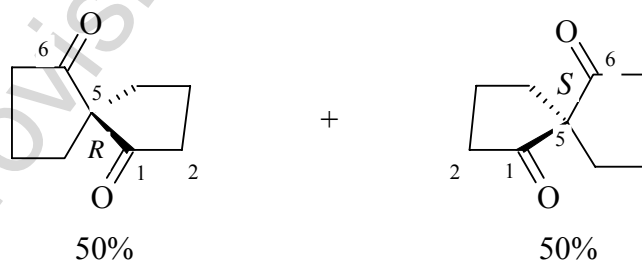
(7*R*)-trisp[4.1.1.4⁹.2⁷.2⁵]heptadecane (PIN)

Example 3:



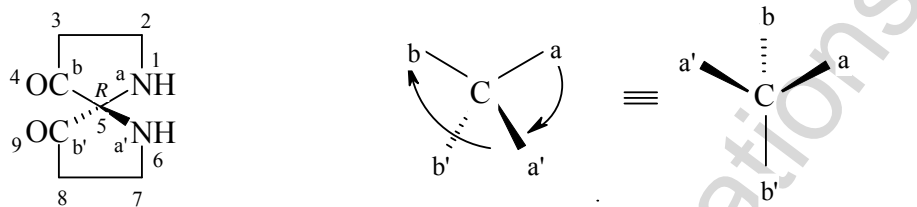
rel-(5*R*)-spiro[4.4]nonane-1,6-dione (PIN)
(5*R*^{*})-spiro[4.4]nonane-1,6-dione

Example 4:



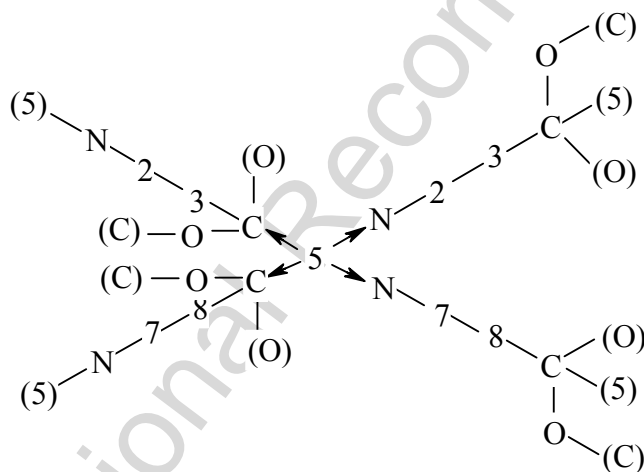
rac-(5*R*)-spiro[4.4]nonane-1,6-dione (PIN)
(5*RS*)-spiro[4.4]nonane-1,6-dione

Example 5:

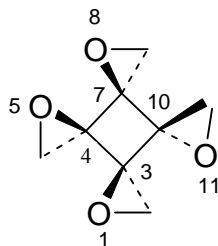


(5*R*)-1,6-diazaspiro[4.4]nonane-4,9-tetrone.(PIN)

In this (see section 2.5, ref. 31), the analysis to determine the priority amongst pairs 'a' > 'a'' > 'b' > 'b'' starts at the nitrogen atom numbered 1, then to the nitrogen atom numbered 6; they are ranked a and b, respectively. The branch, as shown in the digraph below, leading to the group that has precedence, i.e., 'a' > 'b'', is chosen as group 'c'.



Example 6:



(3*R*,4*s*,7*S*,10*s*)-tetraoxatetraspiro[2.0.2⁴.0.2⁷.0.2¹⁰.0³]dodecane (PIN)
1*r*,5*c*,8*c*,11*t*-tetraoxatetraspiro[2.0.2⁴.0.2⁷.0.2¹⁰.0³]dodecane

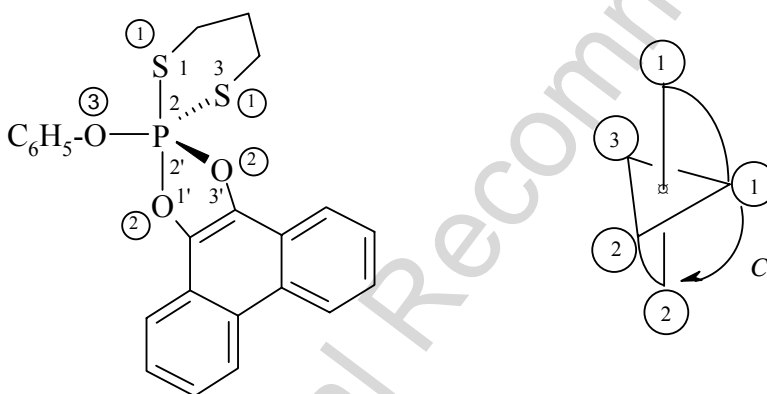
In this example, chiral and pseudoasymmetric centers are present. Application of sequence rules (3) and (4) are necessary.

Guide to name construction:

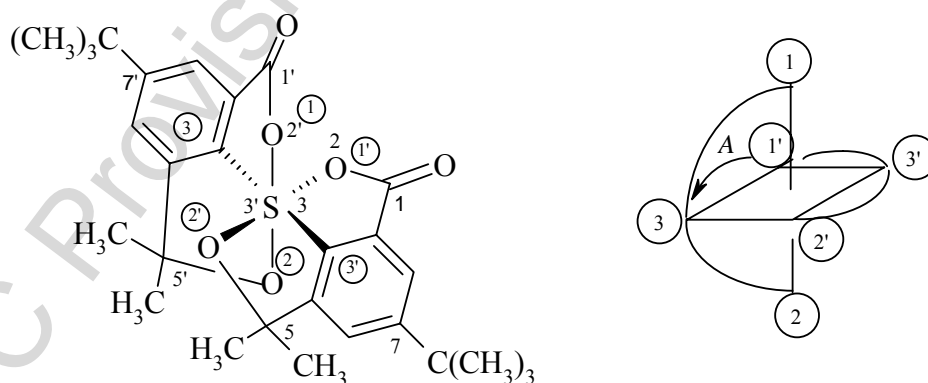
- the numbering is chosen that gives a 'cis' attachment at the first point of difference (see P-14.4 k); thus '1*r*,5*c*,8*c*,11*t*', not '1*r*,5*t*,8*c*,11*c*';
- configurations at C-3 and C-7 are determined by using sequence rule (4), *like* precedes *unlike*, in accordance with the methodology described in P-92.1.1.2;
- configurations at C-4 and C-10 are determined by using sequence rule (5), 'R' precedes 'S', in accordance with the methodology described in P-92.1.4.

P-93.2.3.3 Nontetrahedral stereogenic centers

As described in P-92.1.8, stereodescriptors used in coordination chemistry describe the relative and the absolute configuration of spiro compounds with λ^4 , λ^5 and λ^6 -hetero spiro atoms. Examples:



(*TBPY-5-12-C*)-2-phenoxy-2 λ^5 -spiro[1,3,2-dithiaphosphinane-2,2'-phenanthro[9,10-*d*][1,3,2]dithiaphosphole] (PIN)

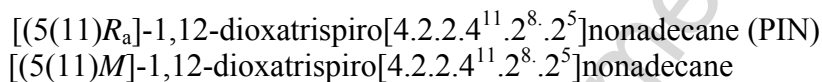
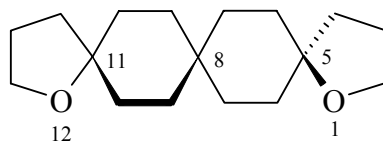


(*OC-6-22'-A*)-7,7'-di-*tert*-butyl-5,5,5',5'-tetramethyl-1*H*,1'*H*,5*H*,5'*H*-3 λ^6 ,3'-spirobi[[1,2]oxathiolo[4,3,2-*hi*][2,1]benzoxathiole]-1,1'-dione (PIN)

P-93.2.3.4 Axial chirality of spiro compounds

The stereodescriptors '*M*' and '*P*', or '*R_a*' and '*S_a*' are used to describe axial chirality of spiro compounds. The stereodescriptors '*R_a*' and '*S_a*' are used in preferred IUPAC names. Locants denoting the first and the last spiro atoms involved in the configuration are placed before the stereodescriptors.

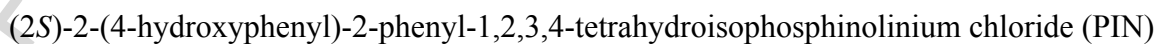
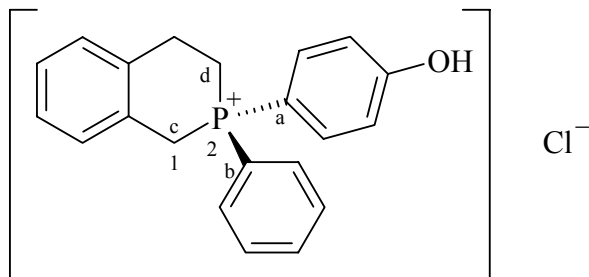
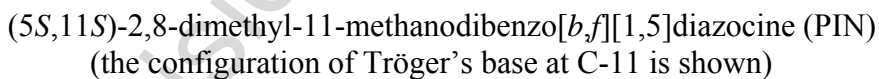
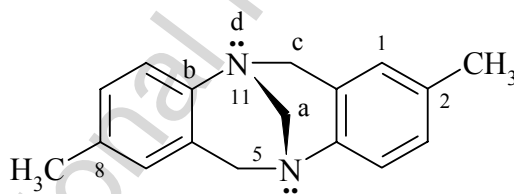
Example:

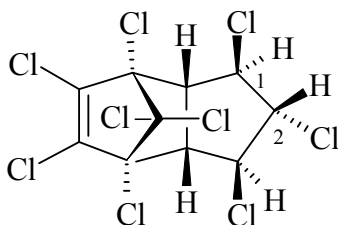


P-93.2.4 Fused and bridged fused compounds

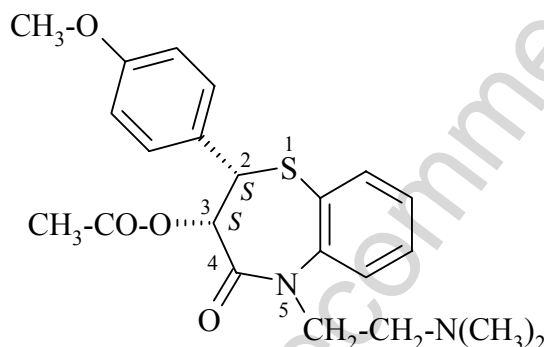
P-93.2.4.1 A great variety of chiral and achiral carbocyclic and heterocyclic compounds are described by the appropriate symbols '*R*', '*S*', '*r*', and '*s*'. A few examples illustrates the chirality associated with carbon and heteroatoms. The first example is the Tröger's base showing the rare chirality associated with amines (see ref. 38).

Examples:





(1*R*,2*r*,3*S*,3*aR*,4*S*,7*R*,7*aS*)-1,2,3,4,5,6,7,8,8-nonachloro-2,3,3*a*,4,7,7*a*-hexahydro-4,7-methano-1*H*-indene

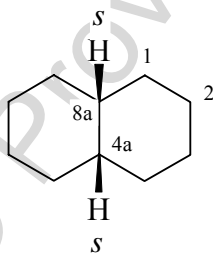


(2*S*,3*S*)-5-[2-(dimethylamino)ethyl]-2-(4-methoxyphenyl)-4-oxo-2,3,4,5-tetrahydro-1,5-benzothiazepin-3-yl acetate (PIN)

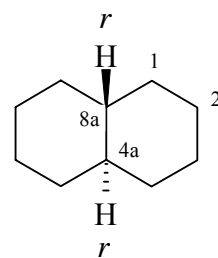
P-93.2.4.2 Configuration of saturated fused systems

Saturated fused systems exhibit ‘*cis-trans*’ isomerism. The CIP ‘*r*’ and ‘*s*’ stereodescriptors are preferred to ‘*cis*’ and ‘*trans*’ to describe the pseudoasymmetric centers when appropriate. The ‘*cisoid*’ and ‘*transoid*’ non CIP stereodescriptors are, although they are not preferred in preferred IUPAC names.

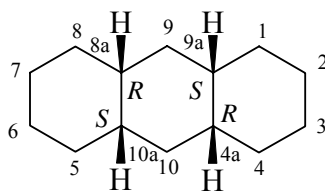
Examples:



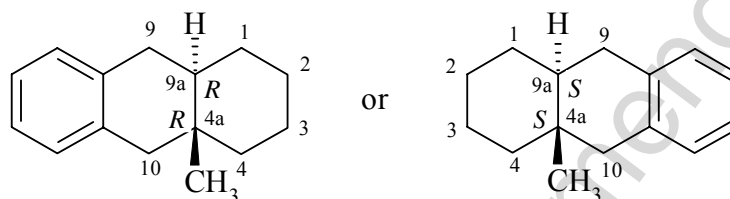
(4*as*,8*as*)-decahydronaphthalene (PIN)
cis-decahydronaphthalene



(4*ar*,8*ar*)-decahydronaphthalene (PIN)
trans-decahydronaphthalene



(4a*R*,8a*R*,9a*S*,10a*S*)-tetradecahydroanthracene (PIN)

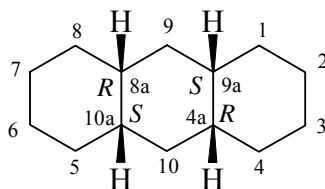


rel-(4a*R*,9a*R*)-4a-methyl-1,2,3,4,4a,9,9a,10-octahydroanthracene (PIN)
(4a*R**,9a*R**)-4a-methyl-1,2,3,4,4a,9,9a,10-octahydroanthracene

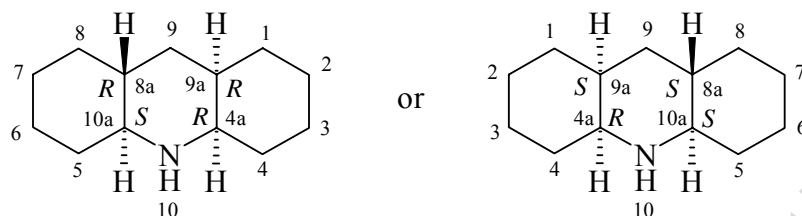
The descriptors '*cisoid*' and '*transoid*'

Steric relations at more than one pair of saturated fusion atoms in a fused system are denoted by '*cis*' and '*trans*', each followed by a hyphen, and, if necessary, the corresponding locant of the lower-numbered fusion atom and a second hyphen, all placed before the name of the ring system. Steric relations between the nearest atoms of *cis* or *trans* fusion pairs have been described by descriptors '*cisoid*' or '*transoid*' followed by a hyphen and when required, the corresponding locants and a second hyphen, the whole placed between the designations of the '*cis*' or '*trans*' junctions concerned. The term 'nearest atom' denotes those atoms linked together through the smallest number of atoms, irrespective of the numbering of the system. When a choice remains between nearest atoms, the pair containing the lower numbered atom is selected. The descriptors '*cisoid*' and '*transoid*' are not abbreviated. These descriptors are no longer recommended. The notation '*R*' and '*S*', with the descriptor '*rel*' is used instead for describing an enantiomer whose relative configuration only is known

Examples:



(4a*R*,8a*R*,9a*S*,10a*S*)-tetradecahydroanthracene (PIN)
cis-cisoid-cis-tetradecahydroanthracene (no longer recommended)
(this compound is achiral)

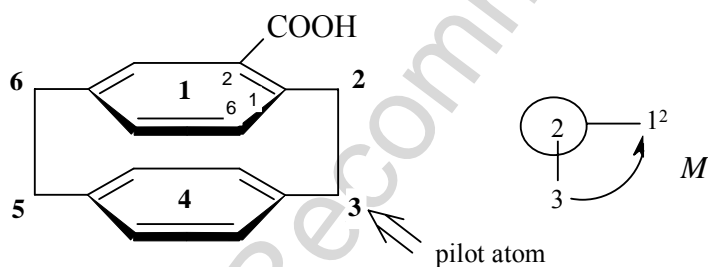


rel-(4a*R*,8a*R*,9a*R*,10a*S*)-tetradecahydroacridine (PIN)
cis-4a-*cisoid*-4a,10a-*trans*-10a-tetradecahydroacridine (no longer recommended)

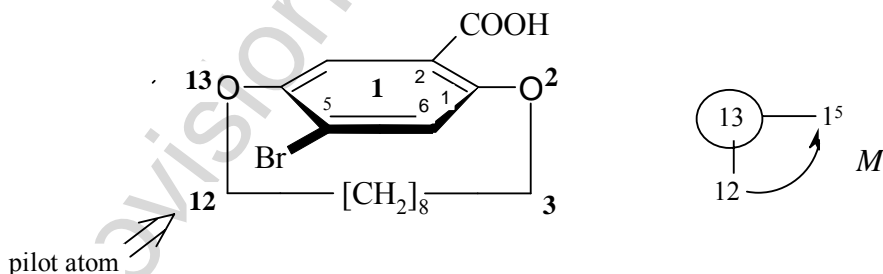
P-93.2.5 Cyclophanes

The descriptors '*R_p*' and '*S_p*' are preferred to '*P*' and '*M*', respectively

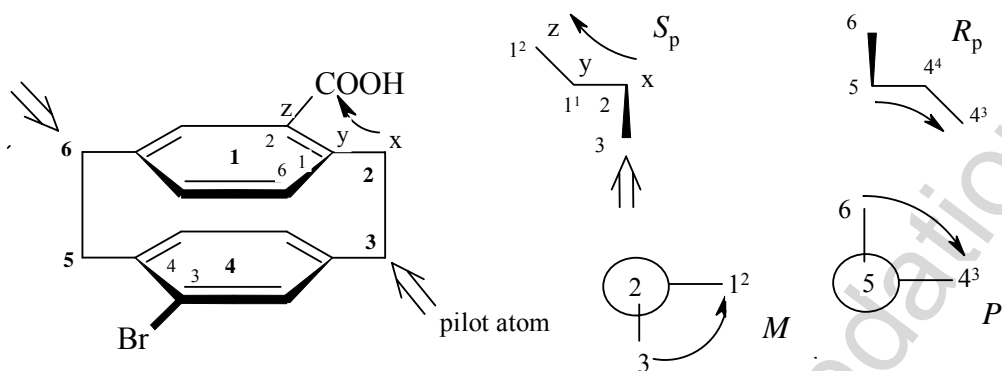
Example:



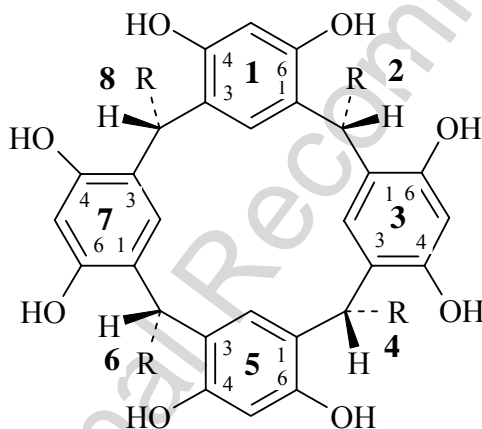
(*S_p*)-1,4(1,4)-dibenzenacyclohexaphane-1²-carboxylic acid (PIN)
(*M*)-1,4(1,4)-dibenzenacyclohexaphane-1²-carboxylic acid



(*S_p*)-1⁵-bromo-1(1,4)-benzene-2,13-dioxacyclotridecaphane-1²-carboxylic acid (PIN)
(*M*)-1⁵-bromo-1(1,4)-benzene-2,13-dioxacyclotridecaphane-1²-carboxylic acid



(1*S_p*,4*R_p*)-4³-bromo-1,4(1,4)-dibenzacyclohexaphane-1²-carboxylic acid (PIN)
(1*M*,4*P*)-4³-bromo-1,4(1,4)-dibenzacyclohexaphane-1²-carboxylic acid



R = -CH₂-[CH₂]₇-CH₃

(2*s*,4*s*,6*s*,8*s*)-2,4,6,8-tetranonyl-1,3,5,7(1,3)-tetrabenzacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octol (PIN)

2*r*,4*c*,6*c*,8*c*-tetranonyl-1,3,5,7(1,3)-tetrabenzacyclooctaphane-1⁴,1⁶,3⁴,3⁶,5⁴,5⁶,7⁴,7⁶-octol

P-93.2.6 Fullerenes

P-93.2.6.1 Definitions and general methodology

Only general principles for describing stereochemical configuration of fullerenes are discussed briefly and exemplified in this section. Describing stereochemical configuration of fullerenes is extremely complex because of different factors such as the numbering of the fullerene molecule, systematic or trivial (in these recommendations, only the systematic numbering given in ref. 10 is used), the nature and disposition of substituent groups on the fullerene, and the plurality of stereodescriptors necessary to fully describe their stereochemical configuration. For a full discussion of the description of fullerene configuration, one must go to the original publication (Section 17 in ref. 10).

For the purpose of describing stereochemical configuration, fullerenes and their derivatives are classified into four types depending on the origin of their chirality.

- P-93.2.6.1.1 Type 1. Inherently chiral parent fullerenes;
- P-93.2.6.1.2 Type 2. Substituted fullerenes inherently chiral because of their substitution pattern;
- P-93.2.6.1.3 Type 3. Substituted fullerenes noninherently chiral because of their substitution pattern;
- P-93.2.6.1.4 Type 4. Chirality due to chiral substituents.
- P-93.2.6.1.5 Superimposition of stereogenic elements in a fullerene molecule

The four types are classified by the 'substitution test' that consists of changing the substituents in a single fullerene unit into a 'achiral test substituent', 'T', and verifying the chirality of the fullerene so modified by the presence of 'T' substituents (see Fig. 9-1).

P-93..2.6.1.1 Type 1. Inherently chiral parent fullerenes.

The two fullerene molecules described in Section P-27, $(C_{60}-I_h)[5,6]$ fullerene and the $(C_{70}-D_{5h(6)})[5,6]$ fullerene, are achiral; they are not inherently chiral. To the contrary, the $(C_{76}-D_2)[5,6]$ fullerene shown below is inherently chiral. The numbering of an inherently chiral fullerene applies to a specific enantiomer; the other enantiomer has a numbering that is the mirror-image of the first numbering. A description of the handedness of the numbering scheme is sufficient to unambiguously characterize the absolute configuration of the fullerene. The viewer looking at the polygon in which the numbering starts from outside the fullerene cage, traces a path from C-1 to C-2 to C-3, which is never aligned in a fullerene structure. If this path describe a clockwise direction, the configuration is indicated by the stereodescriptor $^{f,x}C$, where the superscript 'f' indicates that the descriptor refers to a fullerene, and the superscript 'x' is either 's' for the systematic numbering or 't' for the trivial numbering described in P-27.3. If the path from C-1 to C-2 to C-3 describes an anticlockwise direction, the descriptor is $^{f,x}A$. Thus, the fullerene on the left hand side below is described by the stereodescriptor $^{f,x}C$; its name is $(^{f,s}C)-(C_{76}-D_2)[5,6]$ fullerene. The fullerene on the right hand side is $(^{f,s}A)-(C_{76}-D_2)[5,6]$ fullerene. The systematic numbering is that used by Chemical Abstracts Service (ref. 16).

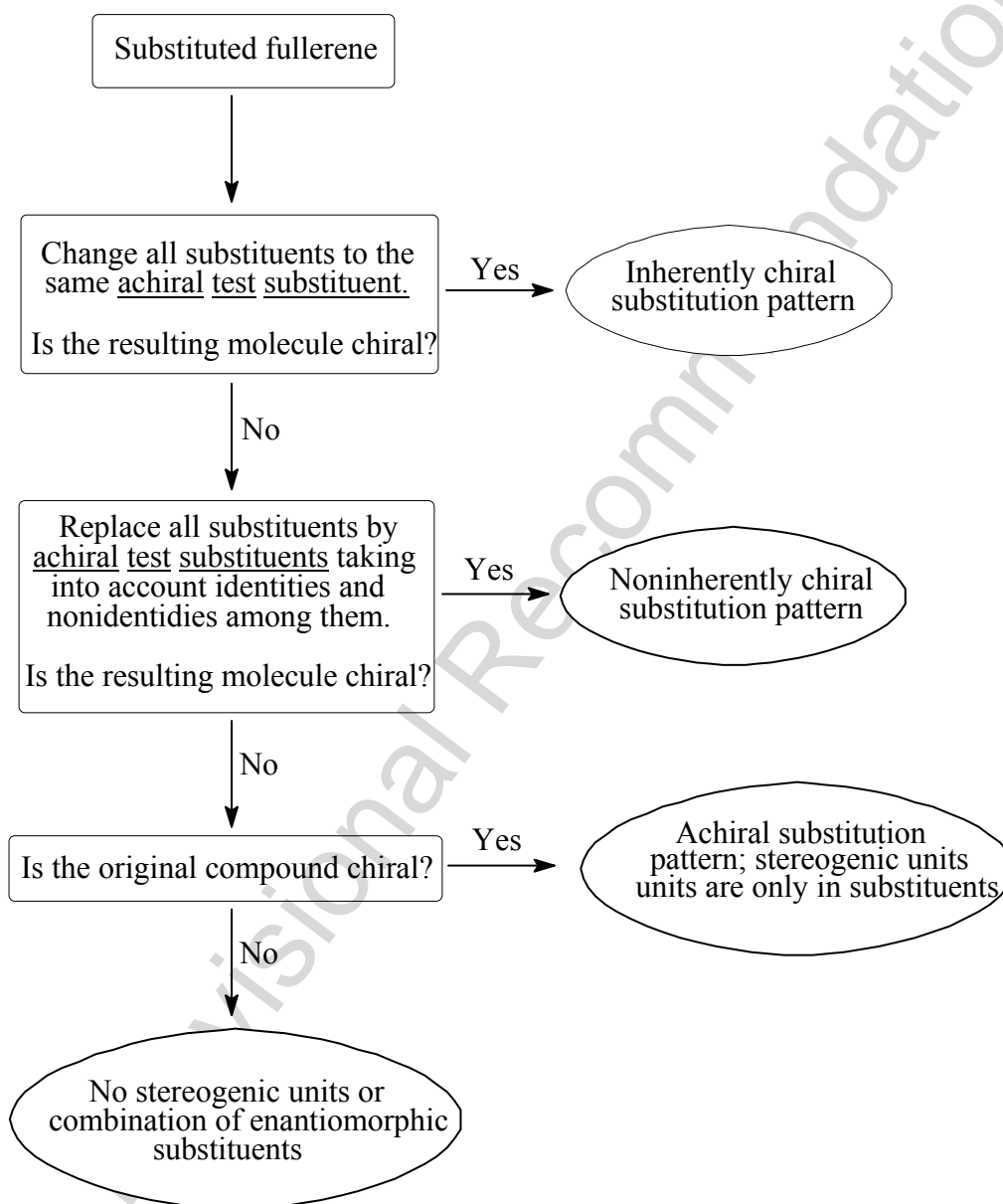
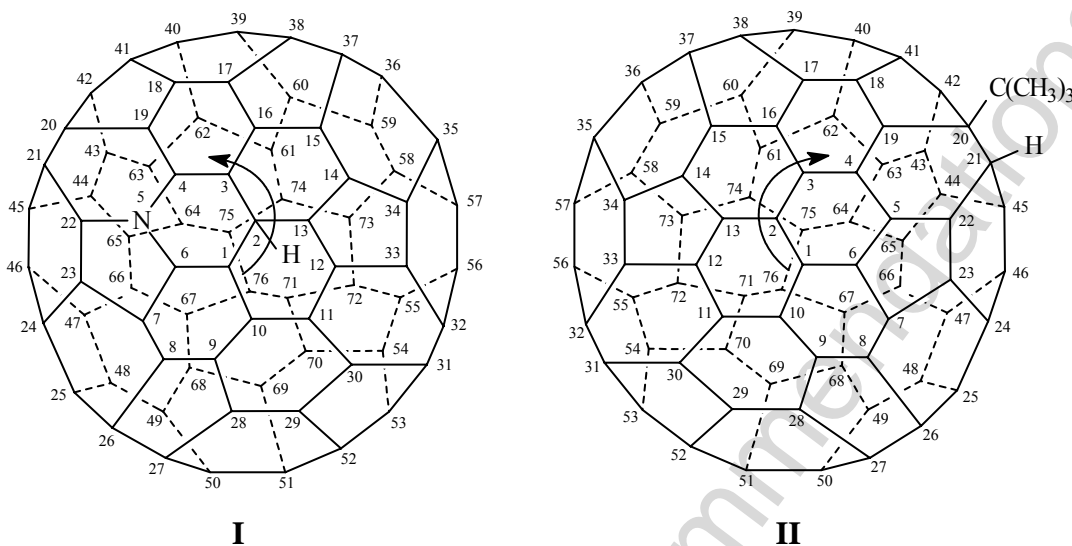


Fig. 9-1 Classification of fullerene chirality by a stepwise substitution pattern

Examples:



I (^{f,s}A)-2*H*-5-Aza-(C₇₆-D₂)[5,6]fullerene

II (^{f,s}C)-20-*tert*-Butyl-20,21-dihydro(C₇₆-D₂)[5,6]fullerene

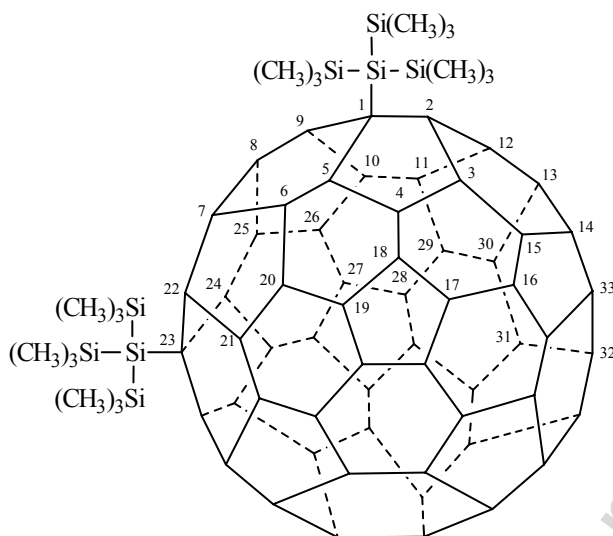
Note: The numbering used in these examples is that currently used in CAS index nomenclature (see ref 16).

P-93.2.6.1.2 Type 2. Substituted fullerenes inherently chiral because of their substitution pattern.

Derivatives of achiral (and chiral) parent fullerenes in which the presence of substituents, chiral or achiral, identical or different, on the fullerene skeleton, creates a chiral substitution pattern are said to have an inherently chiral substitution pattern.

Fullerene compounds of this type are all substituted achiral fullerenes. They have an inherently chiral substitution pattern if the existence of enantiomers is inherent to the geometrical arrangement of the substitution sites on the fullerene parent regardless of whether the substituents are identical or different. In these fullerene derivatives there is a unique numbering scheme that leads to the lowest set of locants for the substituents. As in P-63.2.6.1, the stereodescriptors are '^{f,x}C' and '^{f,x}A'.

Example:



(^{f,s}C)-1,23-Bis[1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl]-1,23-dihydro-(C₆₀-I_h)[5,6]-fullerene

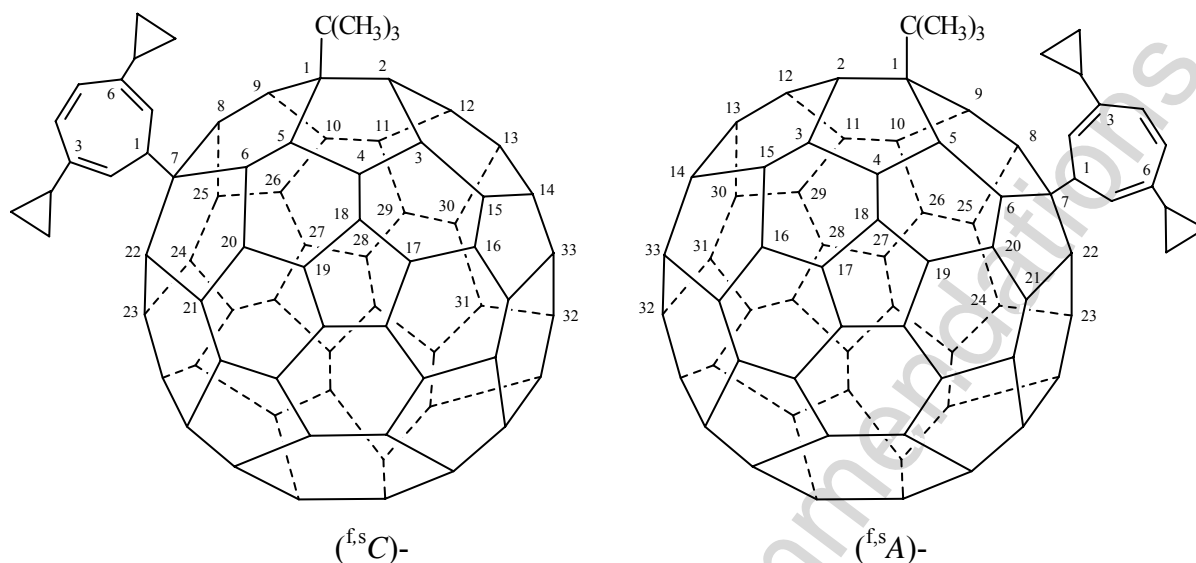
Explanation: Locants for the substituents are 1,23 for clockwise numbering. But for anticlockwise numbering they are 1,29 and since 1,23 is lower than 1,29 according to the principle of lowest locants (see P-14.) and therefore clockwise numbering is preferred. For the enantiomer, the lower locants 1,23 would be obtained on anticlockwise numbering and the descriptor would be (^{f,s}A)-.

P-93.2.6.1.3 Type 3. Substituted fullerenes noninherently chiral because of their substitution pattern.

Derivatives of achiral parent fullerenes in which a chiral substitution pattern on the fullerene is due only to nonidentities among the substituents are have noninherently chiral substitution pattern.

The CIP system is used to rank substituents according to sequence rules (1) or (2) (see P-91.1.1). In the following enantiomeric disubstituted fullerenes, the *tert*-butyl group has precedence over the 3,6-dicyclopropylcyclohepta-2,4,6-trien-1-yl group. Stereodescriptors '^{f,x}C' and '^{f,x}A' are used to describe the absolute configuration, as indicated in P-93-2.6.1., in conformity with the path C-1 to C-2 to C-3 that is clockwise or anticlockwise.

Example:



1-*tert*-Butyl-7-(3,6-dicyclopropylcyclohepta-2,4,6-trien-1-yl)-1,7-dihydro-
(C₆₀-I_h)[5,6]fullerene

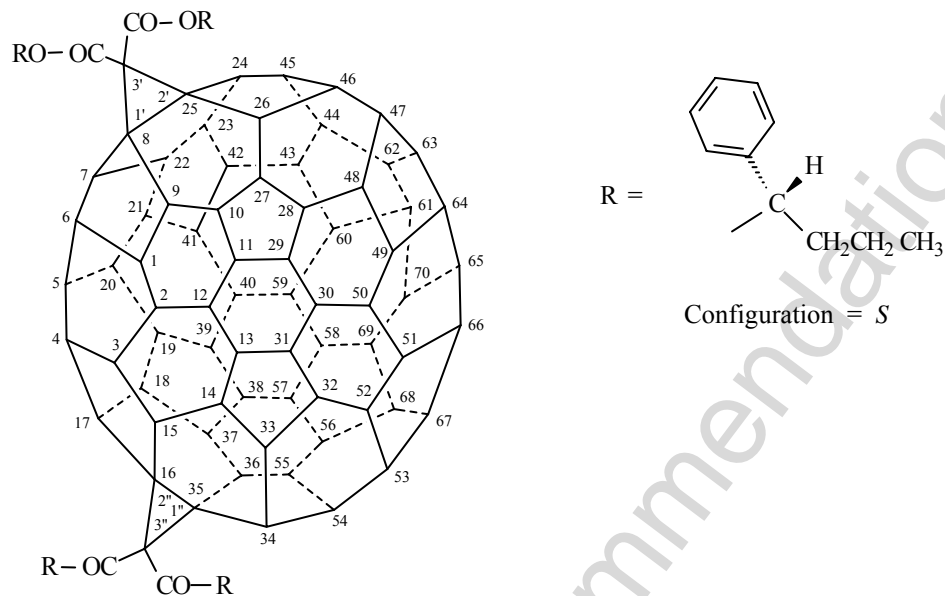
Explanation: This compound is chiral only because the substituents are constitutionally different. The parent fullerene is achiral and it does not have an inherently chiral substitution pattern because replacement of both substituents by the same achiral test substituent, 'T', results in an achiral compound. Therefore it has a noninherently chiral substitution pattern. The *tert*-butyl group is assigned the locant '1' because its CIP priority is higher than that of the 3,6-dicyclopropyl-cyclohepta-2,4,6-trien-1-yl group.

P-93.2.6.1.4 Type 4. Chirality due to chiral substituents.

Derivative of achiral parent fullerenes in which the presence of chiral substituents does not create a chiral substitution pattern have the stereogenic units located exclusively in the substituents.

In derivatives of this type, the chirality located in substituents is expressed by the usual CIP stereodescriptors. In the following example, the '*S*' configuration for the organyl group present in the -CO-O-R substituents is the only stereodescripto needed to express the configuration of the compound.

Example:



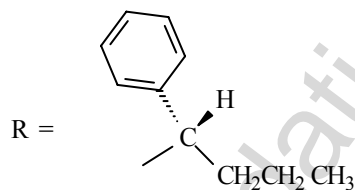
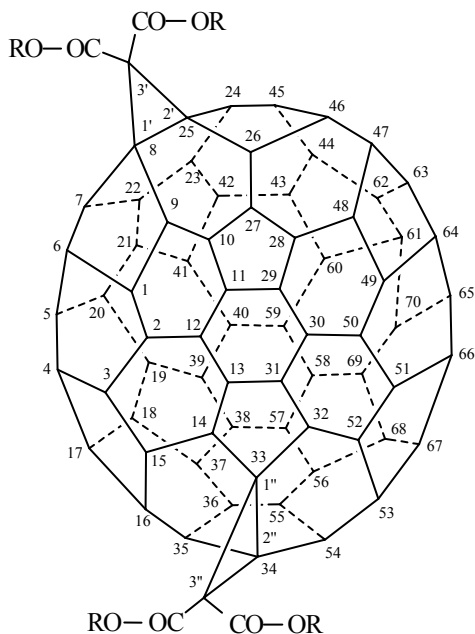
tetrakis[(1*S*)-1-phenylbutyl] 3'*H*,3''*H*-dicyclopropa[8,25:16,35](*C*₇₀-*D*_{5h(6))-[5,6]fullerene-3',3',3'',3''-tetracarboxylate}

Explanations:

- This fullerene derivative is chiral. The parent fullerene is achiral and the derivative has an achiral substitution pattern. The configuration of the substituents are described by CIP stereodescriptors, as described in P-92. .
- If the esters of the acid in the above example were different, the parent fullerene and its substitution pattern would still be achiral and therefore any chirality of the original compound would be due to stereogenic centers located in the substituents.

P-93.2.6.2 Superimposition of stereogenic elements in a fullerene molecule. If a fullerene derivative with an inherently or noninherently chiral substitution pattern carries chiral substituents, the configuration of both types of stereogenic elements has to be indicated. The two types are independent of each other and the configuration of both must be specified for a full description of the compound.

Example:



Configuration = *S*

Configuration = (^{f,s}C)-

tetrakis[(1*S*)-1-phenylbutyl] (^{f,s}C)-3'*H*,3''*H*-dicyclopropa[8,25:33,34]-
(C₇₀-D_{5h(6)})[5,6]fullerene-3',3',3'',3''-tetracarboxylate

Explanation: The chiralities of the stereogenic centers in the esters are super-imposed on the descriptor for the fullerene with the inherently chiral substitution pattern. The enantiomer would be named:

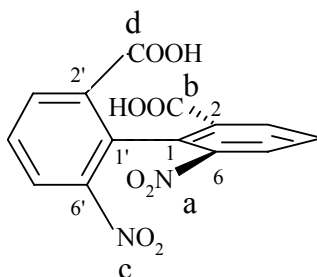
tetrakis[(1*R*)-1-phenyl-butyl] (^{f,s}A)-3'*H*,3''*H*-dicyclopropa[8,25:33,34]-
(C₇₀-D_{5h(6)})[5,6]fullerene-3',3',3'',3''-tetracarboxylate

and the same for the various diastereoisomers.

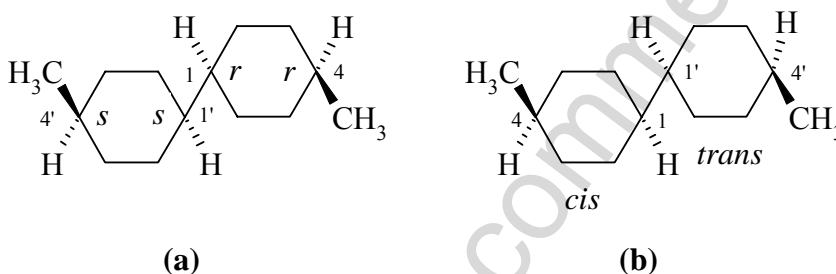
P-93.2.7 Ring assemblies

In preferred IUPAC names, appropriate CIP stereodescriptors are used to describe conformations in accordance with the nature of stereogenic centers. To describe axial chirality, the stereodescriptors '*R_a*' and '*S_a*' are preferred to P and M, respectively'.

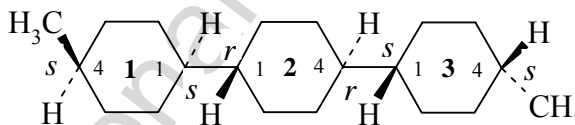
Examples:



(*R_a*)-6,6'-dinitro-1,1'-biphenyl-2,2'-dicarboxylic acid (PIN)
(*M*)-6,6'-dinitro-1,1'-biphenyl-2,2'-dicarboxylic acid



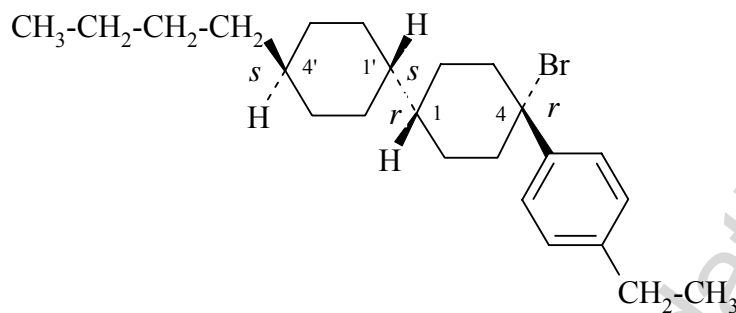
(a) [1*r*,1'*s*,4*r*,4'*s*]-4,4'-dimethyl-1,1'-bicyclohexane (PIN)
(b) [1(4)*cis*,1'(4')*trans*]-4,4'-dimethyl-1,1'-bicyclohexane



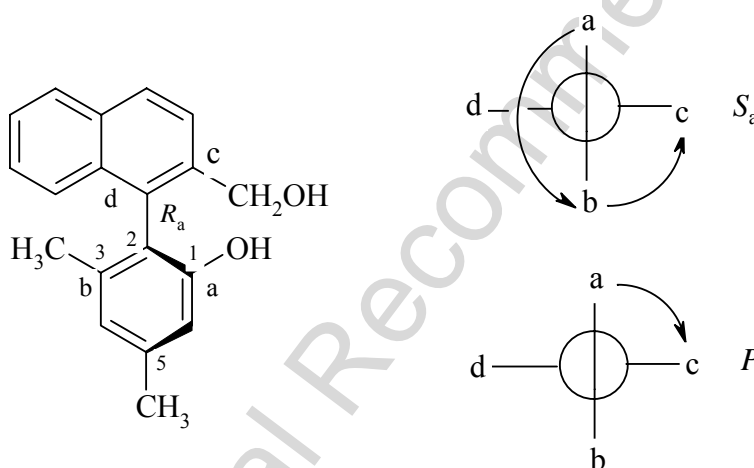
[1¹*s*,1⁴*s*,2¹*r*,2⁴*r*,3¹*s*,3⁴*s*]-1⁴,3⁴-dimethyl-1¹,2¹:2⁴,3¹-tercyclohexane (PIN)
[1¹(1⁴)*cis*,2¹(2⁴)*trans*,3¹(3⁴)*cis*]-1⁴,3⁴-dimethyl-1¹,2¹:2⁴,3¹-tercyclohexane

When more than two positions are substituted in an individual ring, achiral compounds are named by using the stereodescriptors '*r*' and '*s*'. The normal numbering of ring assemblies is applied (see P-28.2 and P-28.3).

Example:

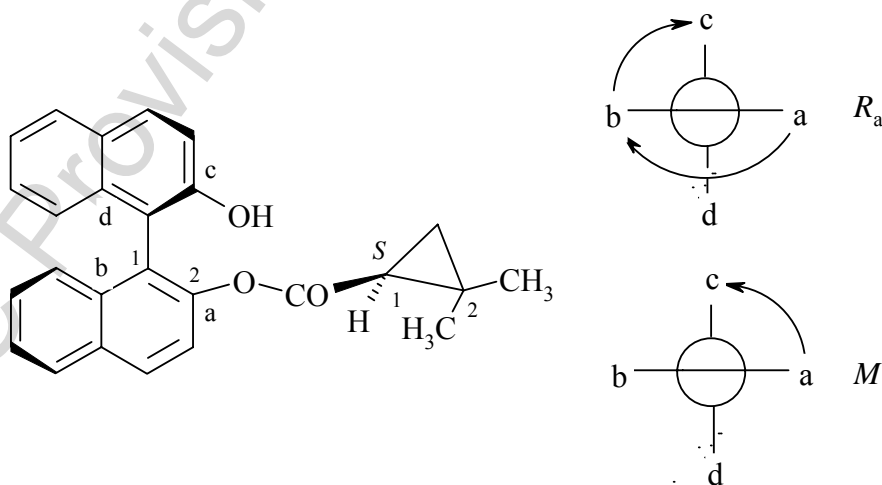


(1*r*,1'*s*,4*r*,4'*s*)-4-bromo-4'-butyl-4-(4-ethylphenyl)-1,1'-bicyclohexane (PIN)



(2*S_a*)-2-[2'-(hydroxymethyl)naphthalen-1-yl]-3,5-dimethylphenol (PIN)

(2*P*)-2-[2'-(hydroxymethyl)naphthalen-1-yl]-3,5-dimethylphenol



(1*R_a*)-2'-hydroxybinaphthalen-2-yl (1*S*)-2,2-dimethylcyclopropane-1-carboxylate (PIN)

(1*M*)-2'-hydroxybinaphthalen-2-yl (1*S*)-2,2-dimethylcyclopropane-1-carboxylate

P-93.3 Assemblies of chains and rings

Preferred stereodescriptors, as described in Sections P-92 and P-93.1 and P-93.2, are used to describe assemblies of rings and chains.

P-93.3.1 Specification of chirality

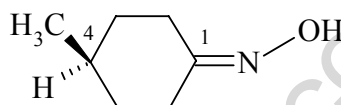
P-93.3.2 Specification of *cis-trans* isomerism

P-93.3.3 Specification of chirality and *cis-trans* isomerism

P-93.3.1 Specification of chirality

Compounds composed of a ring and a double bond arranged as an allene system exhibit axial chirality which is described by the chirality stereodescriptors R_a or S_a that are preferred to M and P , respectively.

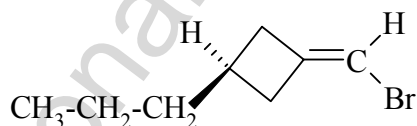
Examples:



(R_a)-(4-methylcyclohexylidene)hydroxylamine (PIN)

(M)-(4-methylcyclohexylidene)hydroxylamine

(M)-4-methylcyclohexanone oxime



(S_a)-(3-(bromomethylidene)-1-propyl)cyclobutane (PIN)

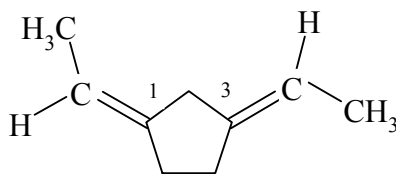
(P)-(3-(bromomethylidene)-1-propyl)cyclobutane

P-93.3.2 Specification of '*cis-trans*' isomerism

Cumulenes having an odd number of double bonds in which a double bond has been replaced by a ring are considered here. Their configuration is described by the stereodescriptors associated with '*cis-trans*' isomerism, i.e., ' Z ' or ' E '.

P-93.3.2.1 When the configuration of each double bond can be directly determined by applying the method recommended for double bonds described in P-92.1.6.2, stereodescriptors ' Z ' or ' E ' are used to describe the configuration of each double bond.

Example:



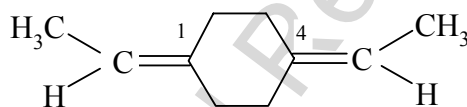
(1*Z*,3*E*)-1,3-diethylidenecyclopentane (PIN)

P-93.3.2.2 Two methods are used to describe the configuration of assemblies that cannot be named by the method described above in P-93.3.3.2.1:

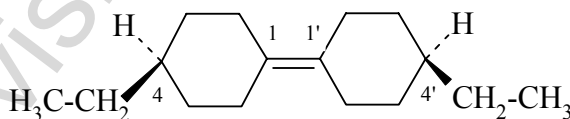
- (1) the entire molecule is described by using the stereodescriptors '*Z*' and '*E*', or '*cis*' and '*trans*', when the system is assimilated to an extended double bond;
- (2) auxiliary stereodescriptors are used as in P-921.6.2.1 to determine the configuration of each double bond;

Stereodescriptors describing the entire molecule are preferred to those determined by applying the method of auxiliary descriptors; stereodescriptors '*Z*' and '*E*' are preferred to '*cis*' and '*trans*'.

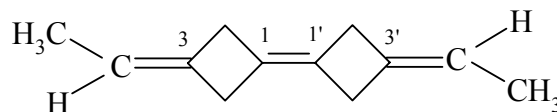
Examples:



[1(4)*Z*]-1,4-diethylidenecyclohexane (PIN) [method (1)]
[1(4)-*cis*]-1,4-diethylidenecyclohexane
1,4-di[(*Z*)-ethylidene]cyclohexane [method (2)]



[4(4')-*Z*]-4,4'-diethyl-1,1'-bi(cyclohexylidene) (PIN) [method (1)]
[4(4')-*cis*]-4,4'-diethyl-1,1'-bi(cyclohexylidene)

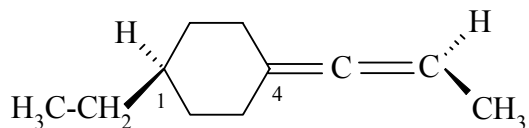


[3(3')*E*]-3,3'-diethylidene-1,1'-bi(cyclobutylidene) (PIN)
[3(3')-*trans*]-3,3'-diethylidene-1,1'-bi(cyclobutylidene)
3,3'-di[(*E*)-ethylidene-1,1'-bi(cyclobutylidene)]

P-93.3.3 Specification of configuration in rings and chains

Stereodescriptors must be adapted to the many configurations that have to be described in compounds where rings and chains can be chiral. CIP stereodescriptors are preferred to non CIP stereodescriptors in preferred names.

Examples:

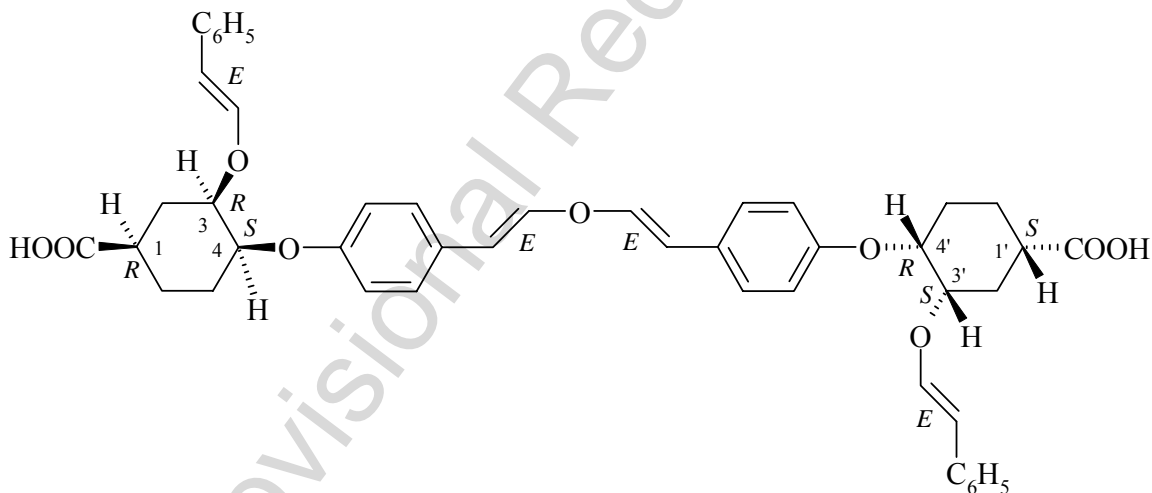


[1(4)-Z]-1-ethyl-4-(prop-2-en-1-ylidene)cyclohexane] (PIN)

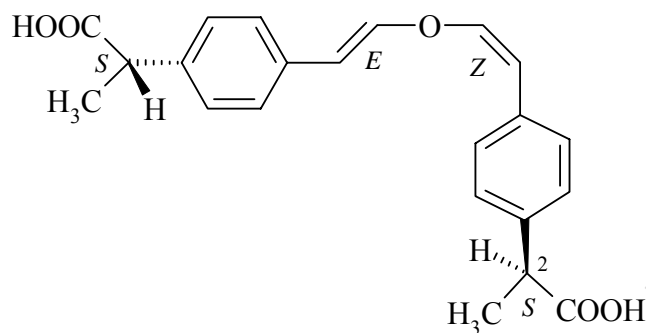
[1(4)-*cis*]-1-ethyl-4-(prop-2-en-1-ylidene)cyclohexane

(1*S*,4*S_a*)-1-ethyl-4-(prop-2-en-1-ylidene)cyclohexane

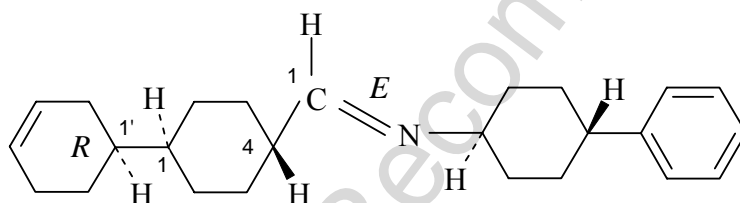
(the configuration of this compound can be described as *Z* for the entire molecule, or as a combination of a chiral center *S* at C-1 and axial chirality *S_a* for the allenic portion of the molecule)



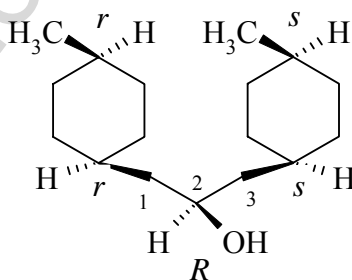
(1*R*,1'*S*,3*R*,3'*S*,4*S*,4'*R*)-4,4'-{oxybis[(1*E*)-ethene-2,1-diyl-4,1-phenyleneoxy]}bis(3-[(1*E*)-2-phenylethenyl]oxy)cyclohexane-1-carboxylic acid) (PIN)



(2*S*)-2-[4-[(1*E*)-{2-[(1*Z*)-2-[4-[(1*S*)-1-carboxyethyl]phenyl]ethenyl]oxy}ethenyl]phenyl]propanoic acid
(a multiplicative name is not allowed; lack of identical components in the linking substituent)



(1*E*)-1-[(1'*R*,1*r*,4*r*)-1,1'-bi(cyclohexan)-3'-en-4-yl]-*N*-[(1*r*,4*r*)-4-phenylcyclohexyl]methanimine (PIN)
(1*E*)-1-[(1'*R*,1(4)-*trans*)-1,1'-bi(cyclohexan)-3'-en-4-yl]-*N*-[(*trans*)-4-phenylcyclohexyl]methanimine



(2*R*)-1-[(1*r*,4*r*)-4-methylcyclohexyl]-3-[(1*s*,4*s*)-4-methylcyclohexyl]propan-2-ol (PIN)

Guide to name construction:

- in accordance with the corresponding digraph, stereodescriptors 'r' and 's' are assigned to the two positions 1 and 4 of the cyclohexane rings as indicated in P-92.1.4.2;
- the cyclohexane ring having the stereodescriptors '1*r*','4*r*' is attached to carbon C-1 of the chain;

- (c) by using 'Sequence Rule 4' ('r' precedes 's'), the configuration 'R' is assigned to carbon C-2 of the chain.

P-94 Conformation and conformational descriptors

P-95.1 Definition

A conformation is the spatial arrangement of the atoms affording distinction between stereoisomers which can be interconverted by rotations about formally single bonds, as exemplified for conformers A and B in Fig. 2.

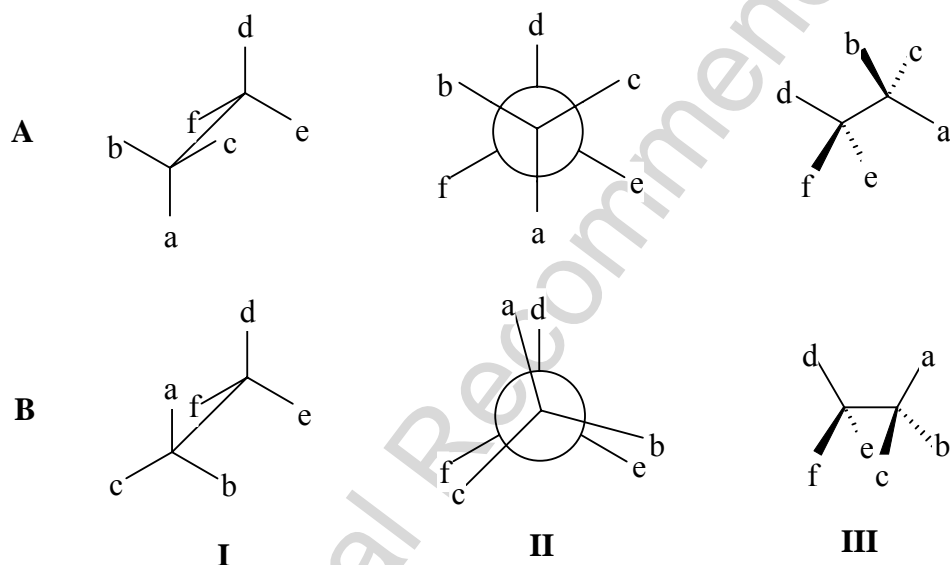


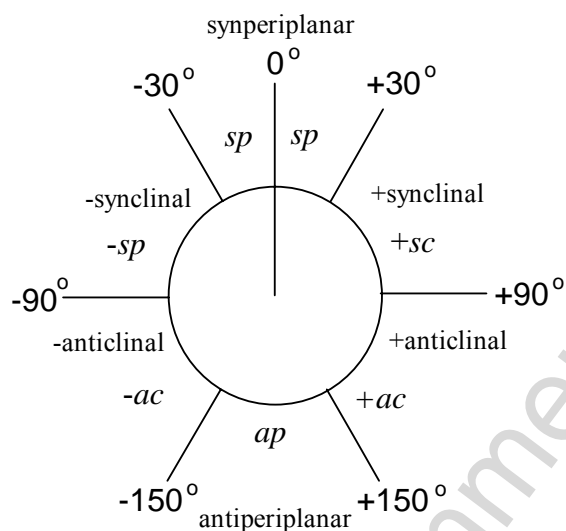
Fig. 9-2. Three different representations of two conformers A and B.

- I** Sawhorse projection
II Newman projection
III Zig-zag projection

P-94.2 Torsion angle

In an assembly of attached atoms X-A-B-Y, where neither X nor Y is collinear with A and B, the smaller angle subtended by the bonds X-A and Y-B in a plane projection obtained by viewing the assembly along the axis A-B is termed the 'torsion angle', denoted by the italicized Greek lower-case letter θ . The torsion angle is considered positive or negative according as the bond atom X or Y requires rotation to the right (clockwise) or left (anticlockwise), respectively, in order that its direction may coincide with that of the bond to the rear selected atom Y or X. The multiplicity of the bonding of the various atoms is irrelevant. A torsion angle also exists if the axis for rotation is formed by a collinear set of more than two atoms directly attached to each other.

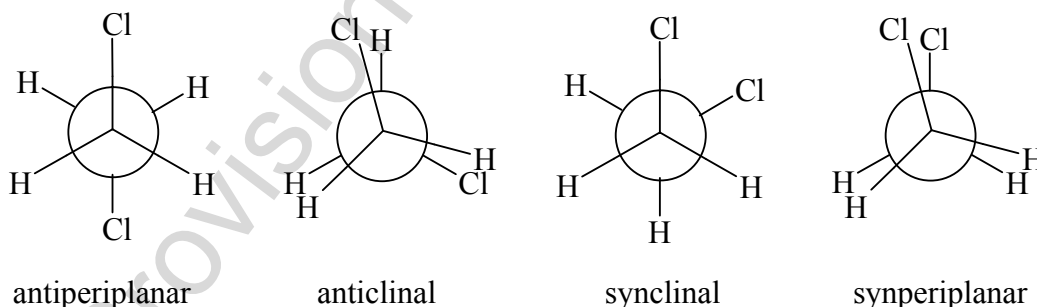
Conformations are described as synperiplanar (*sp*), synclinal (*sc*), anticlinal (*ac*), or antiperiplanar (*ap*), according as the torsion angle is within $\pm 30^\circ$ of 0° ; $\pm 60^\circ$, $\pm 120^\circ$, or $\pm 180^\circ$, respectively; the letters in parentheses are the corresponding abbreviations.



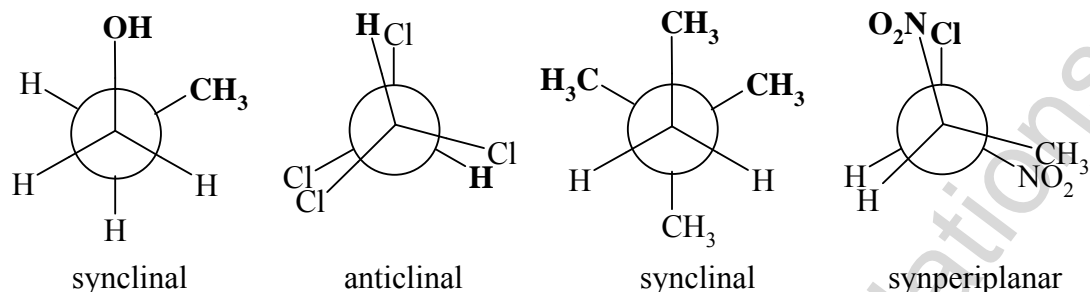
To choose the appropriate stereodescriptor, atoms or groups are selected from each set to define the torsion angle according to the following criteria:

- if all the atoms or groups of a set are different, that one of each set that has priority by the sequence rule;
- if one of a set is unique, that one;
- if all of a set are identical, that one which provides the smallest torsion angle.

Examples:



(The two chlorine atoms decide the conformation)

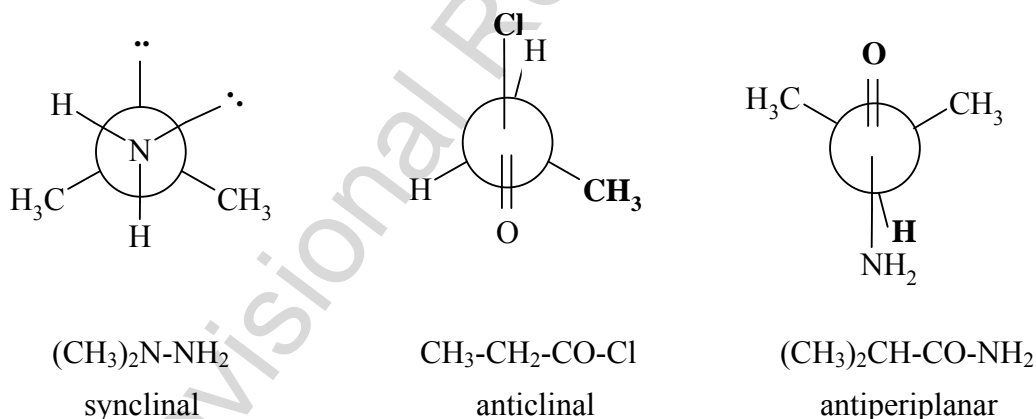


Criteria for:

rear atom	2	2	3	1
front atom	2	2	2	1

If A and B in X-A-B-Y are trigonal centers, a lone pair of electrons represented by two dots is taken into consideration to decide the description of the conformation, as illustrated by the example below describing the conformation of 1,1-dimethylhydrazine, $(\text{CH}_3)_2\text{N-NH}_2$; the lone pairs of electrons are the phantom atoms of the sequence rules symbolism. Similarly, trigonal centers involving double bonds are analyzed with the sequence rules by using duplicate atoms to determine the order of precedence.

Examples:



Criterion for:

rear atom	2	2	2
front atom	2	1	1

P-94.3 Specific stereodescriptors

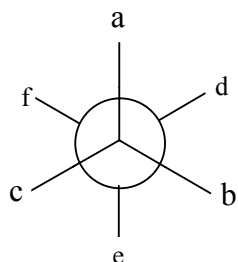
Stereodescriptors are used to denote specific conformers, both aliphatic and alicyclic.

P-94.3.1 Eclipsed, staggered and gauche (or skew) conformations

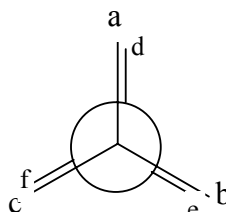
P-94.3.1.1 Two atoms or groups attached to two adjacent atoms are said to be 'eclipsed' if the torsion angle between them is zero. They are said to be 'staggered' when they are as far apart as possible from an eclipsed conformation. 'Gauche' or 'skew' are synonymous with synclinal, which is preferred. The stereodescriptors '*trans*' or '*anti*' are not recommended in place of

anticlinal, nor 'cis' or 'syn' in place of synclinal. Eclipsed and staggered are stereodescriptors used to denote the conformations when all ligands are identical.

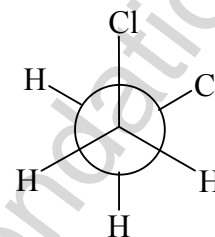
Examples:



staggered conformation
(all attached groups
are staggered)

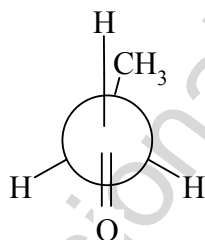


eclipsed conformation
(the pairs 'a-d', 'b-e',
and 'c-f' are eclipsed)

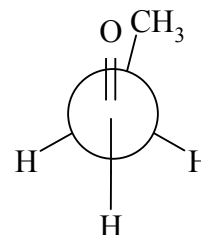


synclinal (preferred)
gauche or skew

P-94.3.1.2 For a structure containing the grouping $R_3C-C(Y)=X$ (with identical or different R groups) the conformation in which the torsion angle is such that X is antiperiplanar to one of the R group, and, in a Newman projection, the double bond bisects one of the R-C-R angle, is called a 'bisecting conformation'. The other conformation, in which X is synperiplanar to one of the R group, is called an eclipsing conformation.



bisecting conformation



eclipsing conformation

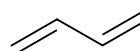
Projections of CH_3-CH_2-CHO

P-94.3.1.3 Stereodescriptors 's-cis' and 's-trans'

The spatial arrangement of two conjugated double bonds about the intervening single bond is described as 's-cis' if synperiplanar and 's-trans' if antiperiplanar. This descriptor should not be applied to other systems such as N-alkyl amides (use 'E/Z' or 'sp/ap').



s-cis

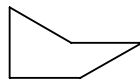


s-trans

P-94.3.2 Stereodescriptors for denoting the conformations of alicyclic rings

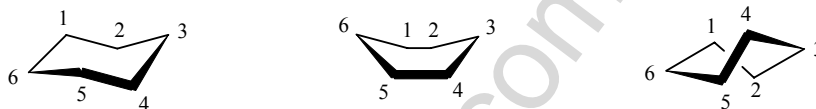
P-94.3.2.1 Envelope conformation

The envelope conformation is the conformation of a five-membered ring in which four atoms are coplanar and one atom projects out of the plane.



P-94.3.2.2 Chair, boat and twist conformations

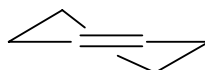
When carbon atoms 1,2,4 and 5 of a six-membered ring occupy coplanar positions and when carbon atoms 3 and 6 are on opposite sides of the plane the conformation is called a chair form. It is a boat form when carbon atoms 3 and 6 are on the same side of the plane. The conformation passed through in the interconversion of two boat forms of six-membered ring is called the twist form; this term is preferred to skew boat, skew form or stretched form.



In carbohydrate stereochemistry, the term twist refers to a five-membered ring and the twist conformation is referred to as skew.

P-94.3.2.3 Half-chair

A molecule of a monounsaturated six-membered ring is described as being in a 'half-chair' conformation according as the atoms not directly linked to the double bond lie on opposite sides of the plane.



P-94.3.2.4 Crown conformation

The conformation of a saturated cyclic molecular entity, containing an even number (≥ 8) of atoms in the ring, in which these atoms lie alternatively in each of two parallel planes and are symmetrically equivalent (D_{4d} for cyclooctane, D_{5d} for cyclodecane, etc), is called a 'crown conformation'.



cyclooctane



cyclodecane

P-94.3.2.5 Tub conformation

The conformation of an eight-membered ring in which the four atoms forming one pair on diametrically opposite bonds in the ring lie in one plane and all other ring atoms lie on one side of that plane is called a 'tub conformation'.



P-94.3.2.6 In-out isomerism

In-out isomerism is found in bicyclic systems having long enough bridges to allow the bridgehead exocyclic bond or lone pair of electrons to point either inside the structure or outside.

Examples:

