

# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ORGANIC CHEMISTRY DIVISION  
COMMISSION ON NOMENCLATURE OF ORGANIC CHEMISTRY (III.1)  
COMMISSION ON PHYSICAL ORGANIC CHEMISTRY (III.2)

## BASIC TERMINOLOGY OF STEREOCHEMISTRY

(IUPAC Recommendations 1996)

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# Basic terminology of stereochemistry (IUPAC Recommendations 1996)

*Abstract:* This is a glossary of the more important, and most widely-used, stereochemical terms. It extends the list of those defined in the IUPAC Nomenclature of Organic Chemistry, Section E: Stereochemistry (Recommendations 1974)<sup>1</sup> and includes some terms from the Glossary of Terms used in Physical Organic Chemistry (Recommendations 1994).<sup>4</sup> Additional terms have been added from inorganic and macromolecular chemistry. Some misleading terms are included together with guidance on correct usage or acceptable alternatives.

Many of the symbols used in stereochemical nomenclature are mentioned but details of their assignment or their incorporation into chemical names are left to the appropriate recommendations. Terminology related to techniques used in the determination of stereochemistry are largely excluded as well as terms used to describe reaction mechanisms.

## Introduction





When the IUPAC Commission on Nomenclature of Organic Chemistry prepared section E: Stereochemistry (Recommendations 1974)<sup>1</sup> the document was primarily intended to describe the naming of stereochemical features as part of the overall nomenclature of organic compounds.<sup>2</sup> In the absence of any IUPAC recommendations on stereochemical terminology Section E included appropriate aspects of the vocabulary of the subject. In 1983 the Commission on Physical Organic Chemistry published a Glossary of terms used in that field.<sup>4</sup> In view of the previous publication of section E stereochemical terms were excluded from this Glossary. However it became apparent that a separate glossary of stereochemical terms would facilitate the work of both commissions and accordingly a joint working party was established with additional representation from the Commission on Nomenclature of Inorganic Chemistry and the Commission on Macromolecular Nomenclature.


The working party considered a very long list of possible terms for inclusion but decided to initially concentrate on those terms which were essential for the work of the commissions and any others which were very widely used, or misused. In the latter case, as well as condemnation of inappropriate terms, guidance on the correct usage, or acceptable alternatives were to be provided. The preparation of a more comprehensive Glossary of Stereochemical Terms was left to a possible second edition, or possibly in a combined glossary with other physical organic chemistry terms.

Many of the symbols used in stereochemical nomenclature are mentioned in this document but it is not intended to provide details of their assignment or how they are incorporated into chemical names. Interested readers are referred in the text to the original published papers and some details are given in the appropriate IUPAC recommendations on organic,<sup>2</sup> inorganic,<sup>5</sup> and macromolecular<sup>6</sup> chemical nomenclature.

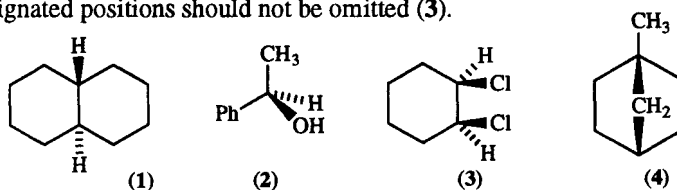
Terminology which relates to techniques used in the determination of stereochemistry<sup>7</sup> is also largely excluded. Some stereochemical terms used to describe reaction mechanisms are already included in the Glossary of Physical Organic Chemistry.<sup>4</sup>

## Graphic Representation of Three-Dimensional Structures<sup>8</sup>

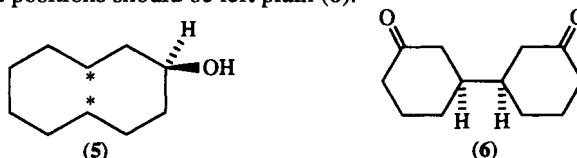
Structural diagrams which depict stereochemistry must be prepared with extra care to ensure there is no ambiguity. In general plain lines depict bonds approximately in the plane of the drawing; bonds to atoms above the plane are shown with a bold wedge  (starting from an atom in the plane of the drawing at the narrow end of the wedge); and bonds to atoms below the plane are shown with short parallel lines . As an alternative a bold bond  may be used instead of a bold wedge. A broken line-----has been used instead of parallel lines but this is better reserved for a partial bond, delocalisation, or a hydrogen bond. The use of a wedge of parallel lines  is not recommended as it is ambiguous. It is used commonly

in two directly opposite ways. Different workers define the narrow end as being in the plane of the drawing or furthest from the viewer. If stereochemistry is unknown this can be indicated explicitly by a wavy line . The use of dots or open circles at a centre to show stereochemistry is strongly deprecated. Other specific conventions mentioned in the Glossary include Fischer projection, Newman projection, sawhorse projection and wedge projection.

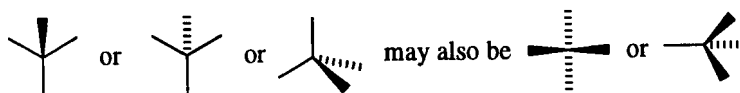
Strict rules for drawing stereochemistry are not possible. In general it is most clear if all rings of an *ortho*-fused ring system (or saturated derivatives) are kept in the plane of the drawing and bridgehead substituents are shown above or below the plane (1). With an acyclic structure (2) or other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



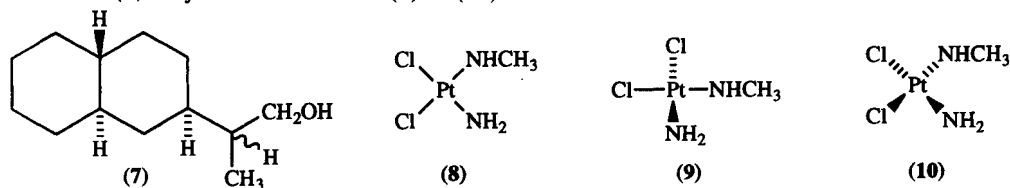
The stereochemistry due to substituents attached to a ring should not be shown at a re-entrant angle [marked with an asterisk on (5)]; although this is suitable for a carbonyl or *N*-methyl]. Any bond between two stereochemically designated positions should be left plain (6).



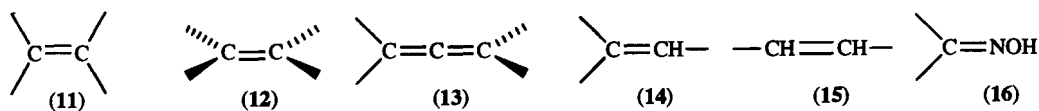
With tetrahedral stereochemistry the following are recommended:



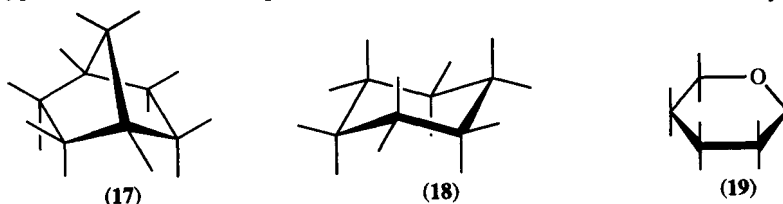
A wavy line can be used to indicate either that the stereochemistry is unknown (7), but only one form is present, or, if explained in the text, that both isomers are present and will be defined when required. If it is intended not to show any stereochemistry it is best to only use plain lines for all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



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



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



## References

1. IUPAC, Commission on Nomenclature of Organic Chemistry, Section E: Stereochemistry (Recommendations 1974), *Pure Appl. Chem.* **45**, 11-30 (1976), see also ref. 2, 3.
2. IUPAC, Commission on Nomenclature of Organic Chemistry, *Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F and H*, 1979, Pergamon Press, pp. 473-490; see also IUPAC, Commission on the Nomenclature of Organic Chemistry, *A Guide to IUPAC Nomenclature of Organic Chemistry*, 1993, Blackwell Scientific Publications, pp. 149-154.
3. International Union of Biochemistry and Molecular Biology, *Biochemical Nomenclature and Related Documents*, 2nd edition, 1992, Portland Press, pp.1-18.
4. IUPAC, Commission on Physical Organic Chemistry, *Glossary of Terms Used in Physical Organic Chemistry*, *Pure Appl. Chem.*, **66**, 1077-1184 (1994).
5. IUPAC, Commission on Nomenclature of Inorganic Chemistry, *Nomenclature of Inorganic Chemistry (Recommendations 1990)*, 3rd edition, 1990, Blackwell Scientific Publications, pp. 159-189.
6. IUPAC, Commission on Macromolecular Nomenclature, *Compendium of Macromolecular Nomenclature*, 1991, Blackwell Scientific Publications, pp. 25-46.
7. IUPAC, Analytical Chemistry Division, *Compendium of Analytical Nomenclature*, 2nd edition, 1987, Blackwell Scientific Publications; IUPAC, *Compendium of Chemical Terminology (IUPAC Recommendations)*, 1987, Blackwell Scientific Publications.
8. K.L. Loening, in *Chemical Structures* edited W.A. Warr, 1988, Springer Verlag, pp. 413-423.

## Glossary

Italics indicate a term covered by this glossary (or a symbol that is usually italicised).

### Absolute Configuration

The spatial arrangement of the atoms of a chiral molecular entity (or group) and its stereochemical description e.g. *R* or *S*. See also relative configuration and  $\alpha$  (*alpha*),  $\beta$  (*beta*) (3).

*ac* See *torsion angle*.

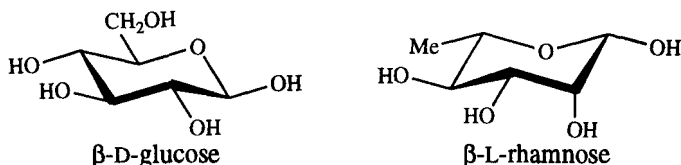
*Achiral* See *chirality*.

*Achirotopic* See *chirotopic*.

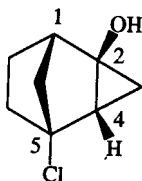
$\alpha$  (**Alpha**),  $\beta$  (**Beta**)

These stereodescriptors are used in a number of different ways.

1. Relative stereodescriptors used in carbohydrate nomenclature to describe the configuration at the anomeric carbon by relating it to the anomeric reference atom. For simple cases the anomeric reference atom is the same as the configurational reference atom. Thus in  $\alpha$ -D-glucopyranose the reference atom is C-5 and the OH at C-1 is on the same side as the OH at C-5 in the Fischer projection. See 'Tentative rules for Carbohydrate Nomenclature. Part 1', *Eur. J. Biochem.*, **21**, 455-477 (1971).

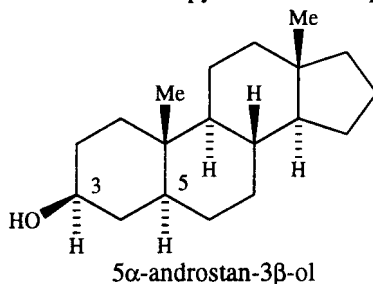


2. Relative stereodescriptors used by *Chemical Abstracts Service* to describe the configuration of a cyclic molecule (including suitable polycyclic systems) with several stereogenic centres whereby the  $\alpha$  side of the reference plane is the side on which the substituent with CIP priority lies at the lowest numbered stereogenic centre. The other side is  $\beta$ .



tricyclo[3.2.1.0<sup>2,4</sup>]octan-2-ol, 5-chloro, (1 $\alpha$ ,2 $\alpha$ ,4 $\alpha$ ,5 $\beta$ )-

3. Absolute stereodescriptors originally devised for steroid nomenclature. However in this sense it is only meaningful if there is an agreed absolute configuration and orientation of the structure so as to define the plane and which way up the molecule is represented. Substituents above the plane of the steroid are described as  $\beta$  and shown as a solid line (— or —), those below the plane are described as  $\alpha$  and shown by a broken line (-----). The extension of this system to tetrapyrroles has been documented and it has been widely used elsewhere. See 'Nomenclature of Steroids', *Pure Appl. Chem.* **61**, 1783-1822 (1989); 'Nomenclature of Tetrapyrroles', *Pure Appl. Chem.* **59**, 779-832 (1987).



5 $\alpha$ -androstan-3 $\beta$ -ol

### Ambo

A prefix used to indicate that a molecule with two (or more) chiral elements is present as a mixture of the two racemic diastereoisomers in unspecified proportions. For example, the dipeptide formed from L-alanine and DL-leucine is L-alanyl-*ambo*-leucine. (See 'Nomenclature and Symbolism for Amino Acids and Peptides', *Pure Appl. Chem.* **56**, 595-624 (1984); 'Nomenclature of Tocopherols and Related Compounds', *Pure Appl. Chem.* **54**, 1507-1510 (1982).)

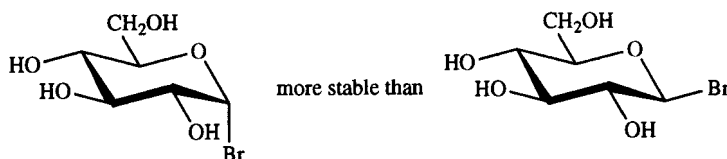
### Angle Strain

Strain due to a departure in bond angle from "normal" values. The term is often used in the context of non-aromatic cyclic compounds in which the internal angles differ from the regular tetrahedral angle of 109° 28'; in this sense angle strain is also known as Baeyer strain.

**Anisometric** See *isometric*.

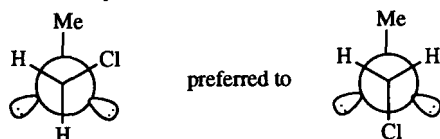
### Anomeric Effect

Originally the thermodynamic preference for polar groups bonded to C-1 (the anomeric carbon of a glycopyranosyl derivative) to take up an *axial* position.

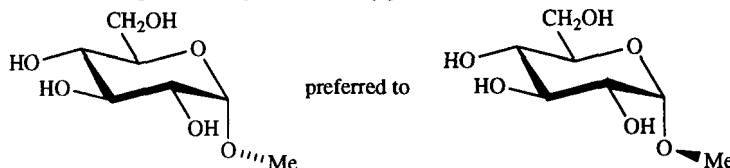


This effect is now considered to be a special case of a general preference (the generalised anomeric effect) for *synclinal* (*gauche*) conformations about the bond C-Y in the system X-C-Y-C where X and Y are

heteroatoms having nonbonding electron pairs, commonly at least one of which is nitrogen, oxygen or fluorine. For example in chloro(methoxy)methane the anomeric effect stabilises the synclinal conformation.



In alkyl glycopyranosides the anomeric effect operates at two sites (i) along the endocyclic C-1 oxygen bond (endo-anomeric effect) and (ii) along the exocyclic C-1 oxygen bond (exo-anomeric effect).



The opposite preference is claimed for some systems *e.g.* glycopyranosyltrialkylammonium salts, and has been referred to as the reverse anomeric effect.

### Anomers

*Diastereoisomers* of glycosides, hemiacetals or related cyclic forms of sugars, or related molecules differing in *configuration* only at C-1 of an aldose, C-2 of a 2-ketose, etc.

### Anti

1. See *torsion angle*.
2. See *endo, exo, syn, anti*.
3. See also 'Glossary of Terms Used in Physical Organic Chemistry', *Pure Appl. Chem.* **66**, 1077-1184 (1994) for use as a term to describe antarafacial addition or elimination reactions.
4. It was formerly used to describe the stereochemistry of oximes and related systems (See *E,Z*).

**Anticlinical** See *torsion angle*.

**Antiperiplanar** See *torsion angle*.

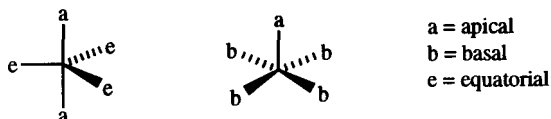
**Antipodes** (usage strongly discouraged)

Obsolete synonym for enantiomers.

**ap** See *torsion angle*.

### Apical, Basal, Equatorial

In trigonal bipyramidal structures (*e.g.* a five-coordinate trigonal bipyramid with phosphorus as central atom) the term apical refers to the two positions that are collinear with the central atom or to the bonds linking these positions to the central atom. The three equivalent bonds (or positions) in a plane passing through the central atom and perpendicular to the direction of the apical bonds are described as equatorial (See *axial, equatorial* for alternative use). The term apical is also used for the bond pointing from the atom at or near the centre of the base to the apex of a pyramidal structure. The positions at or near the base of the pyramid, or the bonds linking those positions to the central atom of the base are described as basal. The apical bonds have also been called axial.



### Asymmetric

Lacking all *symmetry elements* (other than the trivial one of a one-fold axis of symmetry), *i.e.* belonging to the symmetry point group C1. The term has been used loosely (and incorrectly) to describe the absence of an

rotation-reflection axis (alternating axis) in a molecule, i.e. as meaning chiral, and this usage persists in the traditional terms *asymmetric carbon atom*, *asymmetric synthesis*, *asymmetric induction*, etc.

### Asymmetric Carbon Atom

The traditional name (van't Hoff) for a carbon atom that is attached to four different entities (atoms or groups) e.g. Cabcd. See also *chirality centre*.

**Asymmetric Centre** See *chirality centre*.

**Asymmetric Destruction** See *kinetic resolution*.

### Asymmetric Induction

The traditional term describing the preferential formation in a chemical reaction of one *enantiomer* or *diastereoisomer* over the other as a result of the influence of a chiral feature present in the substrate, reagent, catalyst or environment.

### Asymmetric Synthesis

A traditional term used for *stereoselective synthesis* of chiral compounds.

### Asymmetric Transformation

The conversion of a racemate into a pure *enantiomer* or into a mixture in which one enantiomer is present in excess, or of a *diastereoisomeric* mixture into a single diastereoisomer or into a mixture in which one diastereoisomer predominates. This is sometimes called *deracemisation*.

If the two enantiomers of a *chiral* substrate A are freely interconvertible and if an equal amount or excess of a non-racemising second enantiomerically pure chemical species, say (R)-B, is added to a solution of racemic A, then the resulting equilibrium mixture of adducts A•B will, in general, contain unequal amounts of the diastereoisomers (R)-A•(R)-B and (S)-A•(R)-B. The result of this equilibration is called *asymmetric transformation of the first kind*.

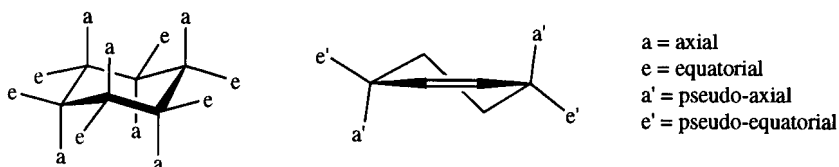
If, in such a system, the two diastereoisomeric adducts differ considerably in solubility so that only one of them, say (R)-A•(R)-B, crystallises from the solution, then the equilibration of diastereoisomers in solution and concurrent crystallisation will continue so that all (or most) of the substrate A can be isolated as the crystalline diastereoisomer (R)-A•(R)-B. Such a "crystallisation-induced asymmetric transformation" is called an *asymmetric transformation of the second kind*. See also *stereoconvergence*

### Atropisomers

A subclass of *conformers* which can be isolated as separate *chemical species* and which arise from restricted rotation about a single bond (see *rotational barrier*) e.g. *ortho*-substituted biphenyl, 1,1,2,2-tetra-*tert*-butylethane

### Axial, Equatorial

In the chair form of cyclohexane ring bonds to ring atoms (and molecular entities attached to such bonds) are termed axial or equatorial according to whether the bonds make a relatively large or small angle, respectively, with the plane containing or passing closest to a majority of the ring atoms. Thus the axial bonds are approximately parallel to the  $C_3$  axis and the equatorial bonds approximately parallel to two of the ring bonds. These terms are also used for the chair form of other saturated six-membered rings. The corresponding bonds occurring at the allylic positions in mono-unsaturated six-membered rings are termed pseudo-axial (or quasi-axial) and pseudo-equatorial (or quasi-equatorial). The terms axial and equatorial have similarly been used in relation to the puckered conformation of cyclobutane, crown conformer of cyclooctane, etc. and the terms pseudo-axial and pseudo-equatorial in the context of the non-planar structures of cyclopentane and cycloheptane. (See *apical*, *basal*, *equatorial* for an alternative use of axial and equatorial with bipyramidal structures)

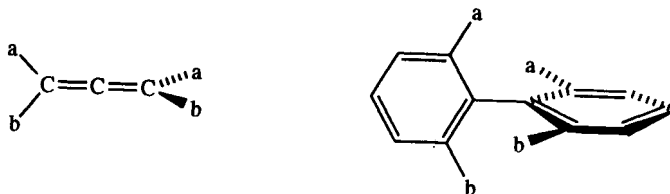




## Axial Chirality

Term used to refer to stereoisomerism resulting from the non-planar arrangement of four groups in pairs about a *chirality axis*. It is exemplified by allenes  $abC=C=Ccd$  (or  $abC=C=Cab$ ) and by the atropisomerism of *ortho*-substituted biphenyls.

The *configuration* in molecular entities possessing axial chirality is specified by the stereodescriptors  $R_a$  and  $S_a$  (or by  $P$  or  $M$ ).



**Axis of Chirality** See *chirality axis*.

**Axis of Helicity** See *helicity*.

**Baeyer Strain** See *angle strain*.

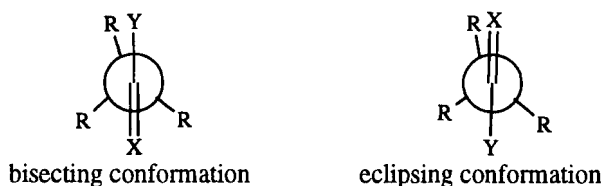
**Basal** See *apical, basal, equatorial*.

**Berry Pseudorotation** See *pseudorotation*.

$\beta$  (**Beta**) See  $\alpha$  (*alpha*),  $\beta$  (*beta*)

## Bisecting Conformation, Eclipsing Conformation

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



bisecting conformation

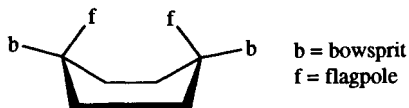
eclipsing conformation

**Boat** See *chair, boat, twist*; and *half-chair, half-boat*.

**Bond Opposition Strain** See *eclipsing strain*.

## Bowsprit, Flagpole

In the boat form of cyclohexane and related structures there are two ring atoms lying out of the plane of the other four; exocyclic bonds to these two atoms pointing in a direction roughly parallel to that plane are called bowsprit, the other two are called flagpole.



b = bowsprit  
f = flagpole

## Bredt's Rule

See entry in 'Glossary of Terms Used in Physical Organic Chemistry', *Pure Appl. Chem.* **66**, 1077-1184 (1994).

## C.I.P. System

Short for Cahn-Ingold-Prelog system (see *CIP Priority*).

**Cahn-Ingold-Prelog System** See *CIP Priority*.

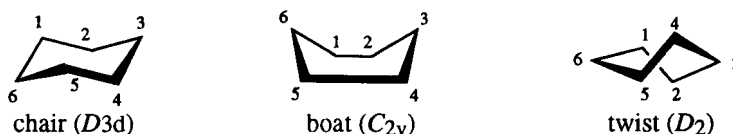
**Centre of Chirality** See *chiral centre*.

### Chair, Boat, Twist

If carbon atoms 1, 2, 4 and 5 of cyclohexane occupy coplanar positions and when carbon atoms 3 and 6 are on opposite sides of the plane the *conformation* (of symmetry group  $D_{3d}$ ) is called a chair form.

The same term is applied to similar conformations of analogous saturated six-membered ring structures containing hetero-atoms and/or bearing substituent groups, but these conformations may be distorted from the exact  $D_{3d}$  symmetry. For cyclohexane and most such analogues, the chair form is the most stable conformation. If the cyclohexane conformation has no centre of symmetry but possesses two planes of symmetry, one of them bisecting the bonds between atoms 1 and 2 and between 4 and 5 and the other plane passing through atoms 3 and 6 (which lie out of the plane and on the same side of the plane containing 1, 2, 4 and 5), that conformation (of symmetry group  $C_{2v}$ ) is called a boat form and it is generally not a stable form. Again, this term is also applied to structural analogues.

The conformation of  $D_2$  symmetry passed through in the interconversion of two boat forms of cyclohexane is called the twist form (also known as skew boat, skew form and stretched form). See also *half-chair*.



In a five-membered ring a conformation in which two adjacent atoms are maximally displaced, in opposite directions, relative to the plane containing the other three carbon atoms has been called a half-chair but is better called a twist conformation (see also *envelope conformation*).

In carbohydrate chemistry the term twist refers to a five-membered ring and the  $D_2$  symmetry six-membered ring is referred to as skew.

**Chair-Chair Interconversion** See *ring reversal*.

### Chemical Species

A set of chemically identical atomic or molecular structural units in a solid array or of chemically identical *molecular entities* that can explore the same set of molecular energy levels on the time scale of the experiment.

For example, two conformational isomers may interconvert sufficiently slowly to be detected by their separate n.m.r. spectra and hence to be considered to be separate chemical species on a time scale governed by the radiofrequency of the spectrometer used. On the other hand, in a slow chemical reaction the same mixture of conformers may behave as a single chemical species, *i.e.* there is a virtually complete equilibrium population of the total set of molecular energy levels belonging to the two conformers.

Except where the context requires otherwise, the term is taken to refer to a set of molecular entities containing isotopes in their natural abundance.

[‘Glossary of Terms Used in Physical Organic Chemistry’, *Pure Appl. Chem.* **66**, 1077-1184 (1994)].

### Chiral

Having the property of *chirality*.

As applied to a molecule the term has been used differently by different workers. Some apply it exclusively to the whole molecule, whereas others apply it to parts of a molecule. For example, according to the latter view, a meso-compound is considered to be composed of two chiral parts of opposite chirality sense; this usage is to be discouraged. See *enantiomorph*.

In its application to an assembly of molecules, some restrict the term to an assembly in which all of the molecules have the same *chirality sense*, which is better called *enantiopure*. Others extend it to a *racemic* assembly, which is better just called a *racemate*. Use of the term to describe molecular assemblies should be avoided.

## Chirality

The geometric property of a rigid object (or spatial arrangement of points or atoms) of being non-superposable on its mirror image; such an object has no symmetry elements of the second kind (a mirror plane,  $\sigma = S_1$ , a centre of inversion,  $i = S_2$ , a rotation-reflection axis,  $S_{2n}$ ). If the object is superposable on its mirror image the object is described as being achiral. See also *handedness*.

### Chirality Axis

An axis about which a set of ligands is held so that it results in a spatial arrangement which is not superposable on its mirror image. For example with an allene  $abC=C=Ccd$  the chiral axis is defined by the  $C=C=C$  bonds; and with an *ortho*-substituted biphenyl the atoms C-1, C-1', C-4 and C-4' lie on the chiral axis.

### Chirality Centre

An atom holding a set of ligands in a spatial arrangement which is not superposable on its mirror image. A chirality centre is thus a generalised extension of the concept of the *asymmetric carbon atom* to central atoms of any element, for example  $N^+abcd$ ,  $Pabc$  as well as  $Cabcd$ .

### Chirality Element

General name for a *chirality axis*, *chirality centre* or *chirality plane*. Also referred to as an element of chirality.

### Chirality Plane

A planar unit connected to an adjacent part of the structure by a bond which results in restricted torsion so that the plane cannot lie in a symmetry plane. For example with (*E*)-cyclooctene the chiral plane includes the double bond carbon atoms and all four atoms attached to the double bond; with a monosubstituted paracyclophane the chiral plane includes the monosubstituted benzene ring with its three hydrogen atoms and the three other atoms linked to the ring (*i.e.* from the substituent and the two chains linking the two benzene rings).

### Chirality Sense

The property that distinguishes enantiomorphs. The specification of two enantiomorphs by reference to an oriented space *e.g.* of a screw, a right threaded one or a left threaded one. The expression 'opposite chirality' is short for 'opposite chirality sense'.

### Chiroptic/Chiroptical

A term referring to the optical techniques (using refraction, absorption or emission of anisotropic radiation) for investigating chiral substances [*e.g.* measurements of optical rotation at a fixed wavelength, optical rotatory dispersion (ORD), circular dichroism (CD), and circular polarisation of luminescence (CPL)].

### Chirotopic

The description of an atom (or point, group, face, *etc.* in a molecular model) that resides within a *chiral* environment. One that resides within an achiral environment has been called achirotopic.

### CIP Priority

In the CIP rules the conventional order of ligands established for the purpose of unambiguous designation of *stereoisomers*. It is deduced by application of sequence rules, the authoritative statement of which appears in R.S. Cahn, C.K. Ingold and V. Prelog, *Angew. Chem.* **78**, 413-447 (1966), *Angew. Chem. Internat. Ed. Eng.* **5**, 385-415, 511 (1966) ; and V. Prelog and G. Helmchen, *Angew. Chem.* **94**, 614-631 (1982), *Angew. Chem. Internat. Ed. Eng.* **21**, 567-583 (1982).

### cis, trans

Descriptors which show the relationship between two ligands attached to separate atoms that are connected by a double bond or are contained in a ring. The two ligands 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  $\sigma$ -bonds and passes

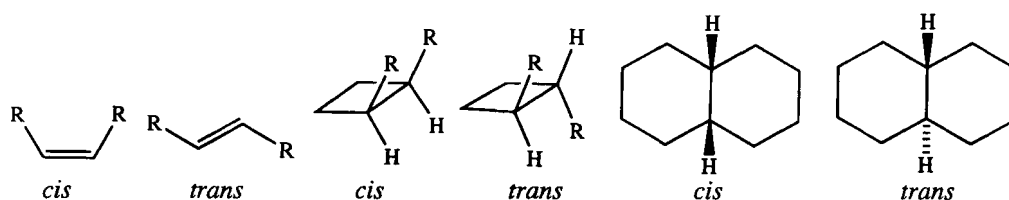
through the double bond. For a ring (the ring being in a conformation, real or assumed, without re-entrant angles at the two substituted atoms) it is the mean plane of the ring(s). For alkenes the terms *cis* and *trans* may be ambiguous and have therefore largely been replaced by the *E, Z* convention for the nomenclature of organic compounds. If there are more than two entities attached to the ring the use of *cis* and *trans* requires the definition of a reference substituent (See IUPAC, *Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F and H*, Pergamon Press, 1979, p. 478, Rule E-2.3.3, E-2.3.4; IUPAC, *A Guide to IUPAC Nomenclature of Organic Chemistry*, Blackwell Scientific Publications, 1993, pp. 149-151, Rule R-7.1.1).

**cisoid Conformation** (usage strongly discouraged)

See *s-cis, s-trans*. The terms *cisoid* and *transoid* are also used to describe the stereochemistry of fused ring systems (See IUPAC, *Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F and H*, Pergamon Press, 1979, p. 478, Rule E-3.2).

### *cis-trans* Isomers

*Stereoisomeric* olefins or cycloalkanes (or hetero-analogues) which differ in the positions of atoms (or groups) relative to a reference plane: in the *cis*-isomer the atoms are on the same side, in the *trans*-isomer they are on opposite sides.



**Clinal** See *torsion angle*.

### Compensation

1. For *internal compensation*, see *meso-compound*.
2. See *external compensation*.

### Configuration

In the context of stereochemistry, the term is restricted to the arrangements of atoms of a molecular entity in space that distinguishes *stereoisomers*, the *isomerism* between which is not due to *conformation* differences. See also *absolute configuration*; *relative configuration*.

### Conformation

The spatial arrangement of the atoms affording distinction between stereoisomers which can be interconverted by rotations about formally single bonds. Some authorities extend the term to include inversion at trigonal pyramidal centres and other *polytopal rearrangements*. See also *conformer*; *bisecting conformation*; *eclipsing conformation*; *chair*; *boat*; *twist*; *crown conformation*; *envelope conformation*; *half-chair*; *staggered conformation*; *tub conformation*.

### Conformational Analysis

The assessment of the relative energies (or thermodynamic stabilities), reactivities, and physical properties of alternative *conformations* of a molecular entity, usually by the application of qualitative or semi-quantitative rules or by semi-empirical calculations.

### Conformer

One of a set of *stereoisomers*, each of which is characterised by a *conformation* corresponding to a distinct potential energy minimum. See also *rotamer*.

**Conglomerate** See *racemic conglomerate*.

### Constitution

The description of the identity and connectivity (and corresponding bond multiplicities) of the atoms in a molecular entity (omitting any distinction arising from their spatial arrangement).

## Constitutional Isomerism

Isomerism between structures differing in *constitution* and described by different line formulae *e.g.*  $\text{CH}_3\text{OCH}_3$  and  $\text{CH}_3\text{CH}_2\text{OH}$ .

## Crown Conformation

A conformation of a saturated cyclic molecular entity, containing an even number ( $\geq 8$ ) of atoms in the ring, in which these atoms lie alternately in each of two parallel planes and are symmetrically equivalent ( $D_{4d}$  for cyclooctane,  $D_{5d}$  for cyclodecane *etc.*). It is analogous to the *chair* conformation of cyclohexane. See also *tub conformation*.



**D, L, DL** See *Fischer-Rosanoff convention*.

**d, l, dl** (usage strongly discouraged)

Obsolete alternatives for respectively the prefixes (+)- and (-)- [used to designate the sign of optical rotation of enantiomers under specified condition (and hence to distinguish the enantiomers)] and (±)- for a racemate.

## $\Delta$ (Delta), $\Lambda$ (Lambda)

Designations of stereoisomers of tris(didentate) metal complexes and other octahedral complexes. See *helicity*, also IUPAC, *Nomenclature of Inorganic Chemistry*, 3rd ed. 1990, Blackwell Scientific Publications, I-10.7.2.1, I-10.7.2.3.

**Deracemisation** See *asymmetric transformation*.

## Desymmetrisation

The modification of an object which results in the loss of one or more symmetry elements, such as those which preclude *chirality* (mirror plane, centre of inversion, rotation-reflection axis), as in the conversion of a *prochiral* molecular entity into a chiral one.

## Desymmetrisation Step

The removal of the smallest possible number of symmetry elements from a molecule with (ref. 1) or without (ref. 2) the restriction to pointwise substitution.

1. K. Mislow and J. Siegel, *J. Am. Chem. Soc.* **106**, 3319-3328 (1984)

2. E.A. Halevi, *J. Chem. Res. (S)* 206-207 (1985)

## Diastereoisomerisation

The interconversion of *diastereoisomers*.

## Diastereoisomerism

*Stereoisomerism* other than *enantiomerism*. Diastereoisomers (or diastereomers) are stereoisomers not related as mirror images. Diastereoisomers are characterised by differences in physical properties, and by some differences in chemical behaviour towards achiral as well as chiral reagents.

**Diastereoisomers (Diastereomers)** See *diastereoisomerism*.

## Diastereoisomer Excess/Diastereoisomeric Excess

This is defined by analogy with *enantiomer excess*, as  $D_1 - D_2$  [and the percent diastereoisomer excess as  $100(D_1 - D_2)$ ], where the mole fractions of two diastereoisomers in a mixture or the fractional yields of two diastereoisomers formed in a reaction are  $D_1$  and  $D_2$  ( $D_1 + D_2 = 1$ ). The term is not applicable if more than two diastereoisomers are present. Frequently this term is abbreviated to d.e. See *stereoselectivity*; *diastereoisomerism*.

**Diastereomeric Ratio**

This is defined by analogy with *enantiomeric ratio* as the ratio of the percentage of one *diastereoisomer* in a mixture to that of the other.

**Diastereomers** See *diastereoisomerism*.

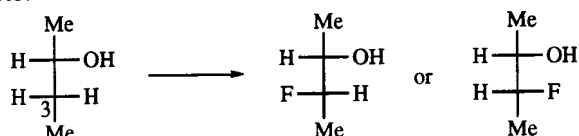
**Diastereoselectivity** See *stereoselectivity*.

**Diastereomorphism**

The relationship between objects (or models) analogous to that between *diastereoisomeric* molecular entities.

**Diastereotopic**

Constitutionally equivalent atoms or groups of a molecule which are not symmetry related. Replacement of one of two diastereotopic atoms or groups results in the formation of one of a pair of *diastereoisomers*. In the example below the two hydrogen atoms of the methylene group C-3 are diastereotopic. See also *prochirality*; *enantiotopic*; *heterotopic*.

**Dihedral Angle**

The angle between two intersecting planes on a third plane normal to the intersection of the two planes. See *torsion angle*.

**Dissymmetry**

Obsolescent synonym for *chirality*.

**E, Z**

The approved *stereodescriptors* of stereoisomeric alkenes  $\text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{R}^4$  ( $\text{R}^1 \neq \text{R}^2$ ,  $\text{R}^3 \neq \text{R}^4$ ; neither  $\text{R}^1$  nor  $\text{R}^2$  need be different from  $\text{R}^3$  or  $\text{R}^4$ ), cumulenes  $\text{R}^1\text{R}^2\text{C}=[\text{C}=\text{C}]_n=\text{CR}^3\text{R}^4$  and related systems *e.g.*  $\text{R}_1\text{R}_2\text{C}=\text{NOH}$ ,  $\text{HON}=\text{C}\{[\text{CH}_2]_n\}_2\text{C}=\text{NOH}$ . The group of highest *CIP* priority attached to one of the terminal doubly bonded atoms of the alkene, oxime, *etc.* or cumulene (*i.e.*  $\text{R}_1$  or  $\text{R}_2$ ) is compared with the group of highest precedence attached to the other (*i.e.*  $\text{R}_3$  or  $\text{R}_4$ ). The stereoisomer is designated as *Z* (*zusammen* = together) if the groups lie on the same side of a reference plane passing through the double bond and perpendicular to the plane containing the bonds linking the groups to the double-bonded atoms; the other stereoisomer is designated as *E* (*entgegen* = opposite). The descriptors may be applied to structures with a fractional bond order between one and two; and to double bonds involving elements other than carbon. They are not used to describe ring substitution relationships. See also *cis-trans isomers*.

**Eclipsed, Eclipsing**

Two atoms or groups attached to adjacent atoms are said to be eclipsed if the *torsion angle* between the three bonds is zero (or approximately so). See *bisecting conformation*, *eclipsing strain*.

**Eclipsing Conformation** See *bisecting conformation*.

**Eclipsing Strain**

Intramolecular strain present due to *non-bonding interactions* between two *eclipsed* atoms or groups. It is, for example, one of the interactions responsible for the existence of a *rotational barrier* and hence *restricted rotation* about the C-C bond in ethane. It has also been called *Pitzer strain*, *torsional strain*, and *bond opposition strain*.

**Element of Chirality** See *chirality element*.

**Enantioconvergence** See *stereoconvergence*.

**Enantioenriched** See *enantiomerically enriched*

**Enantiomer**

One of a pair of molecular entities which are mirror images of each other and non-*superposable*. See also *enantiomorph*.

**Enantiomer Excess/Enantiomeric Excess**

For a mixture of (+)- and (-)-enantiomers, with composition given as the mole or weight fractions  $F_{(+)}$  and  $F_{(-)}$  (where  $F_{(+)} + F_{(-)} = 1$ ) the enantiomer excess is defined as  $|F_{(+)} - F_{(-)}|$  (and the percent enantiomer excess by  $100|F_{(+)} - F_{(-)}|$ ). Frequently this term is abbreviated as e.e. See *optical purity*.

**Enantiomeric Ratio**

The ratio of the percentage of one *enantiomer* in a mixture to that of the other e.g. 70(+):30(-).

**Enantiomerically Enriched/Enantioenriched**

A sample of a chiral substance whose enantiomeric ratio is greater than 50:50 but less than 100:0

**Enantiomerically Pure/Enantiopure**

A sample all of whose molecules have (within limits of detection) the same chirality sense. Use of homochiral as a synonym is strongly discouraged.

**Enantiomeric Purity** See *enantiomer excess*.

**Enantiomerisation**

The interconversion of *enantiomers*. See *racemisation*.

**Enantiomerism**

The isomerism of *enantiomers*.

**Enantiomorph**

One of a pair of *chiral* objects or models that are non-*superposable* mirror images of each other. The adjective enantiomorphous is also applied to mirror-image related groups within a molecular entity.

**Enantiopure** See *enantiomerically pure*.

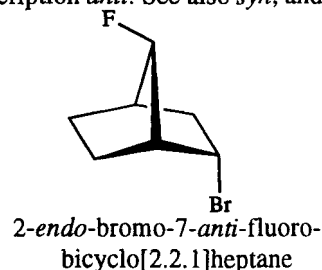
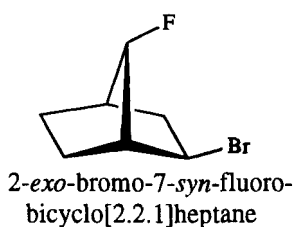
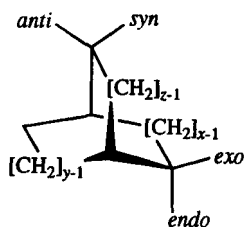
**Enantioselectivity** See *stereoselectivity*.

**Enantiotopic**

Constitutionally identical atoms or groups in molecules which are related by symmetry elements of the second kind only (mirror plane, inversion centre or rotation-reflection axis). For example the two groups *c* in a grouping Cabcc are enantiotopic. Replacement of one of a pair of enantiotopic groups forms one of a pair of enantiomers. Analogously, if complexation or addition to one of the two faces defined by a double bond or other molecular plane gives rise to a chiral species, the two faces are called enantiotopic. See also *prochiral*; *diastereotopic*.

**endo, exo, syn, anti**

Descriptors of the relative orientation of groups attached to non-bridgehead atoms in a bicyclo[*x.y.z*]alkane ( $x \geq y > z > 0$ ). If the group is orientated towards 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 towards 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*. See also *syn*, and *anti*.



**ent**

A prefix used to indicate the enantiomer for natural products and related molecules where the trivial name only refers to one *enantiomer*, e.g. *ent*-kaurene is the enantiomer of kaurene.

**Envelope Conformation**

The conformation (of symmetry group  $C_s$ ) of a five-membered ring in which four atoms are coplanar, and one atom (the flap) projects out of the plane.

**Epimerisation**

Interconversion of *epimers*.

**Epimers**

Diastereoisomers that have the opposite *configuration* at only one of two or more tetrahedral *stereogenic* centres present in the respective molecular entities.

**Equatorial**

1. For the use of this term in the context of cyclohexane see *axial, equatorial*.
2. For the use of this term in the context of a bipyramidal structure see *apical, basal, equatorial*.

**erythro, threo**

Descriptors of the diastereoisomers of an acyclic structure or partial structure having two stereogenic centres. This notation is derived from carbohydrate nomenclature; 'Tentative Rules for Carbohydrate Nomenclature', *Eur. J. Biochem.* **21**, 455-477 (1971). The extension of this system has given rise to conflicting interpretations of these prefixes. It is recommended that for such cases the *l,u* or  $R^*,S^*$  system should be used.

**exo** See *endo, exo, syn, anti*.

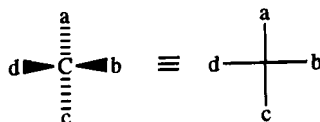
**External Compensation** (usage strongly discouraged)

The absence of *optical activity* in a *racemate*.

**Fiducial Group** See *helicity* and *torsion angle*.

**Fischer Projection (or Fischer-Tollens Projection)**

A *projection formula* in which vertically drawn bonds are considered to lie below the projection plane and horizontal bonds to lie above that plane. Thus for the molecule Cabcd:

**Fischer-Rosanoff Convention (or Rosanoff Convention)**

An arbitrary convention according to which (+)-glyceraldehyde, now known to be (*R*)-2,3-dihydroxypropanal, was named D-glyceraldehyde (with the enantiomer L-glyceraldehyde and its racemate DL-glyceraldehyde) and taken to have the absolute configuration represented by the *Fischer projection formula* shown below.





The atom numbered 1 according to normal nomenclature rules is conventionally placed at the top of the main chain, which is drawn vertically and other groups are drawn on either side of that main chain. The convention is still in use for  $\alpha$ -amino acids and for sugars; see 'Nomenclature and Symbolism for Amino Acids and Peptides, Recommendations 1983', *Pure Appl. Chem.* **56**, 595-624 (1984); and 'Tentative Rules for Carbohydrate Nomenclature', *Eur. J. Biochem.* **21**, 455-477 (1971).

**Flagpole** See *bowsprit*, *flagpole*.

### Free Rotation, Hindered Rotation, Restricted Rotation

In a stereochemical context the rotation about a bond is called "free" when the *rotational barrier* is so low that different *conformations* are not perceptible as different chemical species on the time scale of the experiment.

The inhibition of rotation of groups about a bond due to the presence of a sufficiently large *rotational barrier* to make the phenomenon observable on the time scale of the experiment is termed hindered rotation or restricted rotation.

### Gauche

Synonymous with a *synclinal* alignment of groups attached to adjacent atoms. See also *torsion angle*.

### Gauche Effect

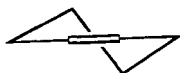
1. The stabilisation of the *gauche* (synclinal) conformation in a two carbon unit bonded vicinally to electronegative elements *e.g.* 1,2-difluoroethane.
2. The destabilisation of the *gauche* (synclinal) conformation in a two carbon unit bonded vicinally to large, soft and polarisable elements such as sulfur and bromine.

### Geometric Isomerism (usage strongly discouraged)

Obsolete synonym for *cis-trans isomerism*.

### Half-chair

The *conformation* of a six-membered ring structure in which four contiguous atoms are in a plane and the other two atoms lie on opposite sides of the plane is called a half-chair. See also *chair*, *boat*, *twist*.



### Handedness

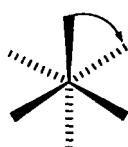
This term has been used in two ways, either *chirality* or *chirality sense*.

### Helicity

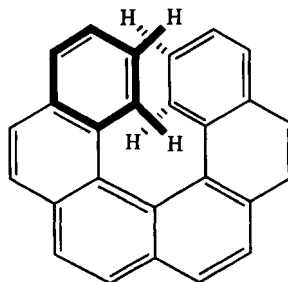
The *chirality* of a helical, propeller or screw-shaped molecular entity. A right-handed helix is described as *P* (or plus), a left-handed one as *M* (or minus).



*M* or  $\Delta$



*P* or  $\Delta$



(*M*)-hexahelicene

The application of this system to the description of conformations considers the *torsion angle* between two specified (fiducial) groups that are attached to the atoms linked by that bond. The sign of the smaller torsion angle between the fiducial groups defines the chirality sense of the helix. Rules for the selection of fiducial groups according to priority are given by R.S. Cahn, C.K. Ingold and V. Prelog, *Angew. Chem.* **78**, 413-

447 (1966), *Angew. Chem. Internat. Ed. Eng.* **5**, 385-415, 511 (1966). See also axial chirality;  $\Delta$  (*delta*),  $\Lambda$  (*lambda*).

**Heterotopic** See *stereoheterotopic*.

**Hindered Rotation** See *free rotation, hindered rotation, restricted rotation*.

**Homochiral** See *enantiomerically pure/enantiopure*.

### Homomorphic

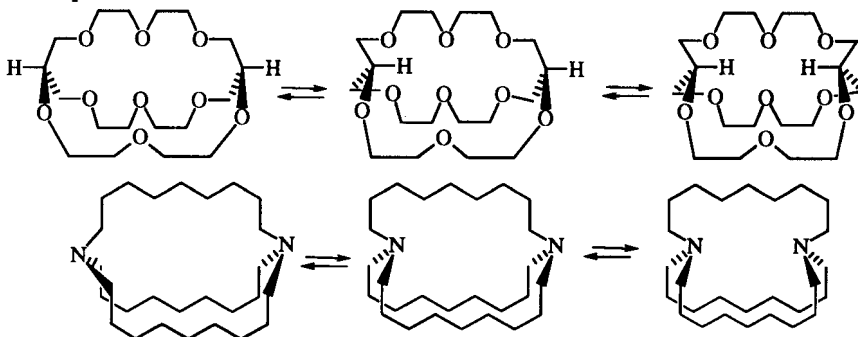
Superposable ligands are called homomorphic.

### Homotopic

Atoms or groups of a molecule which are related by an  $n$ -fold rotation axis ( $n = 2, 3, \text{etc}$ ) are called homotopic. For example, chiral tartaric acid ( $C_2$  axis), chloroform ( $C_3$  axis) and cyclohexaamylose ( $\alpha$ -cyclodextrin,  $C_6$  axis) have respectively two homotopic carboxyl groups, three homotopic chlorine atoms and six homotopic D-glucose residues. See *prochirality*.

### In-Out Isomerism

*Isomerism* 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.



**Induction, Stereochemical** See *asymmetric induction*.

**Internal Compensation** (usage strongly discouraged) See *meso*-compound.

### Inversion

1. See *Walden inversion*.
2. See *pyramidal inversion*.
3. See *ring inversion*.
4. A symmetry operation involving a centre of inversion ( $i$ ).

### Isomer

One of several chemical species (or molecular entities) that have the same stoichiometric molecular formula but different constitutional formulae or different *stereochemical formulae* and hence potentially different physical and/or chemical properties.

### Isomeric

Adjective derived from *isomer*.

### Isomerism

The relationship between *isomers*.

### Isometric, Anisometric

Two molecular entities that are superposable or can be made superposable by reflection of one of them in a mirror are isometric; otherwise they are anisometric.

## Isotopomers

Isomers having the same number of each isotopic atom but differing in their positions. The term is a contraction of isotopic isomer.

Isotopomers can either be *constitutional isomers* (e.g.  $\text{CH}_2\text{DCHO}$  and  $\text{CH}_3\text{CDO}$ ) or isotopic *stereoisomers* (e.g. (*R*)- and (*S*)- $\text{CH}_3\text{CHDOH}$ ).

## Kinetic Resolution

The achievement of partial or complete resolution by virtue of unequal rates of reaction of the *enantiomers* in a *racemate* with a *chiral agent* (reagent, catalyst, solvent, etc.).

L See D, L, DL.

*l*

1. An obsolete prefix for (*-*)-, see *d, l, dl*.
2. See *l,u* for like and unlike diastereoisomers.

*l, u*

*Stereodescriptors of diastereoisomers with two chirality elements.* When the two chirality elements are both *R* or both *S* the molecular entity is described as having an *l* relationship (*l* = like), when one chirality element is *R* and the other *S* the molecular entity is described as having a *u* relationship (*u* = unlike). The notation can be extended to molecules with more than two chirality elements whereby the *l,u* relationships of the chiral elements are considered in pairs. See V. Prelog and G. Helmchen, *Angew. Chem.* **94**, 614-631 (1982), *Angew. Chem. Internat. Ed. Eng.* **21**, 567-583 (1982).

$\Lambda$  (**Lambda**) See  $\Delta$  (*delta*).

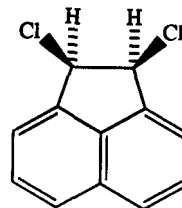
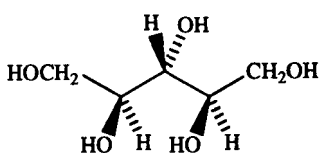
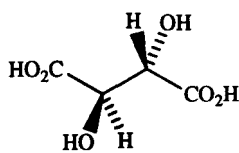
M See *helicity*.

*meso*

A prefix to indicate the presence of a symmetry element of the second kind (see *chirality*) in a chemical species which is usually one of a set of *diastereoisomers* that also includes a chiral member. See *meso*-compound.

## *meso*-Compound

A term for the achiral member(s) of a set of *diastereoisomers* which also includes one or more chiral members. For example:



Minus See *plus, minus*

## Molecular Entity

Any chemically or isotopically distinct atom, molecule, ion, ion pair, radical, radical ion, complex, conformer *etc.*, which can be identified as a separately distinguishable entity.

It depends on the context with what degree of precision a molecular entity is to be described. For example 'hydrogen molecule' is an adequate definition of a certain molecular entity for some purposes, whereas for others it is necessary to distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the hydrogen molecule.

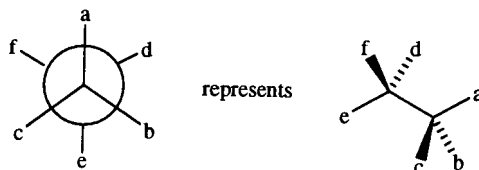
[*Glossary of Terms Used in Physical Organic Chemistry*, *Pure Appl. Chem.* **66**, 1077-1184 (1994)].

### Mutarotation

The change in optical rotation accompanying *epimerisation*. In sugar chemistry this term usually refers to epimerisation at the hemiacetal carbon atom.

### Newman Projection

A *projection formula* representing the spatial arrangement of bonds on two adjacent atoms in a molecular entity. The structure appears as viewed along the bond between these two atoms, and the bonds from them to other groups are drawn as projections in the plane of the paper. The bonds from the atom nearer to the observer are drawn so as to meet at the centre of a circle representing that atom. Those from the further atom are drawn as if projecting from behind the circle.



### Nonbonded Interactions

Intramolecular attractions or repulsions between atoms that are not directly linked to each other, affecting the thermodynamic stability of the chemical species concerned. See also *eclipsing strain*; *transannular strain*.

### Optical Activity

A sample of material able to rotate the plane of polarisation of a beam of transmitted plane-polarised light is said to possess optical activity (or to be optically active). This optical rotation is the classical distinguishing characteristic (sufficient but not necessary) of systems containing unequal amounts of corresponding *enantiomers*. An enantiomer causing rotation in a clockwise direction (when viewed in the direction facing the oncoming light beam) under specified conditions is called dextrorotatory and its chemical name or formula is designated by the prefix (+)-; one causing rotation in the opposite sense is laevorotatory and designated by the prefix (-)-. Materials with optical activity also exhibit other *chiroptic* phenomena.

### Optical Antipodes (usage strongly discouraged)

Obsolete synonym for *enantiomers*.

### Optical Isomerism (usage strongly discouraged)

Obsolescent synonym for *stereoisomers* with different optical properties. It should be described as diastereoisomerism or enantiomerism.

### Optical Purity

The ratio of the observed optical rotation of a sample consisting of a mixture of enantiomers to the optical rotation of one pure enantiomer. See *enantiomeric excess*.

### Optical Resolution (usage strongly discouraged) See *resolution*.

### Optical Rotation See *optical activity*.

### Optical Yield

In a chemical reaction involving *chiral* reactants and products, the ratio of the *optical purity* of the product to that of the precursor, reactant or catalyst. This should not be confused with *enantiomeric excess*.

### Optically Labile (usage strongly discouraged)

A term describing a system in which stereoisomerisation results in a change of optical rotation with time.

### Out-isomer See *in-out isomerism*.

### P, M See *helicity*.

### Percent Diastereoisomer Excess See *diastereoisomer excess*.

### Percent Enantiomer Excess See *enantiomer excess*.

**Periplanar** See *torsion angle*.

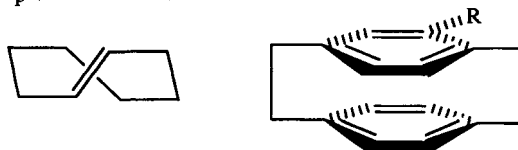
### Perspective Formula

A geometric representation of stereochemical features of a molecule or model which appears as a view from an appropriate direction. See *Fischer projection*, *Newman projection*, *projection formula*, *sawhorse projection*, *wedge projection*, *zig-zag projection*. See also *stereochemical formula*.

**Pitzer Strain** See *eclipsing strain*.

### Planar Chirality

Term used by some authorities to refer to *stereoisomerism* resulting from the arrangement of out-of-plane groups with respect to a plane (*chirality plane*). It is exemplified by the *atropisomerism* of (*E*)-cyclooctene (chiral plane = double bond and attached atoms) or monosubstituted paracyclophane (chiral plane = substituted ring). The configuration of molecular entities possessing planar chirality is specified by the stereodescriptors  $R_p$  and  $S_p$  ( or *P* and *M*).



### Plus, Minus

See 1. *d*, *l*, *dl* for (+), (−) and (±)

2. *helicity* for *P* and *M*.

### Point Group

The classification of the symmetry elements of an object. It is denoted in the Schoenflies notation by an italic symbol, such as  $C_3$ ,  $D_2$ ,  $T_d$ , etc.

### Polytopal Rearrangement

Stereoisomerisation interconverting different or equivalent spatial arrangements of ligands about a central atom or of a cage of atoms, where the ligand or cage defines the vertices of a polyhedron. For example *pyramidal inversion* of amines, *Berry pseudorotation* of  $PF_5$ , rearrangements of polyhedral boranes. See E.L. Muetterties, *J. Am. Chem. Soc.* **91**, 1636-1643 (1969).

### Primary Structure

In the context of macromolecules such as proteins, the constitutional formula, usually abbreviated to a statement of the sequence and if appropriate cross-linking of chains. See also *secondary structure*, *tertiary structure*, *quaternary structure*.

**Priority** See *CIP priority*.

### Prochirality

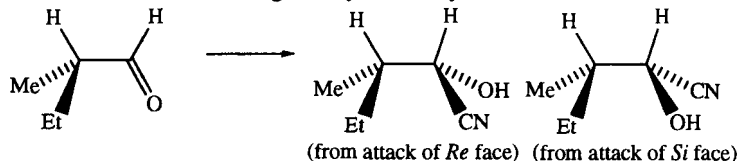
This term is used in different, sometimes contradictory ways; four are listed below.

1. The geometric property of an achiral object (or spatial arrangement of points or atoms) which is capable of becoming *chiral* in a single *desymmetrisation* step. An achiral molecular entity, or a part of it considered on its own, is thus called prochiral if it can be made chiral by the replacement of an existing atom (or achiral group) by a different one.

An achiral object which is capable of becoming chiral in two desymmetrisation steps is sometimes described as *proprochiral*. For example the proprochiral  $CH_3CO_2H$  becomes prochiral as  $CH_2DCO_2H$  and chiral as  $CHDTCO_2H$ .

2. The term prochirality also applies to an achiral molecule or entity which contains a trigonal system and which can be made chiral by the addition to the trigonal system of a new atom or achiral group. For example addition of hydrogen to one of the enantiotopic faces of the prochiral ketone  $CH_3CH_2COCH_3$  gives one of the enantiomers of the chiral alcohol  $CH_3CH_2CHOHCH_3$ ; the addition of  $CN^-$  to one of the

*diastereotopic* faces of the chiral aldehyde shown below converts it into one of the diastereoisomers of the cyanohydrin. The two faces of the trigonal system may be described as *Re* and *Si*.



- The term prochiral also applies to a tetrahedral atom of an achiral or chiral molecule which is bonded to two stereoheterotopic groups. For example, the prochiral molecule  $\text{CH}_3\text{CH}_2\text{OH}$  can be converted into the chiral molecule  $\text{CH}_3\text{CHDOH}$  by the isotopic replacement of one of the two enantiotopic hydrogen atoms of the methylene group. The carbon atom of the methylene group is called prochiral. The prochiral molecule  $\text{HO}_2\text{CCH}_2\text{CHOHCH}_2\text{CO}_2\text{H}$  can be converted into a chiral product by esterification of one of the two enantiotopic  $-\text{CH}_2\text{CO}_2\text{H}$  groups. The carbon atom of the  $\text{CHOH}$  group is called prochiral. The chiral molecule  $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$  can be converted into one of the diastereoisomers of  $\text{CH}_3\text{CHOHCHDCH}_3$  by the isotopic replacement of one of the two *diastereotopic* hydrogen atoms of the methylene group. The carbon atom of the methylene group is called prochiral. The stereoheterotopic groups in these cases may be described as *pro-R* or *pro-S*. Reference to the two stereoheterotopic groups themselves as prochiral, although common, is strongly discouraged. See *chirality centre*.
- The term prochirality is also applied to the enantiotopic faces of a trigonal system.

### Prochirality Centre

An atom of a molecule which becomes a *chirality centre* by replacing one of the two *stereoheterotopic* ligands attached to it by a different ligand is said to be a prochirality centre *e.g.* C-1 of ethanol; C-3 of butan-2-ol.

### *pro-E*, *pro-Z*

One of a pair of identical groups *c* attached to a double bond (as in  $\text{abC}=\text{Cc}_2$ ) is described as *pro-E* if, when it is arbitrarily assigned *CIP* priority over the other group *c*, the *stereodescriptor* of the molecule becomes *E*. The other group *c* is then described as *pro-Z*.

### Projection Formula

A formal two-dimensional representation of a three-dimensional molecular structure obtained by projection of bonds (symbolised as lines) onto a plane with or without the designation of the positions of relevant atoms by their chemical symbols.

A projection formula which indicates the spatial arrangement of bonds is called a *stereochemical formula* or *stereoformula*. Examples of stereoformulae are *Fischer projection*, *Newman projection*, *sawhorse projection*, *wedge projection* and *zig-zag projection*. See also *perspective formula*.

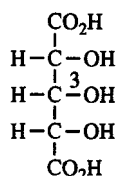
**Proprochirality** See *prochirality*.

### *pro-R*, *pro-S*

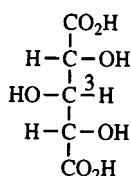
A *stereoheterotopic* group *c* (as in tetrahedral  $\text{Xabc}_2$ ) is described as *pro-R* if, when it is arbitrarily assigned *CIP* priority over the other stereoheterotopic group *c*, the configuration of the thus generated chiral centre is assigned the *stereodescriptor R*. The other group *c* is then described as *pro-S*. This method for distinguishing between stereoheterotopic groups can be applied to other kinds of prochiral molecular entities or *prochiral* parts of molecular entities considered on their own. See *prochirality centre*.

### Pseudo-asymmetric Carbon Atom

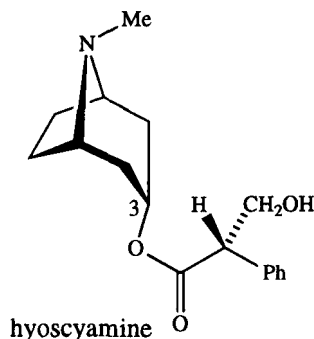
The traditional name for a tetrahedrally coordinated carbon atom bonded to four different entities, two and only two of which have the same constitution but opposite chirality sense. The *r/s* descriptors of pseudo-asymmetric carbon atoms are invariant on reflection in a mirror (*i.e.* *r* remains *r*, and *s* remains *s*), but are reversed by the exchange of any two entities (*i.e.* *r* becomes *s*, and *s* becomes *r*). An example is C-3 of ribaric (C-3 is *r*), xylaric acid (C-3 is *s*) or hyoscyamine (C-3 is *r*). The hyphen in pseudo-asymmetric may be omitted.



ribaric acid



xylaric acid



hyoscyamine

**Pseudo-axial** See *axial, equatorial*.

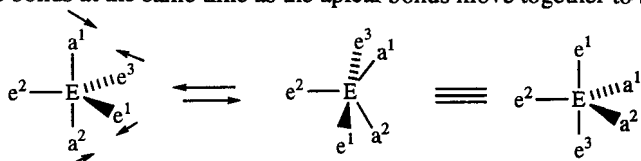
**Pseudo-equatorial** See *axial, equatorial*.

### Pseudorotation

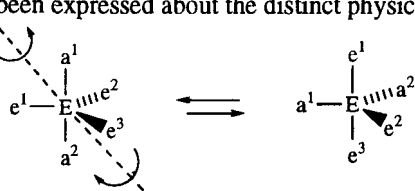
Stereoisomerisation resulting in a structure that appears to have been produced by rotation of the entire initial molecule and is *superposable* on the initial one, unless different positions are distinguished by substitution, including isotopic substitution.

One example of pseudorotation is a facile interconversion between the many envelope and twist conformers of a cyclopentane due to the out of plane motion of carbon atoms.

Another example of pseudorotation (Berry pseudorotation) is a polytopal rearrangement that provides an intramolecular mechanism for the isomerisation of trigonal bipyramidal compounds (e.g.  $\lambda^5$ -phosphanes), the five bonds to the central atom E being represented as  $e^1, e^2, e^3, a^1$  and  $a^2$ . Two *equatorial* bonds move apart and become *apical* bonds at the same time as the apical bonds move together to become equatorial.

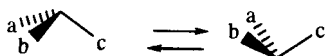


A related conformational change of a trigonal bipyramidal structure is described as turnstile rotation. The process may be visualised as follows. An apical and an equatorial bond rotate as a pair *ca.*  $120^\circ$  relative to the other three bonds. (Doubts have been expressed about the distinct physical reality of this mechanism.)



### Pyramidal Inversion

A polytopal rearrangement in which the change in bond directions to a three-coordinate central atom having a pyramidal arrangement of bonds (tripodal arrangement) causes the central atom (apex of the pyramid) to appear to move to an equivalent position on the other side of the base of the pyramid. If the three ligands to the central atom are different pyramidal inversion interconverts *enantiomers*.



**Quasi-axial** See *axial, equatorial*.

### Quasi-enantiomers

Constitutionally different yet closely related chemical species MX and MY having the opposite chirality sense of the large common chiral moiety M are called quasi-enantiomers. For example (*R*)-2-bromobutane is a quasi-enantiomer of (*S*)-2-chlorobutane. See also *quasi-racemic compound*.

**Quasi-equatorial** See *axial, equatorial*.

### Quasi-racemic Compound

The crystalline product of a 1:1 association between *quasi-enantiomers*.

### Quaternary Structure

The defined organisation of two or more macromolecules with tertiary structure such as a protein that are held together by hydrogen bonds and van der Waals and coulombic forces. See also *primary structure, secondary structure, tertiary structure*.

*r, s*

Stereodescriptors of *pseudo-asymmetric atom*. For references see under *R, S*.

### R, S

The approved designations (devised by Cahn, Ingold and Prelog) of absolute configuration at four-coordinate (quadriligant) and six-coordinate (sexiligant) *stereogenic centres*. For the application of these stereodescriptors in systematic chemical nomenclature see R.S. Cahn, C.K. Ingold and V. Prelog, *Angew. Chem.* **78**, 413-447 (1966), *Angew. Chem. Internat. Ed. Eng.* **5**, 385-415, 511 (1966); and V. Prelog and G. Helmchen, *Angew. Chem.* **94**, 614-631 (1982), *Angew. Chem. Internat. Ed. Eng.* **21**, 567-583 (1982).

*R<sub>p</sub>, S<sub>p</sub>* See *planar chirality*.

*R\**, *S\** See *relative configuration*.

*rac* See *racemate*.

### Racemate

An equimolar mixture of a pair of *enantiomers*. It does not exhibit *optical activity*. The chemical name or formula of a racemate is distinguished from those of the enantiomers by the prefix (±)- or *rac-* (or *racem-*) or by the symbols *RS* and *SR*.

### Racemic

Pertaining to a *racemate*.

### Racemic Compound

A crystalline *racemate* in which the two *enantiomers* are present in equal amounts in a well defined arrangement within the lattice of a homogeneous crystalline addition compound.

### Racemic Conglomerate

An equimolar mechanical mixture of crystals each one of which contains only one of the two *enantiomers* present in a *racemate*. The process of its formation on crystallisation of a racemate is called spontaneous resolution, since pure or nearly pure enantiomers can often be obtained from the conglomerate by sorting.

### Racemic Mixture (usage strongly discouraged)

The term is confusing since it has been used as a synonym for both *racemate* and *racemic conglomerate*.

### Racemisation

The production of a *racemate* from a *chiral* starting material in which one *enantiomer* is present in excess.

### Re, Si

A *stereoheterotopic* face of a trigonal atom is designated *Re* if the ligands of the trigonal atom appear in a clockwise sense in order of *CIP* priority when viewed from that side of the face. The opposite arrangement is termed *Si*. See also *enantiotopic*, and illustrated under *prochirality*.

*rel* See *relative configuration*.



## Relative Configuration

1. The *configuration* of any *stereogenic (asymmetric) centre* with respect to any other *stereogenic centre* contained within the same molecular entity. Unlike *absolute configuration*, relative configuration is reflection-invariant. Relative configuration, distinguishing *diastereoisomers*, may be denoted by the configurational descriptors  $R^*$ ,  $R^*$  (or  $l$ ) and  $R^*$ ,  $S^*$  (or  $u$ ) meaning, respectively, that the two centres have identical or opposite configurations. For molecules with more than two asymmetric centres the prefix *rel-* may be used in front of the name of one enantiomer where  $R$  and  $S$  have been used. If any centres have known absolute configuration then only  $R^*$  and  $S^*$  can be used for the relative configuration. See also  $\alpha$  (*alpha*),  $\beta$  (*beta*) (1) and (3).
2. Two different molecules  $Xabcd$  and  $Xabce$ , may be said to have the same relative configurations if  $e$  takes the position of  $d$  in the tetrahedral arrangement of ligands around  $X$  (*i.e.* the pyramidal fragments  $Xabc$  are superposable). By the same token the *enantiomer* of  $Xabce$  may be said to have the opposite relative configuration to  $Xabcd$ . The terms may be applied to *chiral* molecular entities with central atoms other than carbon but are limited to cases where the two related molecules differ in a single ligand.

Both definitions can be generalised to include *stereogenic units* other than asymmetric centres.

## Resolution

The separation of a *racemate* into the component *enantiomers*. See also *kinetic resolution*, *racemic conglomerate*.

**Restricted Rotation** See *free rotation*, *hindered rotation*, *restricted rotation*.

**Retention of configuration** See *Walden inversion*.

## Ring Reversal (or ring inversion)

The interconversion by rotation about single bonds (coupled with angle deformation in the transition state) of cyclic conformers having equivalent ring shapes (*e.g.* *chair*  $\rightarrow$  *chair*) though not necessarily equivalent spatial positions of substituents (*e.g.* *equatorial*  $\rightarrow$  *axial*)

**Rosanoff Convention** See *Fischer-Rosanoff convention*.

## Rotamer

One of a set of *conformers* arising from restricted rotation about one single bond.

## Rotational Barrier

In a rotation of groups about a bond, the potential energy barrier between two adjacent minima of the molecular entity as a function of the *torsion angle*.

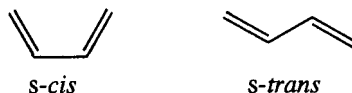
## Rotatory Power

The quantitative measure of *optical activity*.

**RS** See *racemate*.

## s-cis, 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 term should not be applied to other systems such as *N*-alkyl amides (use *E/Z* or *sp/ap*).

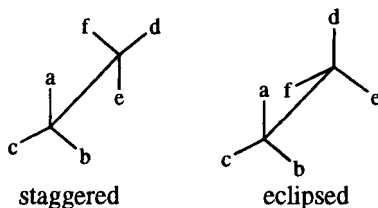


**S** See  $R$ ,  $S$ .

## Sawhorse Projection

A *perspective formula* indicating the spatial arrangement of bonds on two adjacent carbon atoms. The bond between the two atoms is represented by a diagonal line, the left-hand bottom end of which locates the atom

nearer the observer and the right-hand top end the atom that is further away. In general a *Newman* or *zig-zag projection* is preferred.



*sc* See *torsion angle*.

### Secondary Structure

The conformational arrangement ( $\alpha$ -helix,  $\beta$ -pleated sheet, *etc.*) of the backbone segments of a macromolecule such as a polypeptide chain of a protein without regard to the conformation of the side chains or the relationship to other segments. See also *primary structure*, *tertiary structure*, *quaternary structure*.

*Si* See *Re*, *Si*.

**Sequence Rules** See *priority*.

**Skew** See *torsion angle* and *chair*, *boat*, *twist*.

*sp* See *torsion angle*.

### Space Formula

Synonym for *stereochemical formula*.

**Spontaneous Resolution** See *racemic conglomerate*.

*SR* See *racemate*.

### Staggered Conformation

The *conformation* of groups attached to two adjacent atoms is said to be staggered if the *torsion angles* are such that the groups are as far away as possible from an *eclipsed* arrangement.

### Stereochemical Formula (Stereoformula)

A three-dimensional view of a molecule either as such or in a projection. See *projection formula*.

### Stereoconvergence

The predominant formation of the same *stereoisomer* or stereoisomer mixture of a reaction product when two different stereoisomers of the reactant are used in the same reaction. When that product involved in the reaction is one *enantiomer* the result has been called enantioconvergence.

### Stereodescriptor

A prefix to specify *configuration* (absolute or relative) or *conformation*. For example *R,S*; *r,s*; *P,M*; *Re,Si*; *E,Z*; *ap,sp*; *etc.*

### Stereoelectronic

Pertaining to the dependence of the properties (especially the energy) of a molecular entity in a particular electronic state (or of a transition state) on relative nuclear geometry. The electronic ground state is usually considered, but the term can apply to excited states as well. Stereoelectronic effects arise from the different alignment of electronic orbitals in different arrangements of nuclear geometry.

['Glossary of Terms Used in Physical Organic Chemistry', *Pure Appl. Chem.* **66**, 1077-1184 (1994)].

### Stereoelectronic Control

Control of the nature of the products of a chemical reaction (or of its rate) by stereoelectronic factors. The term is usually applied in the framework of an orbital approximation. The variations of molecular orbital energies with relative nuclear geometry (along a reaction coordinate) are then seen as consequences of variations in basis-orbital overlaps.

['Glossary of Terms Used in Physical Organic Chemistry', *Pure Appl. Chem.* **66**, 1077-1184 (1994)].

**Stereoformula** See *projection formula*.

### **Stereogenic Unit (or Stereogen or Stereoelement)**

A grouping within a molecular entity that may be considered a focus of stereoisomerism. At least one of these must be present in every enantiomer (though the presence of stereogenic units does not conversely require the corresponding chemical species to be chiral). Three basic types are recognised for molecular entities involving atoms having not more than four substituents:

- A grouping of atoms consisting of a central atom and distinguishable ligands, such that the interchange of any two of the substituents leads to a stereoisomer. An *asymmetric atom (chirality centre)* is the traditional example of this stereogenic unit.
- A chain of four non-coplanar atoms (or rigid groups) in a stable conformation, such that an imaginary or real (restricted) rotation (with a change of sign of the torsion angle) about the central bond leads to a stereoisomer.
- A grouping of atoms consisting of a double bond with substituents which give rise to *cis-trans isomerism*.

### **Stereoheterotopic**

Either *enantiotopic* or *diastereotopic*. (In contrast the term constitutionally heterotopic has been used to describe identical groups located in constitutionally non-equivalent positions.) See also *pro-R*, *pro-S*.

### **Stereoisomerism**

Isomerism due to differences in the spatial arrangement of atoms without any differences in connectivity or bond multiplicity between the isomers.

**Stereoisomerism, Planar** See *planar chirality*.

### **Stereoisomers**

Isomers that possess identical *constitution*, but which differ in the arrangement of their atoms in space. See *enantiomer*, *diastereoisomer*, *cis-trans isomers*.

### **Stereoisomerism**

A change of *configuration* at a *stereogenic unit* brought about by physical or chemical means. See *epimerisation*.

### **Stereoselective synthesis**

A chemical reaction (or reaction sequence) in which one or more new elements of chirality are formed in a substrate molecule and which produces the stereoisomeric (enantiomeric or diastereoisomeric) products in unequal amounts. Traditionally called *asymmetric synthesis*. See also *stereoselectivity*.

### **Stereoselectivity**

The preferential formation in a chemical reaction of one stereoisomer over another. When the stereoisomers are enantiomers, the phenomenon is called *enantioselectivity* and is quantitatively expressed by the *enantiomer excess*; when they are diastereoisomers, it is called *diastereoselectivity* and is quantitatively expressed by the *diastereoisomer excess*.

### **Stereospecificity**

A reaction is termed stereospecific if starting materials differing only in their configuration are converted into stereoisomeric products. According to this definition, a stereospecific process is necessarily stereoselective but not all stereoselective processes are stereospecific.

[‘Glossary of Terms Used in Physical Organic Chemistry’, *Pure Appl. Chem.* **66**, 1077-1184 (1994)].

### **Steric Strain**

- See strain [See ‘Glossary of terms used in Physical Organic Chemistry’, *Pure Appl. Chem.* **66**, 1077-1184 (1994)].

2. See *angle strain*.
3. See *eclipsing strain*.
4. See *transannular strain*.

### Superposability

The ability to bring two particular stereochemical formulae (or models) into coincidence (or to be exactly superposable in space, and for the corresponding molecular entities or objects to become exact replicas of each other) by no more than translation and rigid rotation.

### Syn

1. See *torsion angle*.
2. See *endo, exo, syn, anti*.
3. See also 'Glossary of Terms Used in Physical Organic Chemistry', *Pure Appl. Chem.* **66**, 1077-1184 (1994) for use as a term to describe suprafacial addition or elimination reactions.
4. It was formerly used to describe the stereochemistry of oximes and related systems (see *E,Z*).

**Synclinal** See *torsion angle*.

**Synperiplanar** See *torsion angle*.

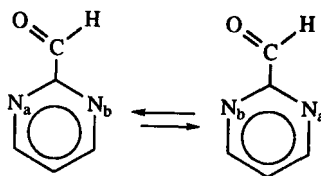
### Tertiary structure

The spatial organisation (including conformation) of an entire protein molecule or other macromolecule consisting of a single chain. See also *primary structure, secondary structure, quaternary structure*.

*threo* See *erythro*.

### Topomerisation

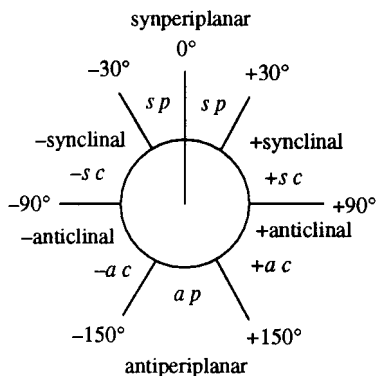
The identity reaction leading to exchange of the positions of identical ligands. The indistinguishable molecular entities involved are called topomers. For example in the reaction below the two identical ligating atoms  $N_a$  and  $N_b$  are interchanged by rotation about the C-aryl bond but may be identified by n.m.r. spectroscopy. This is a degenerate isomerisation [See 'Glossary of terms used in Physical Organic Chemistry', *Pure Appl. Chem.* **66**, 1077-1184 (1994)].



**Topomers** See *topomerisation*.

### Torsion Angle

In a chain of atoms A-B-C-D, the *dihedral angle* between the plane containing the atoms A,B,C and that containing B,C,D). In a *Newman projection* the torsion angle is the angle (having an absolute value between  $0^\circ$  and  $180^\circ$ ) between bonds to two specified (*fiducial*) groups, one from the atom nearer (proximal) to the observer and the other from the further (distal) atom. The torsion angle between groups A and D is then considered to be positive if the bond A-B is rotated in a clockwise direction through less than  $180^\circ$  in order that it may *eclipse* the bond C-D: a negative torsion angle requires rotation in the opposite sense. Stereochemical arrangements corresponding to torsion angles between  $0^\circ$  and  $\pm 90^\circ$  are called *syn* (*s*), those corresponding to torsion angles between  $\pm 90^\circ$  and  $180^\circ$  *anti* (*a*). Similarly, arrangements corresponding to torsion angles between  $30^\circ$  and  $150^\circ$  or between  $-30^\circ$  and  $-150^\circ$  are called *clinal* (*c*) and those between  $0^\circ$  and  $\pm 30^\circ$  or  $\pm 150^\circ$  and  $180^\circ$  are called *periplanar* (*p*). The two types of terms can be combined so as to define four ranges of torsion angle;  $0^\circ$  to  $\pm 30^\circ$  *synperiplanar* (*sp*);  $30^\circ$  to  $90^\circ$  and  $-30^\circ$  to  $-90^\circ$  *synclinal* (*sc*);  $90^\circ$  to  $150^\circ$ , and  $-90^\circ$  to  $-150^\circ$  *anticlinal* (*ac*);  $\pm 150^\circ$  to  $180^\circ$  *antiperiplanar* (*ap*).



The synperiplanar conformation is also known as the *syn*- or *cis*-conformation; antiperiplanar as *anti* or *trans* and synclinal as *gauche* or *skew*. For macromolecular usage the symbols T, C, G<sup>+</sup>, G<sup>-</sup>, A<sup>+</sup> and A<sup>-</sup> are recommended (*ap*, *sp*, *+sc*, *-sc* *+ac* and *-ac* respectively). See 'Stereochemical Definitions and Notations Relating to Polymers', *Pure Appl. Chem.* **51**, 733-752 (1981).

### Torsional Stereoisomers

Stereoisomers that can be interconverted (actually or conceptually) by torsion about a bond axis. This includes *E,Z*-isomers of alkenes, *atropisomers* and *rotamers*.

**Torsional Strain** See *eclipsing strain*.

*trans* See *cis*, *trans*.

### Transannular Strain

In medium-sized ring compounds, the strain due to repulsive *non-bonded interactions* between substituents or hydrogen atoms attached to non-adjacent ring atoms.

**transoid Conformation** (usage strongly discouraged)

See *s-cis*, *s-trans*. See *cisoid* for use of *transoid* as a stereodescriptor.

### Tub Conformation

A *conformation* (of symmetry group  $D_{2d}$ ) of an eight-membered ring in which the four atoms forming one pair of diametrically opposite bonds in the ring lie in one plane and all other ring atoms lie to one side of that plane. It is analogous to the boat conformation of cyclohexane. See also *crown conformation*.



**Turnstile Rotation** See *pseudo-rotation*.

**Twist Form** See *chair*, *boat*, *twist*.

*u* See *l*, *u*.

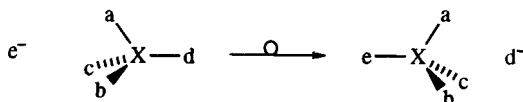
### Valence Isomerism

See 'Glossary of Terms Used in Physical Organic Chemistry', *Pure Appl. Chem.* **66**, 1077-1184 (1994).

### Walden Inversion

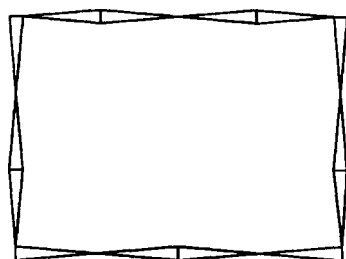
Retention of configuration is the preservation of integrity of the spatial arrangement of bonds to a chiral centre during a chemical reaction or transformation. It is also the configurational correlation when a chemical species Xabcd is converted into the chemical species Xabce having the same *relative configuration*. The configurational change when a chemical species Xabcd (where X is typically carbon), having a tetrahedral arrangement of bonds to X, is converted into the chemical species Xabce having the opposite relative configuration (or when it undergoes an identity reaction in which Xabcd of opposite configuration is produced) is called a Walden inversion or inversion of configuration. The occurrence of a Walden inversion

during a chemical transformation is sometimes indicated in the chemical equation by the symbol shown below in place of a simple arrow pointing from reactants to products.



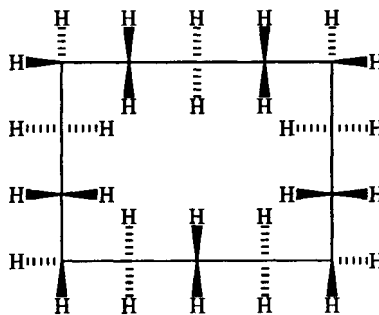
### Wedge Projection

A stereochemical projection, roughly in the mean plane of the molecule, in which bonds are represented by open wedges, tapering off from the nearer atom to the farther atom. See J. Dale, *Acta Chem. Scand.* **27**, 1115-1129 (1973). It is mainly used to illustrate the conformation of larger cycloalkanes *e.g.* cyclotetradecane:



wedge projection

equivalent to



Z See E, Z.

### Zig-zag Projection

A stereochemical projection for an acyclic molecule (or portion of a molecule) where the main chain is represented by a zig-zag line in the plane and the substituents are shown above or below the plane.

