

Glossary

Achiral. A molecule that is superimposable on its mirror image (p. 19) is achiral.

Allenes. Propa-1,2-diene ($\text{CH}_2=\text{C}=\text{CH}_2$) and derivatives. In allenes the two π bonds are orthogonal (see below), as are the two terminal hydrogens at one end, with respect to those at the other.

Ångstrom (Å). Unit of length named after the Swedish physicist, now being superseded by nanometer (nm). $1 \text{ Å} = 10^{-10} \text{ m}$ so that a bond length of 1.54 Å is given by 0.154 nm .

Anisochronous. In NMR spectroscopy this term is used to indicate that two or more nuclei have different chemical shifts.

Anomers. Anomers are cyclic diastereoisomers that differ only at the hemiacetal carbon. The anomeric carbon in a sugar is the only carbon that is bonded to two oxygen atoms.

Anti (see also *Anti addition*; *Anti periplanar*). Substituents are *anti* if they are on opposite sides of a defined reference plane in a molecule. *Anti* is used to assign stereochemistry to products of, for example, asymmetric aldol reactions. The main chain is drawn in the plane of the paper and substituents on opposite sides of the plane are termed *anti*, e.g. diagram 19 in Chapter 3.

Anti addition. *Anti* addition of X–Y occurs when X and Y are added to opposite faces of a double bond.

Anti clinal. When the C–C–C–C dihedral angle is between 90° and 150° , i.e. $120 \pm 30^\circ$, the conformation is said to be *anti clinal*.

Anti periplanar (sometimes called *Anti*). Term given to a molecular fragment, e.g. X–C(1)–C(2)–Y, or C(1)–C(2)–Y (in this second case, a lone pair of electrons in a p-orbital replaces the X–C bond), in which the dihedral angle is 180° , or more generally $180 \pm 30^\circ$.

Atactic. This adjective describes a polymer whose stereogenic centres along the polymer chain are randomly oriented.

Atropisomers. Stereoisomers that arise from restricted rotation around a single bond in which the barrier to rotation is sufficiently high for the stereoisomers to be isolated. Certain *ortho* disubstituted biphenyls are atropisomers, and the stereoisomers referred to in this case are enantiomers.

Axial bonds. In the chair conformation of cyclohexanes, axial bonds are described as being: (a) parallel to the C_3 axis, or (b) perpendicular to a general plane that contains the majority of carbon atoms.

Axial chirality. Chirality that has its origins in the non-planar disposition of groups with respect to an axis, and exemplified by 1,3-dichloroallene (Chapter 5, structure 4), certain alkyldenecyclohexanes (Chapter 5, structure 6) and 4-substituted cyclohexanone oximes.

Bridgehead carbon. In an unsubstituted hydrocarbon that consists of two or more fused or bridged rings, with two or more carbons in common, the bridgehead carbons are tertiary carbons common to two or more rings. Bridgehead carbons can be substituted by, for example, Cl, OH, *etc.* In bicyclo[2.2.1]heptane the bridgehead carbons are C(1) and C(4); in bicyclo[4.4.0]decane they are C(1) and C(6).

Brosylate (4-bromobenzenesulfonate, 4-BrC₆H₄SO₃). Slightly better leaving group than tosylate in substitution and elimination reactions. Usually abbreviated to OBs.

Cahn-Ingold-Prelog (CIP) R/S convention. The most widely used method for assignment of configuration to stereogenic centres (and chiral axes). Substituents at stereogenic centres are given ranking numbers 1, 2, 3 and 4, associated with decreasing atomic number; configuration is then assigned as in Chapter 2, Section 2.2.2. The configuration of chiral axes is given in Chapter 5, Section 5.3.

Canonical forms (also called resonance structures). These are different Lewis structures that are alternative ways of representing the actual structure of a molecule that contains delocalized bonds. One draws several possible structures that all have the same number of unpaired electrons, and in which the relative positions of the nuclei are the same. Each canonical structure contributes in proportion to its stability, so that the structure is a weighted average of all canonical structures. These delocalized canonical structures have no *individual* existence. As an example, aromatic compounds and amides are weighted averages of two or more canonical forms (or Lewis structures); in the case of an amide, these are, for example, $R^1_2N-C(=O)R^2$ and $R^1_2N^+=C(O^-)R^2$.

Chair conformation. The lowest energy conformation of cyclohexane. All the vicinal C–H bonds are staggered; this conformation has very little angle strain or torsion strain.

Chiral. A chiral (or handed) molecule is one that is not superimposable on its mirror image. The adjective is ideally restricted to single molecules. An object such as a helix can also be described as chiral.

Chirality. The property of non-identity of an object with its mirror image. An object, *e.g.* a molecule in a given configuration or conformation, is said to be chiral when it is not identical with its mirror image.

Cis. Groups or atoms are *cis* when they lie on the same side of an identifiable reference plane in a molecule.

Concerted. In a concerted reaction the bonding changes occur in a single step and simultaneously.

Configuration. The three-dimensional arrangement (or sequence) in space of atoms, or functional groups, that characterizes a stereoisomer. In order to change a configuration, bond breaking and bond re-forming in a different sequence must occur. Enantiomers have opposite configurations. Configurations are denoted by *R/S*; *D/L*; *E/Z*. Configuration should be contrasted with *conformation*, in which changes are brought about only by bond rotation.

Conformation. A description of the arrangement or disposition in space of the atoms, or functional groups, in a molecule. Conformations can change by varying a dihedral angle, *i.e.* by rotating about a single bond, but *not* by breaking a bond. Amides (Chapter 4) are a special case.

Conformation (boat). A conformation of cyclohexane that, by virtue of two eclipsed C–C bonds and a 1,4 non-bonded H···H interaction, is of higher energy than the chair conformation. So called because it resembles a boat when viewed sideways on.

Conformation (chair). The lowest energy conformation of cyclohexane, in which all C–C bonds are staggered, and which has very little angle or torsional strain. This conformation resembles a chair when viewed sideways on.

Conformation (eclipsed). When, for example, in ethane the dihedral angle ϕ between a pair of hydrogens on adjacent carbons is 0° ; this is the least stable conformation. In butane, both C–C–C dihedral angles of 0° (synperiplanar) and 120° (anticlinal) are eclipsed; the C–H bonds are eclipsed here also. Some rigid molecules, *e.g.* bicyclo[2.2.1]heptane, have the C–H bonds at C(2), C(3), C(5) and C(6) locked in an eclipsed conformation.

Conformation (skewed). As above, but with the value of ϕ between 0° and 60° ; there are an infinite number of skewed conformations.

Conformation (staggered). As above but with $\phi = 60^\circ$; in the case of ethane, the most stable conformation. Butane has a gauche staggered conformation in which the C–C–C dihedral angle is 60° and an antiperiplanar staggered conformation in which the corresponding dihedral angle is 180° .

Conrotatory. This adjective indicates that both p-orbitals at the terminal carbons (and the substituents at these carbons) of a conjugated acyclic hydrocarbon rotate in the same sense, both clockwise or both anti-clockwise, during ring closure. Also applied to the reverse step, namely ring opening.

Cycloaddition reaction. In the context of pericyclic reactions, this term refers to two molecules, the same or different, with one or more π bonds, that combine to form a cyclic compound with creation of two new σ bonds in a concerted, bimolecular reaction. Of course, cycloaddition reactions may proceed stepwise, but these are not pericyclic reactions.

DL convention. Employed, frequently in conjunction with Fischer projections, to assign configuration to sugars and amino acids, with D-glyceraldehyde (see p. 24) as reference compound.

Dehydrogenases. Enzymes that operate in conjunction with a cofactor, usually NADH. Despite the name, dehydrogenases catalyse both dehydrogenation (oxidation) and reduction reactions, under appropriate conditions.

Dextrorotatory (d). Description given to a chiral compound that rotates the plane of polarized light (usually of wavelength 589.6 nm, the sodium D line) in a clockwise sense as the observer looks into the propagating beam.

Diastereoisomers. Stereoisomers that are not enantiomers. This is a wide definition, which includes geometric isomers such as, for example, (*Z*)- and (*E*)-1,2-dichloroethene. Note that diastereoisomers may be (a) both chiral, (b) one may be chiral and the other not, *e.g.* tartaric acids (Chapter 3) and (c) both may be achiral, *e.g.* *cis*- and *trans*-1,3-disubstituted cyclobutanes and *cis*-1,4- and *trans*-1,4-disubstituted cyclohexanes (Chapter 6).

Diastereotopic. This adjective applies to molecules that contain (a) sp^3 hybridized carbon, *e.g.* C(1), in a molecule of type $RC(1)H_2-C(2)XYZ$ ($X \neq Y \neq Z$) that contains a stereogenic centre, usually, but not necessarily, adjacent to C(1). Replacement, separately, of

each of the C(1) hydrogens by D gives two diastereoisomers, and the hydrogens are said to be diastereotopic. (b) An sp^2 hybridized carbon, such as a carbonyl group in a molecule that contains a stereogenic centre, *e.g.* MeCOCH(Me)Ph. Attack at the two faces of the carbonyl group by a Grignard reagent RMgBr, where $R \neq Me$, gives a pair of diastereoisomeric alcohols, usually in unequal amounts. The faces of the carbonyl group are said to be diastereotopic.

Disrotatory (see Conrotatory). The opposite of conrotatory; in disrotatory ring closures of conjugated acyclic hydrocarbons, the p-orbitals at the terminal carbons, together with the substituents at these carbons, rotate in opposite senses, one clockwise and the other anti-clockwise.

Electrocyclic reactions. A sub-class of pericyclic reactions. Concerted intramolecular ring-forming reactions, *e.g.* of conjugated dienes or trienes in which a new σ bond is formed by way of a cyclic transition state. The cyclic product contains one fewer double bond. Term also applies to the reverse reaction. The simplest example is interconversion of buta-1,3-diene and cyclobutene.

Electrophile (from Greek 'electron loving'). Term defined by Ingold (*J. Chem. Soc.*, 1933, 1191), together with nucleophile (see below). A reagent that acquires a share in the electrons of another (foreign) molecule during a reaction. Exemplified by Br_2 in electrophilic bromination of an alkene, and nitronium ion (NO_2^+) in electrophilic nitration of benzene. In these reactions the alkene and benzene, respectively, are complementary nucleophiles.

Elution. In column chromatography, which is used to separate compounds (including enantiomers), a solution of a substrate is poured onto a column of a packing (or stationary phase) which may be chiral, as in the case of cellulose, or compounds **37** and **38** in Chapter 3. The solvent passes downward through the column and emerges through a tap at the bottom. In so doing there are two opposing factors at work: (a) adsorption of the substrate(s) on the stationary phase, (b) de-adsorption, or 'washing-off' of the substrate by the solvent. This process of adsorption/de-adsorption is repeated continually as the substrate moves down the column. The role of the solvent is elution, and a substrate is eluted more rapidly the less it is adsorbed on the stationary phase. By means of differential diastereomeric interactions with a chiral stationary phase, it is possible to separate enantiomers.

Enantiomeric excess; enantiomeric ratio. Ways of expressing the enantiomeric make-up of a sample. A sample that consists of, say, 90% (+) enantiomer and 10% (–) enantiomer has an enantiomeric excess (ee) of 80% and an enantiomeric ratio of 9:1.

Enantiomerically enriched. See scalemic.

Enantiomerically pure (optically pure). A sample that consists of only one enantiomer.

Enantiomers. A pair of molecules related as non-superimposable mirror images. They rotate the plane of polarized light in opposite directions, and for solutions of equal concentration, by equal amounts. Otherwise their physical properties are identical.

Enantiotopic. Adjective used to describe (a) certain sp^3 hybridized carbons. In a molecule $XYCH_2$ [in which ($X \neq Y$), and neither X nor Y is H or D], replacement, separately, of each of the two hydrogen atoms by D gives two enantiomers, and the hydrogens are said to be enantiotopic. Also used for (b) molecules such as aldehydes, R^1CHO , or certain ketones and alkenes. In ketones R^1R^2CO ($R^1 \neq R^2$), addition of R^3 (via a Grignard reagent) gives a pair of enantiomeric tertiary alcohols depending on whether R^3 has been added to the top or bottom face.

Endo. A substituent on a bridge between bridgehead carbons in a bicyclic molecule that is on the side of the larger bridge is said to be *endo* (see *exo*).

Epimers. Diastereoisomers that differ in configuration at one of two or more stereogenic centres.

Epimerization. A term used to denote the interconversion of two epimers.

Equatorial bond. The six C–H bonds (or generally a C–X bond) of cyclohexane that are approximately perpendicular to the three-fold axis of cyclohexane (Chapter 1, structure 15).

Erythro. A relative stereochemical term used for molecules that have two adjacent stereogenic centres and with two substituents common to both centres. The name is taken from the four-carbon sugar erythrose, oxidation of whose CH_2OH and CHO groups to CO_2H gives *meso*-tartaric acid.

Exo. As *endo*, except that the substituent is now on the side of the smaller bridge. These terms do not specify configuration in an absolute sense.

Fischer projection. A method for diagrammatic representation of chiral molecules, chiefly in conjunction with the *D/L* configuration convention. Used nowadays for sugars and amino acids.

Gauche conformation. In the *gauche* conformation of butane, for example, the two methyl groups are related by a dihedral angle of 60° .

Geminal. Adjective used to describe 1,1-disubstitution; for example, in

dichloromethane (CH_2Cl_2) the chlorines are geminal. In NMR spectroscopy a geminal coupling constant, 2J , occurs between nuclei separated by two bonds.

Geometric isomers. Geometric isomers have different configurations at a double bond, *e.g.* (*E*)- and (*Z*)-1,2-dichloroethene; in this context, *cis/trans* isomerism is also used.

Helicity. The sense of twist of, say, a screw or helix. Defined as right-handed if, in proceeding along the axis of the screw or helix, the sense of twist is clockwise.

Heterolytic. Adjective used to describe the cleavage of a bond X–Y in which Y gains both bonding electrons to give Y^- , leaving X^+ .

Homochiral. Molecules are homochiral if they possess the same sense of chirality, *e.g.* the naturally occurring α -amino acids which all have L configuration. Also used by some to denote enantiomeric purity.

Homolytic bond cleavage. Occurs when a single bond between two atoms in A–B is broken so that both A and B retain one of the bonding electrons.

Homotopic. Adjective that can be used to describe a molecule that contains (a) sp^3 hybridized carbons. In, for example, CH_2Cl_2 , separate replacement of *each* hydrogen by deuterium gives identical molecules. The hydrogens are *homotopic*. Also used for molecules that contain (b) sp^2 hybridized carbons. In, for example, $\text{R}^1\text{R}^2\text{C}=\text{O}$, the carbonyl group is homotopic when $\text{R}^1 = \text{R}^2$. Addition of a different R^3 group (*via* a Grignard reagent) gives identical tertiary alcohols whether addition to the carbonyl group occurs at the top or bottom face.

Hybridization. A mathematical mixing of atomic orbitals (two or more in number) that gives the same number of hybrid orbitals. The hybrid orbitals retain some of the properties of the component atomic orbitals (see Table 1). *Hybrid* is from the Latin for ‘mongrel’.

Table 1 Characteristics of hybrid orbitals in methane, ethene and ethyne^a

A	B	C	D	E
1	3	4 × sp^3	0	109° 28'
1	2	3 × sp^3	1	120°
1	1	2 × sp	2	180°

^aA = number of s orbitals per molecule involved in forming hybrid orbitals. B = number of 2p orbitals per molecule involved in forming hybrid orbitals. C = number and type of hybrid orbitals per molecule formed after hybridization. D = number of p orbitals per molecule remaining after hybridization that can be used to form multiple bonds, as in, say, alkenes and alkynes. E = bond angles at C, *i.e.* $\angle \text{HCH}$ in methane, $\angle \text{HCC}$ in ethene and $\angle \text{HCC}$ in ethyne, respectively, after hybridization. Note that for each row the sum of the entries in columns C and D is 4.

Isochronous. In NMR spectroscopy, two or more nuclei are called isochronous if they have the same chemical shift.

Isotactic. Term used to describe a polymer, *e.g.* polypropene, in which all the methyl groups lie on the same side of the polymer chain (which is usually drawn in the plane of the paper).

Kinetic resolution. Separation of enantiomers by means of a difference of reaction rate of the enantiomers, *e.g.* with an enzyme (or an artificial catalyst), in which case the rate difference is very large. For example, a racemic ethanoate (acetate) can be hydrolysed to one enantiomer of an alcohol; the other enantiomer remains as ethanoate.

Laevorotatory (l). Description given to a chiral compound that rotates the plane of polarized light anti-clockwise as the observer looks into the propagating beam.

Leaving group. In a substitution or elimination reaction, the leaving group X in, say, R_3C-X , leaves with both the bonding electrons. Good leaving groups include I, Br, $^+OH_2$, 4-MeC₆H₄SO₃ (OTs), 4-BrC₆H₄SO₃ (OBs).

Meso. A name given to an achiral stereoisomer of a family of diastereoisomers. A *meso* stereoisomer is achiral by virtue of two self-cancelling stereogenic centres.

Mutarotation. The change in optical rotation when a particular anomer of a sugar, *e.g.* either α - or β -D-glucose, is dissolved in water. Mutarotation occurs in neutral solution and is also catalysed by acid or base. Mutarotation measures the change in rotation of the sample until an optical rotation is obtained that is characteristic of the equilibrium mixture. The interconversion of α and β anomers to yield the equilibrium mixture occurs *via* an open-chain aldehyde form.

Newman projection (see Chapter 2). A diagrammatic representation of the stereochemical relationship between atoms on adjacent carbons. One looks along the carbon-carbon bond, drawn as a circle. Substituents at the front carbon are drawn to the centre of the circle; those at the back stop at the circumference.

Nuclear Overhauser effect (NOE). In the case of 1H NMR spectroscopy, if one saturates the nuclear spin of H^a , there is an enhancement of the signal from a non-equivalent proton, H^b , in the same molecule if these two nuclei are less than *ca.* 0.4 nm apart. It is necessary for the spin-lattice relaxation of H^b to take place by dipole-dipole interactions. Best observed for tertiary, R_3C-H , protons.

Nucleophile (from the Greek, 'nucleus loving'). A reagent that during a reaction shares its electrons with another (foreign) nucleus.

Nucleophiles have either (a) at least one unshared pair of electrons and may be neutral, *e.g.* Me_3N , or negatively charged, *e.g.* I^- . Nucleophiles attack saturated carbon with expulsion of a leaving group ($\text{S}_{\text{N}}2$) or a carbocation ($\text{S}_{\text{N}}1$). (b) A double bond which attacks, for example, bromine in the addition of Br_2 to a double bond, or an aromatic ring which attacks, for example, a nitronium ion in aromatic nitration. In these reactions (a) saturated carbon and the carbocation and (b) bromine and nitronium ion, respectively, themselves act as complementary electrophiles.

OBs. See **Brosylate** (4-bromobenzenesulfonate, $4\text{-BrC}_6\text{H}_4\text{SO}_3$), above.

Optically active compound. A compound, necessarily chiral, and non-racemic, that rotates the plane of polarized light in a particular direction.

Optically pure. Mainly superseded by 'enantiomerically pure'.

Orthogonal. Term used to describe p-orbitals and π bonds in mutually perpendicular planes, as in alkynes, nitriles and allenes. Such orbitals and bonds do not interact. The two HCH planes at each terminal carbon in allene are also orthogonal.

OTs. See **Tosylate** (toluene-4-sulfonate, $4\text{-MeC}_6\text{H}_4\text{SO}_3$), below.

Overhauser effect. See **Nuclear Overhauser effect**.

Pericyclic reactions. These reactions occur by cyclic concerted electron shifts and are sub-divided into cycloadditions, electrocyclic and cheletropic reactions, and sigmatropic rearrangements. The first two types are considered in the text.

Plane of symmetry. The presence of a plane of symmetry in a molecule means that it can be superimposed on its mirror image. Molecules with a plane of symmetry, *in any conformation*, cannot be chiral.

Plane polarized light. Light that emerges from a polarizer, which acts as a filter to block the light waves other than those oscillating in a single plane. An integral part of a polarimeter, and very important to detection of chirality.

Polarimeter. An instrument for determination of the number of degrees by which a particular sample of a chiral compound rotates the plane of polarized light. This enables the specific rotation (see below) to be calculated.

Prochiral. Adjective used to describe (a) a molecule with two enantiotopic atoms, *e.g.* the methylene hydrogens of ethanol, or (b) a molecule such as PhCOMe , with two enantiotopic faces. The term does not usually apply to molecules with diastereotopic atoms and faces, as these

already possess at least one stereogenic centre. Some authors prefer adoption of the term *prostereogenic* instead.

Pseudorotation. Observed in cyclopentane, which has a structure resembling a square-shaped envelope with its flap raised. The ‘flap’ rotates rapidly around the ring in an ‘up and down’ motion of the five ring carbons: this is termed *pseudorotation*, and during a circuit the energy of the molecule varies only by *ca.* 2.5 kJ mol⁻¹ so no significant energy maxima or minima exist.

Racemate. A sample that consists of a 1:1 ratio of enantiomers.

Racemization. Racemization is the conversion of one enantiomer into the racemate.

Regioselective. When, for example, a reagent XY adds to a double bond R¹R²C=CR³R⁴, two products can be formed: R¹R²CX–CR³R⁴Y and R¹R²CY–CR³R⁴X. If one isomer predominates over the other, the reaction is called regioselective.

Resolution. Separation of a 50:50 mixture of enantiomers in order to obtain one, or both, enantiomers.

Resonance structures. See **Canonical structures**, above.

Sawhorse projection. An oblique view of a carbon–carbon single bond that enables the observer to see the stereochemistry of substituents. Three substituents are connected to each carbon by a stick diagram that resembles a Y (the Y can rotate). Introduced in Chapter 2.

Scalemic. A scalemic sample is one that is partially racemized (or enantiomerically enriched).

sp³, sp² and sp orbitals. Hybrid orbitals derived by mathematical mixing of one s- and *n* p-orbitals (where *n* = 1, 2 or 3) to give (*n* + 1) hybrid orbitals. Any remaining unhybridized p-orbitals can be used to form multiple bonds, as in alkenes and alkynes.

Specific rotation, e.g. [α]_D²⁵. The number of degrees (+ or –) by which a solution of a non-racemic chiral compound rotates the plane of polarized light, under conditions of (a) unit concentration and (b) unit path length of cell; by convention, the degree symbol is not shown. Dextrorotatory compounds are assigned (+). For determinations of liquids, density is used for *c* in equation 1 of Chapter 2. The superscript 25 refers to the temperature in degrees centigrade, and the subscript D to the wavelength of the light, usually the sodium D line.

Stereogenic centre (Chiral centre, Asymmetric centre). Most commonly an sp³ hybridized carbon (though, for example, the nitrogen atoms of some ammonium salts, and the S of some sulfoxides can act as

stereogenic centres) to which four different groups are bonded. In the case of sulfoxides, one of the groups is a lone pair of electrons.

Stereoisomers. Isomers that differ in three-dimensional spatial arrangements (configurations) but which have the same connectivity (this term indicates which atom is bonded to which) and includes (see above) enantiomers, diastereoisomers and geometric isomers.

Stereoselective. In stereoselective reactions from a suitable starting material, two (or more) stereoisomers are formed in unequal amounts. For example, in a stereoselective reaction, camphor reacts with LiAlH_4 to give mainly isborneol together with borneol. When one stereoisomer is formed exclusively the reaction is termed completely stereoselective.

Stereospecific. Types of reactions that can be shown by reactants that exist as stereoisomers. If each stereoisomer of a reactant gives a different stereoisomeric product, the reaction is stereospecific. Examples include the $\text{S}_{\text{N}}2$ reaction, *anti* addition of bromine to alkenes, and the Diels–Alder reaction (a *syn* addition in which the relative configuration of substituents on the dienophile is retained).

Suprafacial. A suprafacial reaction takes place at the ends of the same face of a π electron system, usually in an alkene. Used to describe, for example, photochemical $[2 + 2]$ cycloadditions of alkenes, and also the OsO_4 mediated formation of 1,2-diols from alkenes.

Syn (see also *Syn* addition; *Syn* periplanar). Substituents are *syn* if they are on the same side of a defined reference plane in a molecule. *Syn* is also employed to assign stereochemistry to products, *e.g.* of aldol reactions. With the main chain drawn in the plane of the paper, substituents on the same side of the plane are termed *syn*, *e.g.* structure **18** in Chapter 3.

Syn addition. *Syn* addition of X–Y occurs when X and Y are added to the same face of a double bond.

Syn clinal. The conformation of, say, butane when the C–C–C dihedral angle has values between 30° and 90° .

Syn periplanar. The conformation of, say, butane when the C–C–C dihedral angle is 0° . The term is justified up to values of 30° .

Syndiotactic. Adjective used to describe a polymer, *e.g.* polypropene, in which with respect to the polymer chain (drawn in the plane of the paper) the methyl groups are represented as alternately in front of and behind the plane. The monomer units exist as repeating pairs.

Tautomerism. Isomerism brought about by rapid and reversible inter-conversion of, say, a ketone with an α -hydrogen and an enol, as in

$R^1_2CH-C(=O)R^2$ and $R^1_2C=C(OH)R^2$. The conversion is usually acid or base catalysed. The keto form is *usually* more stable, though not when a phenol is the 'enol'.

Threo. Derived from the sugar threose and like *erythro* (see above) used generally. Oxidation of the CHO and CH_2OH groups of threose to CO_2H gives an *optically active* tartaric acid.

Torsion barrier. The free energy difference between the minimum and maximum points when rotation occurs around, for example, the C–C bond in ethane; the value here is *ca.* 12.5 kJ mol⁻¹.

Tosylate (toluene-4-sulfonate, 4-MeC₆H₄SO₃). A good leaving group in substitution and elimination reactions. Usually abbreviated to OTs.

Trans. Groups or atoms are *trans* when they lie on opposite sides of an identifiable reference plane in a molecule.

van der Waals' radius. One measure of the size of an atom or group. If two groups approach more closely than the sum of their van der Waals' radii, electron clouds of the component atoms begin to interpenetrate and a strong mutual repulsion results. As two non-polar groups are brought together from a large separation, an unsymmetrical distribution of electrons in one group induces an opposite distribution in the other. These opposite induced partial charges attract one another, and the attraction increases (non-linearly) the closer the groups approach. At a certain separation, the sum of the van der Waals' radii, the attractive force is at a maximum; closer approach brings about repulsion.

Vicinal. Adjective used to describe 1,2-disubstitution; for example, in butane-1,4-dioic acid (succinic acid, $HO_2C-CH_2CH_2-CO_2H$) the carboxylic acid groups are vicinal, as are the chlorine atoms in 1,2-dichloroethane ($ClCH_2CH_2Cl$). In NMR spectroscopy a vicinal coupling constant, 3J , occurs between nuclei separated by three bonds.