

Glossary

Absolute configuration : The actual three-dimensional structure of a chiral molecule. Absolute configurations are specified verbally by the *R,S* convention and are represented on paper by Fischer projections.

Absorption spectrum : A plot of wavelength of incident light versus amount of light absorbed. Organic molecules show absorption spectra in both the infrared and ultraviolet regions of the electromagnetic spectrum. By interpreting these spectra, useful structural information about the sample can be obtained.

Acetal : A functional group consisting of two ether-type oxygen atoms bound to the same carbon, $R_2C(OR')_2$. Acetals are often used as protecting groups for ketones and aldehydes, since they are stable to basic and nucleophilic reagents but can be easily removed by acidic hydrolysis.

Achiral : Having a lack of handedness. A molecule is achiral if it has a plane of symmetry and is thus superimposable on its mirror image.

Activating group : An electron-donating group such as hydroxyl ($-OH$) or amino ($-NH_2$) that increases the reactivity of an aromatic ring toward electrophilic aromatic substitution. All activating groups are *ortho/para* directing.

Activation energy : The difference in energy levels between ground state and transition state. The amount of activation energy required by a reaction determines the rate at which the reaction proceeds. The majority of organic reactions have activation energies of 10 - 25 kcal/mol.

Acylation : The introduction of an acyl group, $-COR$, onto a molecule. For example, acylation of an alcohol yields an ester ($R'OH \rightarrow R'OCOR$), acylation of an amine yields an amide ($R'NH_2 \rightarrow R'NHCOR$), and acylation of an aromatic ring yields an alkyl aryl ketone ($ArH \rightarrow ArCOR$).

Acylium ion : A resonance-stabilised carbocation in which the positive charge is located at a carbonyl-group carbon, $R-C=O^+$. Acylium ions are strongly electrophilic and are involved as intermediates in Friedel-Crafts acylation reactions.

1,4-Addition : Addition of a reagent to the ends of a conjugated *pi* system. Conjugated dienes yield 1,4 adducts, when treated with electrophiles such as HCl.

Addition polymer : A polymer produced by a chain reaction procedure in which an initiator adds to a carbon-carbon double bond to yield a reactive intermediate. The chain is then built as monomers add successively to the reactive end of the growing chain. Addition polymers are formed by combination of alkene monomers to produce a single huge molecule only.

Aldaric acid : The dicarboxylic acid resulting from oxidation of an aldose.

Aldonic acid : The monocarboxylic acid resulting from mild oxidation of an aldose.

Alicyclic : Referring to an aliphatic cyclic hydrocarbon such as a cycloalkane or cycloalkene.

Aliphatic : Referring to a non-aromatic hydrocarbon such as a simple alkane, alkene, or alkyne.

Alkylation : Introduction of an alkyl group onto a molecule. For example, aromatic rings can be alkylated to yield arenes ($ArH \rightarrow ArR$), alkoxide anions can be alkylated to yield ethers ($R'O \rightarrow R'OR$).

Allylic : Used to refer to the position next to a double bond. For example, $CH_2=CHCH_2Br$ is an allylic bromide.

Angle strain : The strain introduced into a molecule when a bond angle is deformed from its ideal value. Angle strain is particularly important in small-ring cycloalkanes where it results from compression of bond angles to less than their ideal tetrahedral values. For example, cyclopropane has approximately 22 kcal/mol angle strain owing to bond deformations from the 109° tetrahedral angle to 60° .

Anomers : Cyclic stereoisomers of sugars that differ only in their configurations at the hemiacetal (anomeric) carbon.

Anti conformation : The geometric arrangement around a carbon-carbon single bond, in which the two largest substituents are 180° apart, as viewed in a Newman projection.

Anti stereochemistry : Referring to opposite sides of a double bond or molecule. An *anti addition* reaction is one in which the two ends of the double bond are attacked from different sides. For example, addition of Br_2 to cyclohexene yields *trans*-1,2-dibromocyclohexane, the product of anti addition.

Aromaticity : The special characteristics of cyclic conjugated π electron systems that result from their electronic structures. These characteristics include unusual stability, the presence of a ring in the NMR spectrum, and a tendency to undergo substitution reactions rather than addition reactions on treatment with electrophiles. Aromatic molecules must be planar, cyclic, conjugated species that have $4n + 2\pi$ electrons.

Asymmetric centre : See chiral centre.

Atactic polymers : Addition polymers that have a random stereochemical arrangement of substituents on the polymer backbone. These polymers result from high temperature radical-initiated polymerisation of alkene monomers.

Aufbau principle : A guide for determining the ground-state electronic configuration of elements by filling the lowest energy orbitals first.

Axial bond : A bond to chair cyclohexane that lies along the ring axis perpendicular to the rough plane of the ring. (See equatorial bond)



AXIAL BONDS

Base peak : The most intense peak in a mass spectrum.

Bent bonds : The bonds in small rings such as cyclopropane that bend away from the internuclear line and overlap at a slight angle, rather than head-on. Bent bonds are highly strained and highly reactive.

Benzylic : Referring to the position next to an aromatic ring. For example, a benzylic cation is a resonance stabilised, conjugated carbocation having its positive charge located on a carbon atom next to the benzene ring in a π orbital that overlaps with the aromatic π system.

Benzyne : An unstable intermediate having a triple bond in a benzene ring.

Bimolecular reaction : A reaction that occurs between two reagents.

Block co-polymer : A polymer consisting of alternating homopolymer blocks. Block co-polymers are usually prepared by initiating addition polymerisation of one monomer, followed by addition of an excess of a second monomer.

Boat cyclohexane : A three-dimensional conformation of cyclohexane that bears a slight resemblance to a boat. Boat cyclohexane has no angle strain, but has a large number of eclipsing interactions that make it less stable than chair cyclohexane.



BOAT CYCLOHEXANE

Bond angle : The angle formed between two adjacent bonds.

Bond-dissociation energy : The amount of energy needed to homolytically break a bond to produce two radical fragments.

Bond length : The distance between the nuclei of two atoms that are bonded to each other.

Bond strength : See Bond-dissociation energy.

Bronsted acid : A substance that donates a hydrogen ion (proton) to a base.

Carbanion : A carbon-anion, or substance that contains a trivalent, negatively charged carbon atom (R_3C^-). Carbanions are sp^3 hybridised and have eight electrons in the outer shell of the negatively charged carbon.

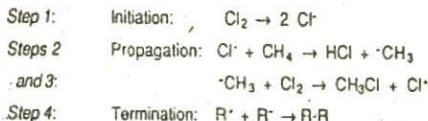
Carbene : A neutral substance that contains a divalent carbon atom having only six electrons in its outer shell ($R_2C:$).

Carbocation : A carbon-cation, or substance that contains a trivalent, positively charged carbon atom having six electrons in its outer shell (R_3C^+). Carbocations are planar and sp^2 hybridised.

Carbocycle : A cyclic molecule that has only carbon atoms in ring.

Carbohydrate : A polyhydroxy aldehyde or polyhydroxy ketone. The name derives from the fact that glucose, the most abundant carbohydrate, has the formula $C_6H_{12}O_6$ and was originally thought to be a hydrate of carbon. Carbohydrates can be either simple sugars such as glucose or complex sugars such as cellulose. Simple sugars are those that cannot be hydrolysed to yield smaller molecules, whereas complex sugars are those that can be hydrolysed to yield simpler sugars.

Chain reaction : A reaction that, once initiated, sustains itself in an endlessly repeating cycle of propagation steps. The free radical chlorination of alkanes is an example of a chain reaction that is initiated by UV light and that then continues in a series of propagation steps.



Chair cyclohexane : A three-dimensional conformation of cyclohexane that resembles the shape of a chair. The chair form of cyclohexane has no angle strain. It represents the lowest energy conformation of the molecule.



CHAIR CYCLOHEXANE

Chemical shift : The position on the NMR chart where a nucleus absorbs. By convention, the chemical shift of tetramethylsilane is arbitrarily set at zero and all other absorptions usually occur downfield (to the left on the chart). Chemical shifts are expressed in delta units, δ , where one delta equals one part per million of the spectrometer operating frequency. The chemical shift of a given nucleus is related to the chemical environment of that nucleus in the molecule, thus allowing one to obtain structural information by interpreting the NMR spectrum.

Chiral : Having handedness. Chiral molecules are those that do not have a plane of symmetry and are therefore not superimposable on their mirror image. A chiral molecule thus exists in two forms, one right-handed and one left-handed. The most common (though not the only) cause of chirality in a molecule is the presence of a carbon atom that is bonded to four different substituents.

Chiral centre : An atom (usually carbon) that is bonded to four different groups and is therefore chiral.

Chromatography : A technique for separating a mixture of compounds into pure components. Chromatography operates on the principle of differential adsorption whereby different compounds adsorb on a stationary support phase and are then carried along at different rates by a mobile phase.

Cis-trans Isomers : Special kind of stereoisomers that differ in their stereochemistry about a double bond or on a ring. Cis-trans isomers are also called geometric isomers.

Concerted : Referring to a reaction that takes place in a single step without intermediates. For example, the Diels-Alder cycloaddition reaction is a concerted process.

Condensation polymer : A polymer produced by a series of polar reactions between two difunctional monomers. The polymer normally has the two monomer units in alternating order and usually has other atoms in addition to carbon in the polymer backbone. Nylon-6,6, a polyamide produced by reaction between a diacid and a diamine, is an example of such a polymer.

Configuration : The three-dimensional arrangement of atoms bonded to a chiral centre relative to the stereochemistry of other chiral centres in the same molecule.

Conformation : The exact three-dimensional shape of a molecule at any given instant, assuming that rotation around single bonds is frozen.

Conjugate base : The anion that results from dissociation of a Bronsted acid.

Conjugation : A series of alternating single and multiple bonds with overlapping p orbitals. For example, 1,3-butadiene is a conjugated diene, 3-buten-2-one is a conjugated enone, and benzene is a cyclic conjugated triene.

Constitutional Isomers : Isomer that have their atoms connected in a different order. For example, butane and 2-methylpropane are constitutional isomers.

Copolymer : A polymer formed by addition polymerisation of a mixture of two or more different monomer units.

Coupling constant : The magnitude (expressed in Hertz) of the spin-spin splitting interaction between nuclei whose spins are coupled. Coupling constants are denoted J .

Covalent bond : A bond formed by sharing electrons between two nuclei.

Cracking : A process used in petroleum refining in which large alkanes are thermally cracked into smaller fragments.

Cycloaddition : A reaction in which two reactants add together in a single step to yield a cyclic product. The Diels-Alder reaction between a diene and a dienophile to give a cyclohexene is the best-known example of a cycloaddition.

Deactivating group : An electron-withdrawing substituent that decreases the reactivity of an aromatic ring towards electrophilic aromatic substitution. Most deactivating groups, such as nitro, cyano and carbonyl are *meta* directors, but halogen substituents are *ortho/para* directors.

Decarboxylation : A reaction that involves loss of carbon dioxide from the starting material. β -Keto acids decarboxylate particularly readily on heating.

Dehydration : A reaction that involves loss of water from the starting material. Most alcohols can be dehydrated to yield alkenes.

Delocalization : A spreading out of electron density over a conjugated π electron system. For example, allylic cations and allylic anions are delocalized because their charges are spread out by resonance stabilisation over the entire π -electron system.

Denaturation : The physical changes that occur in proteins when secondary and tertiary structures are disrupted. Denaturation is usually brought about by heat treatment or by a change in pH and is accompanied by a loss of biological activity.

Deshielding : An effect observed in NMR that causes a nucleus to absorb downfield (to the left) of tetramethylsilane standard. Deshielding is caused by a withdrawal of electron density from the nucleus and is responsible for the observed chemical shifts of vinylic and aromatic protons.

Dextrorotatory : A word used to describe an optically active substance that rotates the plane of polarisation of plane-polarised light in a right-handed (clockwise) direction. The direction of rotation is not, however, related to the absolute configuration of the molecule.

Diastereomer : A term that indicates the relationship between non-mirror-image stereoisomers. Diastereomers are stereoisomers that have the same configuration at one or more chiral centres, but differ at other chiral centres.

Diazotization : The conversion of a primary amine, RNH_2 into a diazonium salt, RN_2^+ by treatment with nitrous acid. Aryl diazonium salts are stable, but alkyl diazonium salts are extremely reactive and are rarely isolable.

Dielectric constant : A measure of the ability of a solvent to act as an insulator of electric charge. Solvents that have high dielectric constants are highly polar.

Dienophile : A compound containing a double bond that can take part in the Diels-Alder cycloaddition reaction. The most reactive dienophiles are those that have electron-withdrawing groups such as nitro, cyano, or carbonyl on the double bond.

Dipolar aprotic solvent : A dipolar solvent that cannot function as a hydrogen ion donor.

Dipole moment : A measure of the polarity of a molecule. A dipole moment arises when the centres of gravity of positive and negative charges within a molecule do not coincide.

Dissociation constant : A measure of the extent to which a molecule dissociates into ions. The dissociation constant for the reaction $\text{AB} \rightleftharpoons \text{A}^+ + \text{B}^-$ is given by the expression:

$$K_{\text{dis}} = \frac{[A^{\dagger}][B]}{[A][B]}$$

where the quantities in brackets represent the molar concentrations of the reactant and products.

DNA : Deoxyribonucleic acid, the biopolymer consisting of deoxyribonucleotide units linked together through phosphate-sugar bonds. DNA is found in the nucleus of cells and contains an organism's genetic information.

Doublet : A two-line NMR absorption caused by spin-spin splitting, when the spin of the nucleus under observation couples with the spin of a neighbouring magnetic nucleus.

Downfield : Used to refer to the left hand portion of the NMR chart.

Eclipsed conformation : The arrangement around a carbon-carbon single bond in which the bonds to substituents on one carbon are parallel to the bonds to substituents on the neighbouring carbon as viewed in a Newman projection. For example, the eclipsed conformation of ethane has the C-H bonds on one carbon lined up with the C-H bonds on the neighbouring carbon.



ECLIPSED CONFORMATION

Elastomers : Amorphous polymers that have the ability to stretch out and then return to their previous shape. These polymers have irregular shapes that prevent crystalline formation and have little cross-linking between chains.

Electromagnetic spectrum : The range of electromagnetic energy, including infrared, ultraviolet and visible radiation.

Electron affinity : The measure of an atom's tendency to gain an electron and form an anion. Elements on the right side of the periodic table such as the halogens have higher electron affinities than elements on the left side.

Electronegativity : The ability of an atom to attract electrons and thereby polarise a bond. As a general rule, electronegativity increases in going across the periodic table from right to left and in going from bottom to top.

Electrophile : An electron-lover, or substance that accepts an electron pair from a nucleophile in a polar bond forming reaction.

Electrophoresis : A technique used for separating charged organic molecules, particularly proteins and amino acids. The mixture to be separated is placed on a buffered gel or paper and an electric potential is applied across the ends of the apparatus. Negatively charged molecules migrate towards the positive electrode and positively charged molecules migrate towards the negative electrode.

Empirical formula : A formula that gives the relative proportions of elements in a compound in smallest whole numbers.

Enantiomers : Stereoisomers of a chiral substance that have a mirror image relationship. Enantiomers must have opposite configurations at all chiral centres in the molecule.

Endothermic : A term used to describe reactions that absorb energy and that therefore have positive enthalpy changes. In reaction energy diagrams, the products of endothermic reactions have higher energy levels than the starting materials.

Entgegen (E) : A term used to describe the stereochemistry of a carbon-carbon double bond. The two groups on each carbon are first assigned priorities according to the Cahn-Ingold-Prelog sequence rules and the two carbons are then compared. If the high priority groups on each carbon are on opposite sides of the double bond, the bond has E geometry.

Enzyme : A biological catalyst. Enzymes are large proteins that catalyse specific biochemical reactions.

Epoxide : A three-membered cyclic ether functional group.

Equatorial bond : A bond to cyclohexane that lies along the rough equator of the ring.



EQUATORIAL BONDS

Equilibrium constant : A measure of the equilibrium position for a reaction. The equilibrium constant for the reaction $A + B \rightleftharpoons C + D$ is given by the expression:

$$K_{eq} = \frac{[C][D]}{[A][B]}$$

where the numbers in brackets refer to the molar concentrations of the reactants and products.

Essential oil : The volatile oil that is obtained by steam distillation of a plant extract.

Excited-state configuration : An electronic configuration having a higher energy level than the ground state.

Exothermic : A term used to describe reactions that release energy and that therefore have negative enthalpy changes. On reaction energy diagrams, the products of exothermic reactions have energy levels lower than those of starting materials.

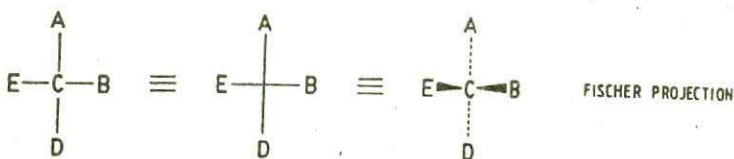
Fat : A solid triacylglycerol derived from animal sources.

Fibres : Thin threads produced by extruding a molten polymer through small holes in a die.

Fibrous protein : Proteins that consist of polypeptide chains arranged side by side in long threads. These proteins are tough, insoluble in water and are used in nature for structural materials such as hair, hooves, and fingernails.

Fingerprint region : The complex region of the infrared spectrum from 1500 cm^{-1} to 400 cm^{-1} . If two substances have identical absorption patterns in the fingerprint region of the IR, they are almost certainly identical.

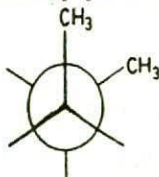
Fischer projection : A means of depicting the absolute configuration of chiral molecules on a flat page. A Fischer projection employs a cross to represent the chiral centre; the horizontal arms of the cross represent bonds coming out of the plane of the page, whereas the vertical-arms of the cross represent bonds going back into the plane of the page.



Frequency : The number of electromagnetic wave cycles that travel past a fixed point in a given unit of time. Frequencies are usually expressed in units of cycles per second, or Hertz.

Functional group : An atom or group of atoms that is part of a larger molecule and that has a characteristic chemical reactivity. Functional groups display the same chemistry in all molecules of which they are a part.

Gauche conformation : The conformation of butane in which the two methyl groups lie 60° apart, as viewed in a Newman projection. This conformation has 0.9 kcal/mol steric strain.



GAUCHE CONFORMATION

Geometric Isomers : An old term for cis-trans isomers.

Globular protein : Proteins that are coiled into compact, nearly spherical shapes. These proteins are generally water soluble, are mobile within the cell and are the structural class to which enzymes belong.

Glycol : A 1,2-diol such as ethylene glycol, HOCH₂CH₂OH.

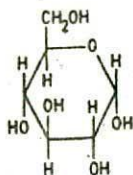
Glycoside : A cyclic acetal formed by reaction of a sugar with another alcohol.

Ground state : The most stable, lowest energy electronic configuration of a molecule.

Haloalcohol : A 1,2-disubstituted haloalcohol such as is obtained on addition of HOBr to an alkene.

Halonium ion : A species containing a positively charged, divalent halogen. Three-membered-ring bromonium ions are implicated as intermediates in the electrophilic addition of bromine to alkenes.

Haworth projection : A means of viewing stereochemistry in cyclic hemiacetal forms of sugars. Haworth projections are drawn so that the ring is flat and is viewed from an oblique angle with the hemiacetal oxygen at the upper right.



HAWORTH PROJECTION
OF GLUCOSE

Heat of combustion : The amount of heat released when a compound is burned in a calorimeter according to the equation :



Heat of hydrogenation : The amount of heat released when a carbon-carbon double bond is hydrogenated. Comparison of heats of hydrogenation for different alkenes allows one to determine the stability of the different double bonds.

Heterocycle : A cyclic molecule whose ring contains more than one kind of atom. For example, pyridine is a heterocycle that contains five carbon atoms and one nitrogen atom in its ring.

Heterolytic bond breakage : The kind of bond breaking that occurs in polar reactions when one fragment leaves with both of the bonding electrons, as in the equation :



Homolytic bond breakage : The kind of bond breaking that occurs in free radical reactions when each fragment leaves with one bonding electron according to the equation :



Homopolymer : A polymer made by addition polymerisation of a single monomer unit.

Huckel's rule : A rule stating that monocyclic conjugated molecules having $4n + 2$ pi electrons ($n =$ an integer) show the unusual stability associated with aromaticity.

Hybrid orbital : An orbital that is derived from a combination of ground-state (s , p , d) atomic orbitals. Hybrid orbitals, such as the sp^3 , sp^2 and sp hybrids of carbon form stronger bonds than ground-state atomic orbitals.

Hydration : Addition of water to a molecule, such as occurs when alkenes are treated with strong sulfuric acid.

Hydroboration : Addition of borane (BH₃) or an alkyl borane to an alkene. The resultant trialkylborane products are useful synthetic intermediates that can be oxidised to yield alcohols.

Hydrogenation : Addition of hydrogen to a double or triple bond to yield the saturated product.

Hydrogen bond : A weak (5 kcal/mol) attraction between a hydrogen atom bonded to an electronegative element and an electron lone pair on another atom.

Hyperconjugation : A weak stabilising interaction that results from overlap of a p orbital with a neighbouring sigma bond. Hyperconjugation is important in stabilising carbocations and in stabilising substituted alkenes.

Inductive effect : The electron attracting or electron withdrawing effect that is transmitted through sigma bonds as the result of a nearby dipole. Electronegative elements have an electron-withdrawing inductive effect, whereas electropositive elements have an electron-donating inductive effect.

Infrared spectroscopy : A kind of optical spectroscopy that uses infrared energy. IR spectroscopy is particularly useful in organic chemistry for determining the kinds of functional groups present in molecules.

Initiator : A substance with an easily broken bond that is used to initiate free radical chain reactions. For example, free radical chlorination of alkanes is initiated when light energy breaks the weak chlorine-chlorine bond to form chlorine free radicals.

Intermediate : A species that is formed during the course of a multi-step reaction but is not the final product. Intermediates are more stable than transition states, but may or may not be stable enough to be isolated.

Intramolecular, Intermolecular : Reactions that occur within the same molecule are intramolecular, whereas reactions that occur between two molecules are intermolecular.

Ionic bond : A bond between two ions due to the electrical attraction of unlike charges. Ionic bonds are formed between strongly electronegative elements (such as the halogens) and strongly electropositive elements (such as the alkali metals).

Ionization energy : The amount of energy required to remove an electron from an atom. Elements on the far right of the periodic table have high ionization energies, and elements on the far left of the periodic table have low ionization energies.

Isoelectric point : The pH at which the number of positive charges and the number of negative charges on a protein or amino acid are exactly balanced.

Isomers : Compounds that have the same molecular formula but have different structures.

Isoprene rule : An observation to the effect that terpenes appear to be made up of isoprene (2-methyl-1,3-butadiene) units connected in a head-to-tail fashion. Monoterpenes have two isoprene units, sesquiterpenes have three isoprene units, diterpenes have four isoprene units and so on.

Isotactic polymer : An addition polymer in which all substituents on the polymer backbone have the same three-dimensional orientation.

Kinetics : Referring to rates of reactions. Kinetics measurements can be extremely important in helping to determine reaction mechanisms.

Leaving group : The group that is replaced in a substitution reaction. The best leaving groups in nucleophilic substitution reactions are those that form the most stable, least basic, anions.

Levorotatory : Used to describe an optically active substance that rotates the plane of polarisation of plane-polarised light in a left-handed (counterclockwise) direction.

Lewis acid : A substance having a vacant low-energy orbital that can accept an electron pair from a base. All electrophiles are Lewis acids, but transition metal salts such as $AlCl_3$ and $ZnCl_2$ are particularly good ones.

Lewis base : A substance that donates an electron lone pair to an acid. All nucleophiles are Lewis bases.

Lewis structure : A representation of a molecule showing covalent bonds as a pair of electron dots between atoms.

Lipid : A naturally occurring substance isolated from cells and tissues by extraction with nonpolar solvents. Lipids belong to many different structural classes, including fats, terpenes, prostaglandins, and steroids.

Lipophilic : Fat-loving. Long non-polar hydrocarbon chains tend to cluster together in polar solvents because of their lipophilic properties.

Lone-pair electrons : Non-bonding electron pairs that occupy valence orbitals. It is the lone-pair electrons that are used by nucleophiles in their reactions with electrophiles.

Magnetic equivalence : Used to describe nuclei that have identical chemical and magnetic environments and that therefore absorb at the same place in the NMR spectrum. For example, the six hydrogens in benzene are magnetically equivalent, as are the six carbons.

Markovnikov's rule : A guide for determining the orientation of electrophilic addition reactions. In the addition of HX to an alkene, the hydrogen atom becomes bonded to the alkene carbon that has fewer alkyl substituents. A modern statement of this same rule is that electrophilic addition reactions proceed *via* the most stable carbocation intermediate.

Mechanism : A complete description of how a reaction occurs. A mechanism must account for all starting materials and all products and must describe the details of each individual step in the overall reaction process.

Meso : A *meso* compound is one that contains chiral centres but is nevertheless achiral by virtue of a symmetry plane.

Micelle : A spherical cluster of soap-like molecules that aggregate in aqueous solution. The ionic *heads* of the molecules lie on the outside where they are solvated by water and the organic *tails* bunch together on the inside of the micelle.

Mobile phase : The solvent (either gas or liquid) used in chromatography to move material along the solid adsorbent phase.

Molecular formula : An expression of the total numbers of each kind of atom present in a molecule. The molecular formula must be a whole-number multiple of the empirical formula.

Molecular ion : The cation produced in the mass spectrometer by loss of an electron from the parent molecule. The mass of the molecular ion corresponds to the molecular weight of the sample.

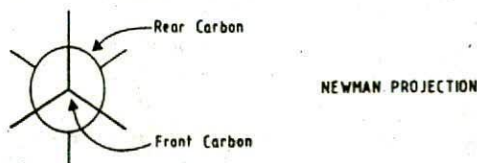
Molecular orbital : An orbital that is the property of the entire molecule rather than of an individual atom. Molecular orbitals result from overlap of two or more atomic orbitals when bonds are formed.

Monomer : The simple starting units from which polymers are made.

Multiplet : A symmetrical pattern of peaks in an NMR spectrum that arises by spin-spin splitting of a single absorption because of coupling between neighbouring magnetic nuclei.

Mutarotation : The spontaneous change in optical rotation observed when a pure anomer of a sugar is dissolved in water. Mutarotation is caused by the reversible opening and closing of the acetal linkage, which yields an equilibrium mixture of anomers.

Newman projection : A means of indicating stereochemical relationships between substituent groups on neighbouring carbons. The carbon-carbon bond is viewed end-on and the carbons are indicated by a circle. Bonds radiating from the centre of the circle are attached to the *front carbon*, and bonds radiating from the edge of the circle are attached to the *rear carbon*.



Normal alkane : A straight-chain alkane, as opposed to a branched alkane. Normal alkanes are denoted by the suffix *n*, as in $n\text{-C}_4\text{H}_{10}$ (*n*-butane).

Nuclear magnetic resonance, NMR : A spectroscopic technique that provides information about the carbon-hydrogen framework of a molecule. NMR works by detecting the energy absorption accompanying the transition between nuclear spin states that occurs when a molecule is placed in a strong magnetic field and irradiated with radio-frequency waves. Different nuclei within a molecule are in slightly different magnetic environments and therefore show absorptions at slightly different frequencies.

Nucleophile : A nucleus-lover, or species that donates an electron pair to an electrophile in a polar bond-forming reaction. Nucleophiles are also Lewis bases.

Olefin : An alternative name for an alkene.

Optical Isomers : Enantiomers. Optical isomers are isomers that have a mirror image relationship.

Optically active : A substance that rotates the plane of polarisation of plane-polarised light. Note that an optically active sample must contain chiral molecules, but that all samples with chiral molecules are not optically active. Thus, a racemic sample is optically inactive even though the individual molecules are chiral.

Orbital : The volume of space in which an electron is most likely to be found.

Ozonide : The product formed by addition of ozone to a carbon-carbon double bond. Ozonides are usually treated with a reducing agent, such as zinc in water, to produce carbonyl compounds.

Paraffins : A trivial name for alkanes.

Pauli exclusion principle : A statement of the fact that not more than two electrons can occupy the same orbital, and that these two must have spins of opposite sign.

Peptides : Amino acid polymers in which the individual amino acid residues are linked by amide bonds.

Peroxide : A molecule containing an oxygen-oxygen bond functional group, $R-O-O-R'$ or $R-O-O-H$. The peroxides present as explosive impurities in ether solvents are usually of the latter type. Since the oxygen-oxygen bond is weak and easily broken, peroxides are often used to initiate radical chain reactions.

Phospholipids : Lipids that contain a phosphate residue. For example, phosphoglycerides contain a glycerol backbone linked to two fatty acids and a phosphoric acid.

Pi bond : The covalent bond formed by sideways overlap of atomic orbitals. For example, carbon-carbon double bonds contain a *pi* bond formed by sideways overlap of two *p* orbitals.

Plane of symmetry : An imaginary plane that bisects a molecule such that one half of the molecule is the mirror image of the other half. Molecules containing a plane of symmetry are achiral.

Plane-polarised light : Ordinary light that has its electric vectors in a single plane rather than in random planes. The plane of polarisation is rotated when the light is passed through a solution of a chiral substance.

Polar reaction : A reaction in which bonds are made when a nucleophile donates two electrons to an electrophile and in which bonds are broken when one fragment leaves with both electrons from the bond.

Polarity : The unsymmetrical distribution of electrons in molecules that results when one atom attracts electrons more strongly than another.

Polymer : A large molecule made up of repeating smaller units. For example, polyethylene is a synthetic polymer made from repeating ethylene units.

Primary, secondary, tertiary, quaternary : Terms used to describe the substitution pattern at a specific site. A primary site has one organic substituent attached to it, a secondary site has two organic substituents, a tertiary site has three and a quaternary site has four.

	Carbon	Hydrogen	Alcohol	Amine
primary	RC_1H_3	RC_1H_5	RC_1H_2OH	RNH_2
secondary	RC_2H_2	RC_2H_4	RC_2CHOH	RC_2NH
tertiary	RC_3H	RC_3H_3	RC_3COH	RC_3N
quaternary	RC_4			

Primary structure : The amino acid sequence in a protein.

Principle of maximum overlap : The strongest bonds are formed when overlap between orbitals is greatest.

Propagation step : The step or series of steps in a free radical chain reaction that carry on the chain. The propagation steps must yield both product and a reactive intermediate to carry on the chain.

Protecting group : A group that is introduced to protect a sensitive functional group towards reaction elsewhere in the molecule. After serving its protective function, the group is then removed. For example, ketones and aldehydes are often protected as acetals by reaction with ethylene glycol.

Protein : A large peptide containing fifty or more amino acid residues. Proteins serve both as structural materials (hairs, horns, fingernails) and as enzymes that control an organism's chemistry.

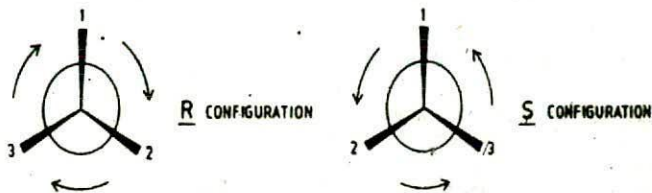
Protic solvent : A solvent such as water or alcohol that can serve as a proton donor. Protic solvents are particularly good at stabilising anions by hydrogen bonding, thereby lowering their reactivity.

Quartet : A set of four peaks in the NMR, caused by spin-spin splitting of a signal by three adjacent nuclear spins.

Quaternary : (see primary).

Quaternary structure : The highest level of protein structure, involving a specific aggregation of individual proteins into a larger cluster.

R,S convention: A method for defining the absolute configuration around chiral centres. The Cahn-Ingold-Prelog sequence rules are used to assign relative priorities to the four substituents on the chiral centre and the centre is oriented such that the group of lowest (fourth priority) faces directly away from the viewer. If the three remaining substituents have a right-handed or clockwise relationship in going from first to second to third priority, then the chiral centre is denoted *R* (*rectus*, right). If the three remaining substituents have a left-handed or counterclockwise relationship, the chiral centre is denoted *S* (*sinister*, left).



Racemic mixture: A mixture consisting of equal parts (+) and (-) enantiomers of a chiral substance. Even though the individual molecules are chiral, racemic mixtures are optically inactive.

Racemisation: The process whereby one enantiomer of a chiral molecule becomes converted into a 50 : 50 mixture of enantiomers, thus losing its optical activity. For example, this might happen during an S_N1 reaction of a chiral alkyl halide.

Radical: When used in organic nomenclature, the word radical refers to a part of a molecule that appears in its name for example, the phenyl in phenyl acetate. Chemically, however, a radical is a species that has an odd number of electrons, such as the chlorine free radical (Cl).

Radical reaction: A reaction in which bonds are made by donation of one electron from each of two reagents and in which bonds are broken when each fragment leaves with one electron.

Reaction energy diagram: A pictorial representation of the course of a reaction, in which potential energy is plotted as a function of reaction progress. Starting materials, transition states, intermediates and final products are all represented and their appropriate energy levels are indicated.

Reducing sugar: Any sugar that reduces silver ion in the Tollens' test or cupric ion in the Fehling's or Benedict's tests. All sugars that are aldehydes or that can be readily converted into aldehydes are reducing. Glycosides, however, are not reducing sugars.

Refining: The process by which petroleum is converted into gasoline and other useful products.

Resolution: The process by which a racemic mixture is separated into its two pure enantiomers. For example, a racemic carboxylic acid might be converted by reaction with a chiral amine base into a diastereomeric mixture of salts, which could be separated by fractional crystallisation. Preparation of the free acids would then yield the two pure enantiomeric acids.

Resonance effect: The effect by which substituents donate or withdraw electron density through orbitals overlap with neighbouring π bonds. For example, an oxygen or nitrogen substituent donates electron density to an aromatic ring by overlap of the *O* or *N* orbital with the aromatic ring p orbitals. A carbonyl substituent, however, withdraws electron density from an aromatic ring by p -orbital overlap. These effects are particularly important in determining whether a given group is *meta* directing or *ortho*, *para*-directing in electrophilic aromatic substitution reactions.

Resonance hybrid: A molecule, such as benzene, that cannot be represented adequately by a single Kekule structure but must instead be considered as an average of two or more resonance structures. The resonance structures themselves differ only in the positions of their electrons, not of their nuclei.

Ring current: The circulation of π electrons induced in aromatic rings by an external magnetic field. This effect accounts for the pronounced downfield shift of aromatic ring protons in the NMR.

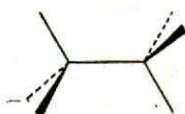
RNA: Ribonucleic acid, the biopolymer found in cells that serves to transcribe the genetic information found in DNA and use that information to direct the synthesis of proteins.

Saccharide: A sugar.

Saponification: An old term for the base-induced hydrolysis of an ester to yield a carboxylic acid salt.

Saturated : A saturated molecule is one that has only single bonds and thus cannot undergo addition reactions. Alkanes, for example, are saturated, but alkenes are unsaturated.

Sawhorse structure : A stereochemical manner of representation that portrays a molecule using a stick drawing and gives a perspective view of the conformation around single bonds.



SAWHORSE STRUCTURE

Second-order reaction : A reaction whose rate-limiting step is bimolecular and whose kinetics are therefore dependent on the concentration of two reagents.

Secondary : (See primary).

Secondary structure : The level of protein substructure that involves organisation of chain sections into ordered arrangements such as β -pleated sheets or α -helices.

Sequence rules : A series of rules devised by Cahn, Ingold and Prelog for assigning relative priorities to substituent groups on a double-bond carbon atom or on a chiral centre. Once priorities have been established, *E,Z*-double bond geometry and *R,S*-configurational assignments can be made.

Shielding : An effect observed in NMR that causes a nucleus to absorb toward the right (upfield) side of the chart. Shielding is caused by donation of electron density to the nucleus.

Sigma bond : A covalent bond formed by head-on overlap of atomic orbitals.

Skew conformation : Any conformation about a single bond that is intermediate between staggered and eclipsed. (See staggered conformation; eclipsed conformation).

Soap : The mixture of long-chain fatty acid salts obtained on base hydrolysis of animal fat.

sp Orbital : A hybrid orbital derived from the combination of an *s* and *p* atomic orbital. The two *sp* orbitals that result from hybridisation are oriented at an angle of 180° to each other.

sp² Orbital : A hybrid orbital derived by combination of an *s* atomic orbital with two *p* atomic orbitals. The three *sp²* hybrid orbitals that result lie in a plane at angles of 120° to each other.

sp³ Orbital : A hybrid orbital derived by combination of an *s* atomic orbital with three *p* atomic orbitals. The four *sp³* hybrid orbitals that result are directed towards the corners of a tetrahedron at angles of 109° to each other.

Spin-spin splitting : The splitting of an NMR signal into a multiplet caused by an interaction between nearby magnetic nuclei whose spins are coupled. The magnitude of spin-spin splitting is given by the coupling constant *J*.

Staggered conformation : The three-dimensional arrangement of atoms around a carbon-carbon single bond in which the bonds on one carbon exactly bisect the bond angles on the second carbon as viewed end-on. (See eclipsed conformation)



STAGGERED CONFORMATION

Stationary phase : The solid support used in chromatography. The molecules to be chromatographically separated adsorb on the stationary phase and are moved along by the mobile phase. Silica gel (hydrated SiO₂) and alumina (Al₂O₃) are often used as stationary phases in column chromatography of organic mixtures.

Stereochemistry : The branch of chemistry concerned with the three-dimensional arrangement of atoms in molecules.

Stereoisomers : Isomers that have their atoms connected in the same order but that have different three-dimensional arrangements. The term stereoisomer includes both enantiomers and diastereomers but does not include constitutional isomers.

Stereospecific : A term indicating that only a single stereoisomer is produced in a given reaction, rather than a mixture.

Steric strain : The strain imposed on a molecule when two groups are too close together and try to occupy the same space. Steric strain is responsible both for the greater stability of *trans* versus *cis* alkenes and for the greater stability of equatorially substituted versus axially substituted cyclohexanes.

Syn stereochemistry : A *syn* addition reaction is one in which the two ends of the double bond are attacked from the same side. For example, OsO_4 induced hydroxylation of cyclohexene yields *cis*-1,2-cyclohexanediol, the product of *syn* addition.

Syndiotactic polymer : An addition polymer in which the substituents on the polymer backbone have a regular alternating stereochemistry.

Terpenes : Lipids that are formally derived by head-to-tail polymerisation of isoprene units.

Tertiary : (see primary)

Tertiary structure : The level of protein structure that involves the manner in which the entire protein chain is folded into a specific three-dimensional arrangement.

Thermoplastic : A polymer that is hard at room temperature but that becomes soft and pliable when heated. Thermoplastics are used for the manufacture of a variety of moulded objects.

Thermosetting resin : A polymer that is highly cross-linked and that sets into a hard, insoluble mass when heated. Bakelite is the best-known example of such a polymer.

Torsional strain : The strain in a molecule caused by electron repulsion between eclipsed bonds. Torsional strain plays a major role in destabilizing boat cyclohexane relative to chair cyclohexane.

Transition state : An imaginary activated complex between reagents, representing the highest energy point on a reaction curve. Transition states are unstable complexes that cannot be isolated.

Triacylglycerol : Lipids such as animal fat and vegetable oil consisting chemically of triesters of glycerol with long-chain fatty acids.

Triplet : A symmetrical three-line splitting pattern observed in the NMR when a proton has two equivalent neighbouring protons.

Ultraviolet (UV) : An optical spectroscopy employing ultraviolet irradiation. UV spectroscopy provides structural information about the extent of *pi* electron conjugation in organic molecules.

Unimolecular reaction : A reaction that occurs by spontaneous transformation of the starting material without the intervention of other reagents. For example, the dissociation of a tertiary alkyl halide in the $\text{S}_{\text{N}}1$ reaction is a unimolecular process.

Unsaturated : An unsaturated molecule is one that has multiple bonds and can undergo addition reactions. Alkenes and alkynes, for example, are unsaturated.

Upfield : Used to refer to the right-hand portion of the NMR chart.

Van der Waals forces : The attractive forces between molecules that are caused by dipole-dipole interactions. Van der Waals forces are one of the primary forces responsible for holding molecules together in the liquid state.

Vicinal : A term that refers to a 1,2-disubstitution pattern. For example, 1,2-dibromoethane is a vicinal dibromide.

Vinyllic : A term that refers to a substituent at a double-bond carbon atom. For example, chloroethylene is a vinyllic chloride and enols are vinyllic alcohols.

Vulcanisation : A process for hardening rubber by heating in presence of elemental sulphur. The sulphur functions by forming cross links between polymer chains.

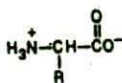
Wavelength : The length of a wave from peak to peak. The wavelength of electromagnetic radiation is inversely proportional to frequency and inversely proportional to energy.

Wavenumber : The wavenumber is the reciprocal of the wavelength in centimeters. Thus, wavenumbers are expressed in cm^{-1} .

Ylides : A neutral dipolar molecule in which the positive and negative charges are adjacent. For example, the phosphoranes used in Wittig reactions are ylides.

Zusammen (Z) : A term used to describe the stereochemistry of a carbon-carbon double bond. The two groups on each carbon are assigned priorities according to the Cahn-Ingold-Prelog sequence rules and the two carbons are compared. If the high priority groups on each carbon are on the same side of the double bond, the bond has Z geometry.

Zwitterion : A neutral dipolar molecule in which the positive and negative charges are not adjacent. For example, amino acids exist as zwitterions. (Zwitterions are also called betains).



An amino acid zwitterion

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