1

Structure and bonding

Key point. Organic chemistry is the study of carbon compounds. *Ionic* bonds involve elements gaining or losing electrons but the carbon atom is able to form four *covalent* bonds by sharing the four electrons in its outer shell. Single (C–C), double (C=C) or triple bonds (C≡C) to carbon are possible. When carbon is bonded to a different element, the electrons are not shared equally, as *electronegative* atoms (or groups) attract the electron density whereas *electropositive* atoms (or groups) repel the electron density. An understanding of the electron-withdrawing or -donating ability of atoms, or a group of atoms, can be used to predict whether an organic compound is a good *acid* or *base*.
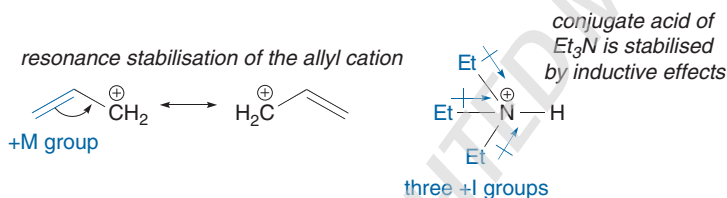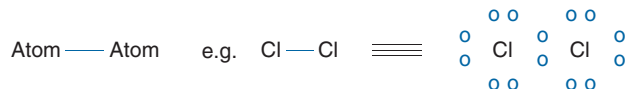

1.1 Ionic versus covalent bonds

- *Ionic bonds* are formed between molecules with opposite charges. The negatively charged anion will electrostatically attract the positively charged cation. This is present in (inorganic) salts.


- *Covalent bonds* are formed when a pair of electrons is shared between two atoms. A single line represents the two-electron bond.

- *Coordinate (or dative) bonds* are formed when a pair of electrons is shared between two atoms. *One* atom donates both electrons and a single line or an arrow represents the two-electron bond.

The cyclic ether is tetrahydrofuran (THF) and BH_3 is called borane (Section 6.2.2.5)

electron acceptor

O⟶BH_3 or $\overset{\oplus}{O}$ — $\overset{\ominus}{BH_3}$

electron donor
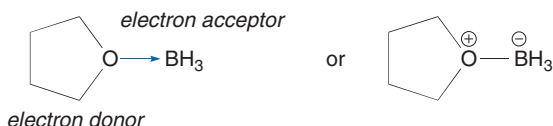
- *Hydrogen bonds* are formed when the partially positive ($\delta+$) hydrogen of one molecule interacts with the partially negative ($\delta-$) heteroatom (e.g. oxygen or nitrogen) of another molecule.
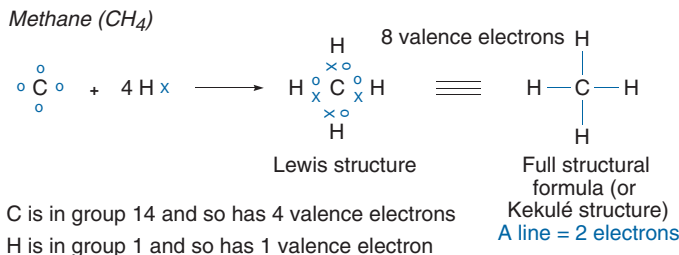
Intramolecular hydrogen bonding in carbonyl compounds is discussed in Section 8.4.1

$$\overset{\delta+}{} \quad \overset{\delta-}{}$$
Molecule–H⋯⋯Heteroatom–Molecule   e.g. $\overset{\delta+}{HO-H}$ ⋯⋯ $\overset{\delta-}{OH_2}$

1.2 The octet rule

To form organic compounds, the carbon atom shares electrons to give a stable 'full shell' electron configuration of eight valence electrons.

Methane is the smallest alkane – alkanes are a family of compounds that contain only C and H atoms linked by single bonds (Section 2.4)

Methane (CH_4)

8 valence electrons

°C° + 4 H× ⟶ H C H   ≡   H—C—H

Lewis structure

Full structural formula (or Kekulé structure)
A line = 2 electrons

C is in group 14 and so has 4 valence electrons
H is in group 1 and so has 1 valence electron

Drawing organic compounds using full structural formulae and other conventions is discussed in Section 2.5

A single bond contains two electrons, a double bond contains four electrons and a triple bond contains six electrons. A lone (or non-bonding) pair of electrons is represented by two dots (· ·).

Carbon dioxide (CO_2)

O C O   ≡   :O=C=O:

Hydrogen cyanide (HCN)
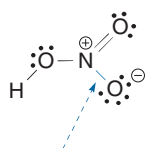
H C N   ≡   H—C≡N:

1.3 Formal charge

Formal positive or negative charges are assigned to atoms, which have an apparent 'abnormal' number of bonds.

Atom(s)	C	N, P	O, S	F, Cl, Br, I
Group number	14	15	16	17
Normal number of 2 electron bonds	4	3	2	1

Formal charge =	group number in periodic table	−	number of bonds to atom	−	number of unshared electrons	−	10

Example: Nitric acid (HNO₃)

Nitrogen with 4 covalent bonds has a formal charge of +1

Formal charge: $15 - 4 - 0 - 10 = +1$

The nitrogen atom donates a pair of electrons to make this bond

Nitric acid is used in synthesis to nitrate aromatic compounds such as benzene (Section 7.2.2)

Carbon forms four covalent bonds. When only three covalent bonds are present, the carbon atom can have either a formal negative charge or a formal positive charge.

The stability of carbocations and carbanions is discussed in Section 4.3

- *Carbanions*–three covalent bonds to carbon and a formal negative charge.

Formal charge on C:
$14 - 3 - 2 - 10 = -1$

8 outer electrons: 3 two-electron bonds and 2 non-bonding electrons
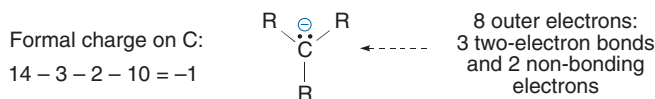
The negative charge is used to show the 2 non-bonding electrons

Carbanions are formed on deprotonation of organic compounds. Deprotonation of a carbonyl compound, at the α-position, forms a carbanion called an enolate ion (Section 8.4.3)

- *Carbocations*–three covalent bonds to carbon and a formal positive charge.

Formal charge on C:
$14 - 3 - 0 - 10 = +1$

6 outer electrons: 3 two-electron bonds
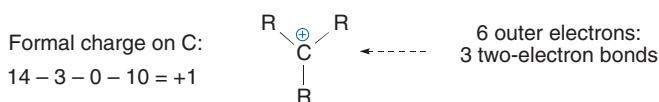
The positive charge is used to show the absence of 2 electrons

Carbocations are intermediates in a number of reactions, including S_N1 reactions (Section 5.3.1.2)

## 1.4 Sigma (σ−) and pi (π−) bonds

The electrons shared in a covalent bond result from overlap of atomic orbitals to give a new molecular orbital. Electrons in 1s and 2s orbitals combine to give sigma (σ−) bonds.

When two 1s orbitals combine *in-phase*, this produces a *bonding molecular orbital*.

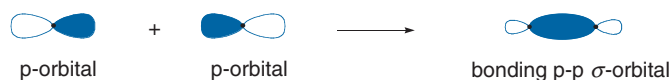Molecular orbitals and chemical reactions are discussed in Section 4.10

s-orbital   +   s-orbital   ⟶   bonding molecular orbital

When two 1s orbitals combine *out-of-phase*, this produces an *antibonding molecular orbital*.

s-orbital   +   s-orbital   ⟶   antibonding molecular orbital
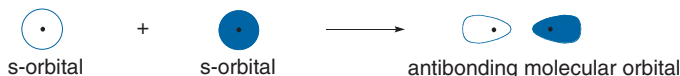
Electrons in p orbitals can combine to give sigma (σ) or pi (π) bonds.

- *Sigma ($\sigma-$) bonds* are strong bonds formed by head-on overlap of two atomic orbitals.

p-orbital   +   p-orbital   ⟶   bonding p-p σ-orbital

p-orbital   +   p-orbital   ⟶   antibonding p-p $\sigma*$-orbital

Alkenes have a C=C bond containing one strong σ-bond and one weaker π-bond (Section 6.1)

- *Pi ($\pi-$) bonds* are weaker bonds formed by side-on overlap of two p-orbitals.

p-orbital   +   p-orbital   ⟶   bonding p-p π-orbital

All carbonyl compounds have a C=O bond, which contains one strong σ-bond and one weaker π-bond (Section 8.1)

p-orbital   +   p-orbital   ⟶   antibonding p-p $\pi*$-orbital
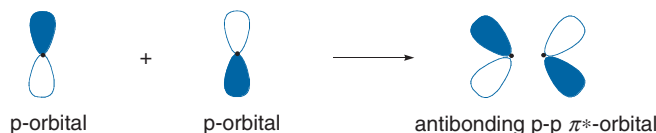
Only σ- or π-bonds are present in organic compounds. All single bonds are σ-bonds while all multiple (double or triple) bonds are composed of one σ-bond and one or two π-bonds.

1.5 Hybridisation

Hund's rule states that when filling up a set of orbitals of the same energy, electrons are added with parallel spins to different orbitals rather than pairing two electrons in one orbital

- The ground-state electronic configuration of carbon is $1s^2 2s^2 2p_x^1 2p_y^1$.
- The six electrons fill up lower energy orbitals before entering higher energy orbitals (Aufbau principle).
- Each orbital is allowed a maximum of two electrons (Pauli exclusion principle).
- The two 2p electrons occupy separate orbitals before pairing up (Hund's rule).
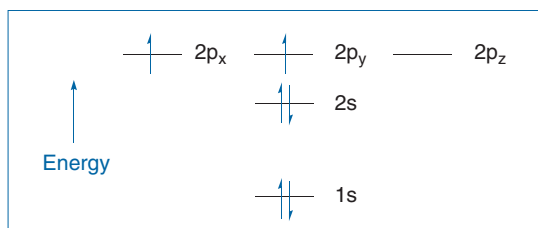
The carbon atom can mix the 2s and 2p atomic orbitals to form four new hybrid orbitals in a process known as *hybridisation*.

- *sp³ Hybridisation*. For four single σ-bonds – carbon is sp³ hybridised (e.g. in methane, CH_4). The orbitals move as far apart as possible, and the lobes point to the corners of a tetrahedron (109.5° bond angle).
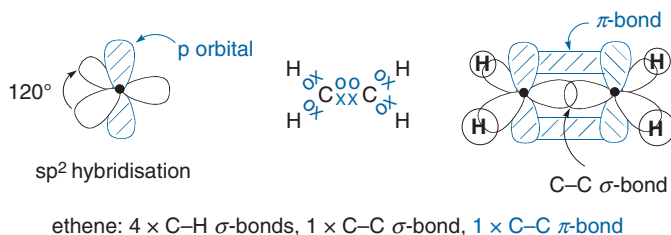

sp3 hybridisation

methane: 4 × C–H σ-bonds
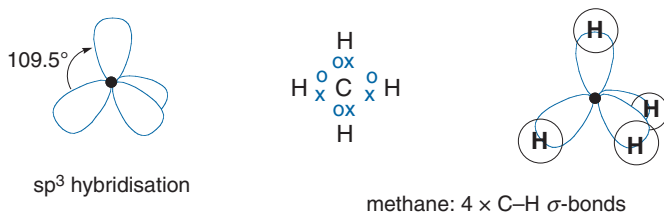
- *sp² Hybridisation*. For three single σ-bonds and one π-bond – the π-bond requires one p-orbital, and hence the carbon is sp² hybridised (e.g. in ethene, $H_2C=CH_2$). The three sp²-orbitals point to the corners of a triangle (120° bond angle), and the remaining p-orbital is perpendicular to the sp² plane.

Alkenes have a C=C bond containing one strong σ-bond and one weaker π-bond (Section 6.1)

All carbonyl compounds have a C=O bond, which contains one strong σ-bond and one weaker π-bond (Section 8.1)

sp2 hybridisation

C–C σ-bond

ethene: 4 × C–H σ-bonds, 1 × C–C σ-bond, 1 × C–C π-bond

- *sp Hybridisation*. For two single σ-bonds and two π-bonds – the two π-bonds require two p-orbitals, and hence the carbon is sp hybridised (e.g. in ethyne, HC≡CH). The two sp-orbitals point in the opposite directions (180° bond angle), and the two p-orbitals are perpendicular to the sp plane.

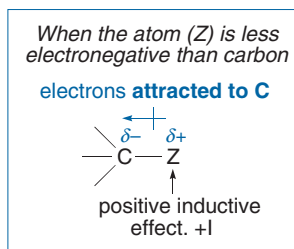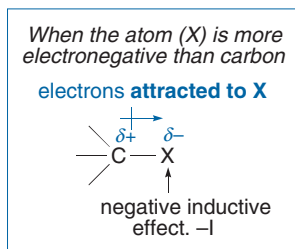Alkynes have a C≡C bond containing one strong σ-bond and two weaker π-bonds (Section 6.1)

sp hybridisation

C–C σ-bond

ethyne: 2 × C–H σ-bonds, 1 × C–C σ-bond, 2 x C–C π-bonds

- For a single C−C or C−O bond, the atoms are sp^3 hybridised and the carbon atom(s) is *tetrahedral*.
- For a double C=C or C=O bond, the atoms are sp^2 hybridised and the carbon atom(s) is *trigonal planar*.
- For a triple C≡C or C≡N bond, the atoms are sp hybridised and the carbon atom(s) is *linear*.

This compound contains four functional groups, including a phenol. Functional groups are introduced in Section 2.1

3 = sp3 2 = sp2 1 = sp

The shape of organic molecules is therefore determined by the hybridisation of the atoms.

Functional groups (Section 2.1) that contain π-bonds are generally more reactive as a π-bond is weaker than a σ-bond. The π-bond in an alkene or alkyne is around $+250\,kJ\,mol^{-1}$, while the σ-bond is around $+350\,kJ\,mol^{-1}$.

Bond	Mean bond enthalpies (kJ mol⁻¹)	Mean bond lengths (pm)
C—C	+347	153
C=C	+612	134
C≡C	+838	120

A hydrogen atom attached to a C≡C bond is more acidic than a hydrogen atom attached to a C=C bond or a C−C bond; this is explained by the change in hybridisation of the carbon atom that is bonded to the hydrogen atom (Section 1.7.4)

The shorter the bond length, the stronger the bond. For C−H bonds, the greater the 's' character of the carbon orbitals, the shorter the bond length. This is because the electrons are held closer to the nucleus.

Rotation about C−C bonds is discussed in Section 3.2

A single C−C σ-bond can undergo free rotation at room temperature, but a π-bond prevents free rotation around a C=C bond. For maximum orbital overlap in a π-bond, the two p-orbitals need to be parallel to one another. Any rotation around the C=C bond will break the π-bond.

1.6 Inductive effects, hyperconjugation and mesomeric effects

1.6.1 Inductive effects

In a covalent bond between two different atoms, the electrons in the σ-bond are not shared equally. The electrons are attracted towards the most electronegative atom. An

arrow drawn above the line representing the covalent bond can show this. (Sometimes an arrow is drawn on the line.) Electrons are pulled in the direction of the arrow.

An inductive effect is the polarisation of electrons through σ-bonds

When the atom (X) is more electronegative than carbon	When the atom (Z) is less electronegative than carbon
electrons **attracted to X**	electrons **attracted to C**
$\delta+ \quad \delta-$ C — X	$\delta- \quad \delta+$ C — Z
negative inductive effect. –I	positive inductive effect. +I

An alkyl group (R) is formed by removing a hydrogen atom from an alkane (Section 2.2).

–I groups	**+I groups**
X = Br, Cl, NO$_2$, OH, OR, SH, SR, NH$_2$, NHR, NR$_2$, CN, CO$_2$H, CHO, C(O)R	Z = R (alkyl or aryl), metals (e.g. Li or Mg)
The more electronegative the atom (X), the stronger the –I effect	The more electropositive the atom (Z), the stronger the +I effect

An aryl group (Ar) is benzene (typically called phenyl, Ph) or a substituted benzene group (Section 2.2)

| *Pauling electronegativity scale*	The inductive effect of the atom rapidly diminishes as the chain length increases
K = 0.82 I = 2.66 C = 2.55 Br = 2.96 N = 3.04 Cl = 3.16 O = 3.44 F = 3.98	$\delta\delta\delta+ \quad \delta\delta+ \quad \delta+ \quad \delta-$ H$_3$C — CH$_2$ — CH$_2$ — CH$_2$ — Cl
The higher the value the more electronegative the atom	experiences a negligible –I effect experiences a strong –I effect
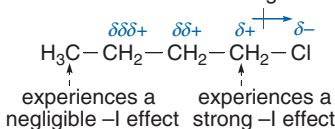
The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions and this can be measured by the dipole moment (μ). The larger the dipole moment (often measured in debyes, D), the more polar the compound.

1.6.2 Hyperconjugation

A σ-bond can stabilise a neighbouring carbocation (or positively charged carbon, e.g. R_3C^+) by donating electrons to the vacant p-orbital. The positive charge is delocalised or 'spread out' and this stabilising effect is called *resonance*.

Hyperconjugation is the donation of electrons from nearby C–H or C–C σ-bonds

C–H σ-bond
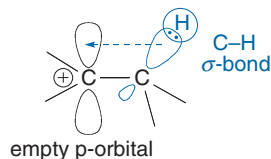
The electrons in the C–H σ-bond spend some of the time in the empty p-orbital

empty p-orbital

The stability of carbocations is discussed in Section 4.3.1

1.6.3 Mesomeric effects

Whilst inductive effects pull electrons through the σ-bond framework, electrons can also move through the π-bond network. A π-bond can stabilise a negative charge, a

positive charge, a lone pair of electrons or an adjacent bond by *resonance* (i.e. delocalisation or 'spreading out' of the electrons). Curly arrows (Section 4.1) are used to represent the movement of π- or non-bonding electrons to give different resonance forms. It is only the electrons, not the nuclei, that move in the resonance forms, and a double-headed arrow is used to show their relationship.

1.6.3.1   Positive mesomeric effect

- When a π-system donates electrons, the π-system has a positive mesomeric effect, +M.

donates electrons: +M group
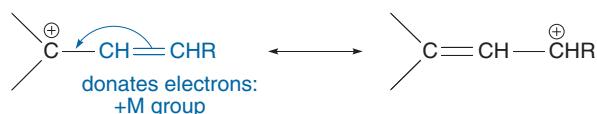
- When a lone pair of electrons is donated, the group donating the electrons has a positive mesomeric effect, +M.

donates electrons: +M group
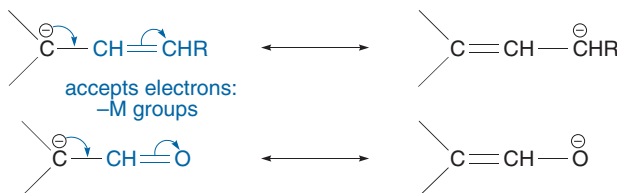
1.6.3.2   Negative mesomeric effect

- When a π-system accepts electrons, the π-system has a negative mesomeric effect, −M.

accepts electrons: −M groups

The actual structures of the cations or anions lie somewhere between the two resonance forms. All resonance forms must have the same overall charge and obey the same rules of valency.

> **–M groups** generally contain an electronegative atom(s) and/or a π-bond(s):
> CHO, C(O)R, CO$_2$H, CO$_2$Me, NO$_2$, CN, aromatics, alkenes
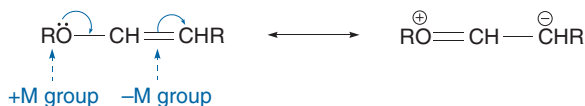>
> **+M groups** generally contain a lone pair of electrons or a π-bond(s):
> C̈l, B̈r, ÖH, ÖR, S̈H, S̈R, N̈H$_2$, N̈HR, N̈R$_2$, aromatics, alkenes
>
> Aromatic (or aryl) groups and alkenes can be *both* +M and –M.

In neutral compounds, there will always be a +M *and* −M group(s): one group donates (+M) the electrons, the other group(s) accepts the electrons (−M).

An amide, such as $RCONH_2$, also contains both a +M group (NH_2) and a −M group (C=O). See Sections 1.7.2 and 9.3.1

All resonance forms are *not* of the same energy. Generally, the most stable resonance forms have the greatest number of covalent bonds, atoms with a complete valence shell of electrons, and/or an aromatic ring. In phenol (PhOH), for example, the resonance form with the intact aromatic benzene ring is expected to predominate.
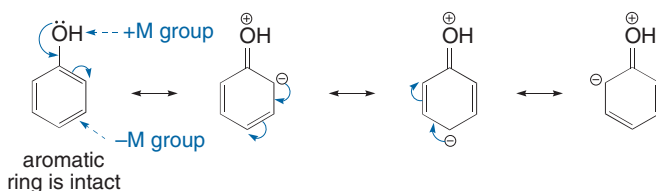
Benzene and other aromatic compounds, including phenol, are discussed in Chapter 7

As a rule of thumb, the more resonance structures an anion, cation or neutral π-system can have, the more stable it is.

1.6.3.3   Inductive versus mesomeric effects

Mesomeric effects are generally stronger than inductive effects. A +M group is likely to stabilise a cation more effectively than a +I group.

Mesomeric effects can be effective over much longer distances than inductive effects provided that *conjugation* is present (i.e. alternating single and double bonds). Whereas inductive effects are determined by distance, mesomeric effects are determined by the relative positions of +M and −M groups in a molecule (Section 1.7).

Conjugated enones, containing a C=C–C=O group, are discussed in Section 8.5.1

1.7   Acidity and basicity

1.7.1   Acids

An acid is a substance that donates a proton (Brønsted-Lowry). Acidic compounds have low pK_a values and are good proton donors as the anions (or conjugate bases), formed on deprotonation, are relatively stable.

Equilibria and equilibrium constants are discussed in Section 4.9.1.1
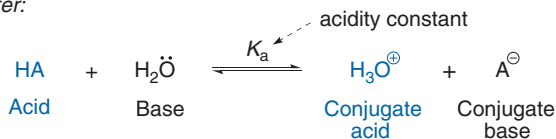
The more stable the conjugate base the stronger the acid

$$K_a \approx \frac{[H_3O^{\oplus}]\,[A^{\ominus}]}{[HA]}$$

As H_2O is in excess

$$pK_a = -\log_{10} K_a$$

The higher the value of K_a, the lower the pK_a value and the more acidic is HA

The pK_a value equals the pH of the acid when it is half ionised. At pH's above the pK_a the acid (HA) exists predominantly as the conjugate base (A⁻) in water. At pH's below the pK_a it exists predominantly as HA.

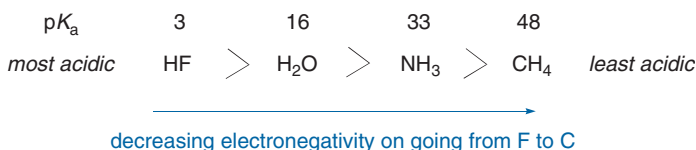pH = 0, strongly acidic

pH = 7, neutral

pH = 14, strongly basic

The influence of solvent polarity on substitution and elimination reactions is discussed in Sections 5.3.1.3 and 5.3.2.3

The pK_a values are influenced by the solvent. Polar solvents will stabilise cations and/or anions by *solvation* in which the charge is delocalised over the solvent (e.g. by hydrogen-bonding in water).
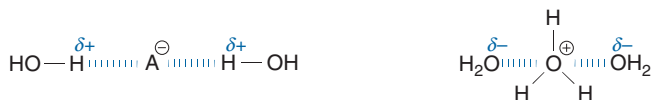
The more electronegative the atom bearing the negative charge, the more stable the conjugate base (which is negatively charged).

pK_a	3	16	33	48
most acidic	HF	> H$_2$O	> NH$_3$	> CH$_4$ least acidic

decreasing electronegativity on going from F to C

Therefore, F⁻ is more stable than H_3C^-.

Inductive effects are introduced in Section 1.6.1

The conjugate base can also be stabilised by −I and −M groups which can delocalise the negative charge. (The more 'spread out' the negative charge, the more stable it is).

Mesomeric effects are introduced in Section 1.6.3

−I and −M groups therefore *lower* the pK_a while
+I and +M groups *raise* the pK_a

1.7.1.1   Inductive effects and carboxylic acids

The carboxylate ion (RCO$_2$⁻) is formed on deprotonation of a carboxylic acid (RCO$_2$H). The anion is stabilised by resonance (i.e. the charge is spread over both oxygen atoms) but can also be stabilised by the R group if this has a −I effect.
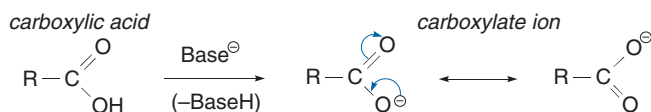
The reactions of carboxylic acids are discussed in Chapter 9

The greater the −I effect, the more stable the carboxylate ion (e.g. FCH$_2$CO$_2$⁻ is more stable than BrCH$_2$CO$_2$⁻) and the more acidic the carboxylic acid (e.g. FCH$_2$CO$_2$H is more acidic than BrCH$_2$CO$_2$H).

F—CH$_2$—CO$_2$H	Br—CH$_2$—CO$_2$H	H$_3$C—CO$_2$H
pK$_a$ 2.7	2.9	4.8
Most acidic as F is more electronegative than Br and has a greater −I effect		**Least** acidic as the CH$_3$ group is a +I group
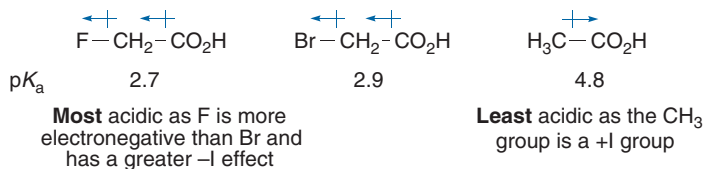
1.7.1.2 Inductive and mesomeric effects and phenols

Mesomeric effects can also stabilise positive and negative charges.

> The *negative* charge needs to be on an adjacent carbon atom for a **−M** group to stabilise it
>
> The *positive* charge needs to be on an adjacent carbon atom for a **+M** group to stabilise it
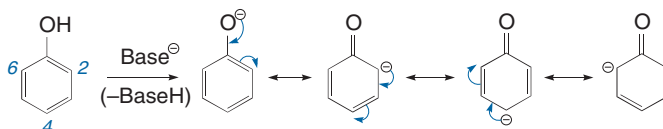
On deprotonation of phenol (PhOH) the phenoxide ion (PhO⁻) is formed. This anion is stabilised by the delocalisation of the negative charge on to the 2-, 4- and 6-positions of the benzene ring.

- If −M groups are introduced at the 2-, 4- and/or 6-positions, the anion can be further stabilised by delocalisation through the π-system as the negative charge can be spread onto the −M group. We can use double-headed curly arrows to show this process.

  Double-headed curly arrows are introduced in Section 4.1

- If −M groups are introduced at the 3- and/or 5-positions, the anion cannot be stabilised by delocalisation, as the negative charge cannot be spread onto the −M group. There is no way of using curly arrows to delocalise the charge on to the −M group.
- If −I groups are introduced on the benzene ring, the effect will depend on their distance from the negative charge. The closer the −I group is to the negative charge, the greater the stabilising effect will be. The order of −I stabilisation is therefore 2-position > 3-position > 4-position.
- The −M effects are much stronger than −I effects (Section 1.6.3).

Examples

> The NO$_2$ group is strongly electron-withdrawing; −I and −M

OH	OH	OH	OH

pK_a 9.9   8.4   7.2   4.0

Least acidic
as no –I or
–M groups on
the ring

The NO_2 can
only stabilise
the anion
inductively

The NO_2
can stabilise
the anion
inductively and
by resonance

Most acidic as
both NO_2 groups
can stabilise the
anion inductively
and by resonance
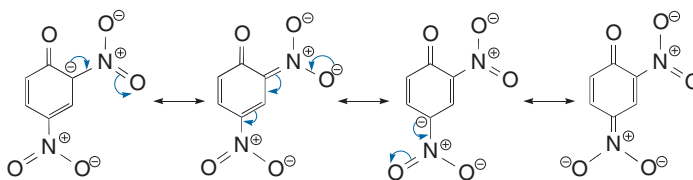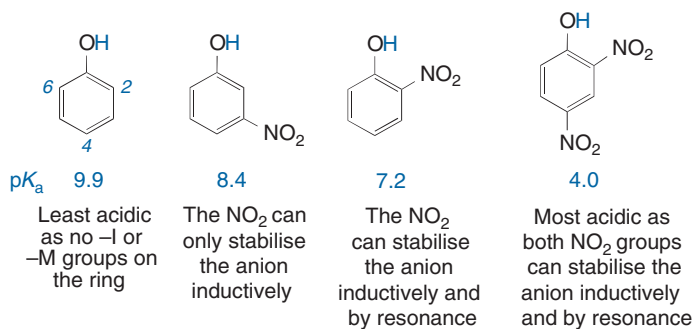
1.7.2 Bases

A base is a substance that accepts a proton (Brønsted-Lowry). Basic compounds
are good proton acceptors as the conjugate acids, formed on protonation, are
relatively stable. Consequently, strong bases (B: or B⁻) give conjugate acids
(BH^+ or BH) with high pK_a values.

In water:

basicity constant

$$\ddot{B} \; + \; H_2O \; \underset{}{\overset{K_b}{\rightleftharpoons}} \; \overset{\oplus}{BH} \; + \; H\overset{\ominus}{O}$$
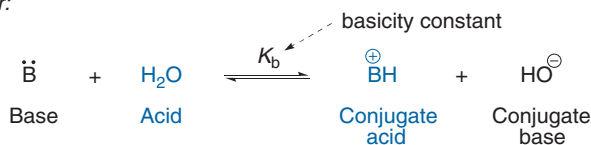
Base   Acid   Conjugate   Conjugate
                     acid   base

The strength of bases is usually described by the K_a and pK_a values of the
conjugate acid.

$$\overset{\oplus}{BH} \; + \; H_2O \; \underset{}{\overset{K_a}{\rightleftharpoons}} \; \ddot{B} \; + \; H_3\overset{\oplus}{O}$$
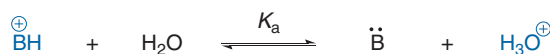
$$K_a \approx \frac{[B\,][H_3\overset{\oplus}{O}]}{[\overset{\oplus}{BH}]}$$

As H_2O is in excess

- If B is a *strong* base then BH^+ will be relatively stable and not easily
  deprotonated. BH^+ will therefore have a *high* pK_a value.
- If B is a *weak* base then BH^+ will be relatively unstable and easily deproto-
  nated. BH^+ will therefore have a *low* pK_a value.

The cation can be stabilised by +I and +M groups, which can delocalise the positive charge. (The more 'spread out' the positive charge, the more stable it is.)

Mesomeric effects are introduced in Section 1.6.3

1.7.2.1 Inductive effects and aliphatic (or alkyl) amines

On protonation of amines (e.g. RNH_2), ammonium salts are formed.

Aliphatic amines have nitrogen bonded to one or more alkyl groups; aromatic amines have nitrogen bonded to one or more aryl groups

$$R \overset{\cdot\cdot}{-} \overset{}{NH_2} \quad + \quad H^{\oplus} \quad \rightleftharpoons \quad R \overset{\oplus}{-} NH_3$$

primary amine   *ammonium ion*

The greater the +I effect of the R group, the greater the electron density at nitrogen and the more basic the amine. The greater the +I effect, the more stable the ammonium ion and the more basic the amine.

Primary (RNH_2), secondary (R_2NH) and tertiary (R_3N) amines are introduced in Section 2.1

no +I group   *three +I groups*

Triethylamine (Et_3N) is commonly used as a base in organic synthesis (Section 5.2.2)

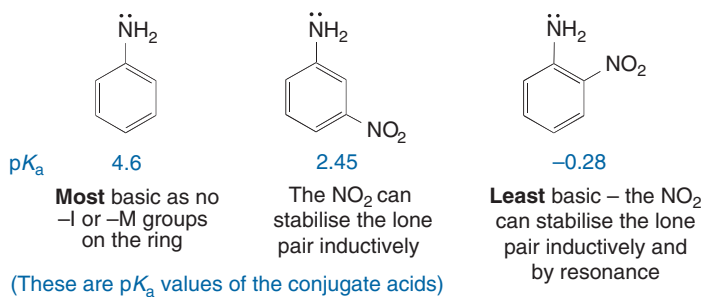|			
pK_a 9.3	10.7	10.9	10.9

The pK_a values *should* increase steadily as more +I alkyl groups are introduced on nitrogen. However, the pK_a values are determined in *water*, and the more hydrogen atoms on the positively charged nitrogen, the greater the extent of hydrogen bonding between water and the cation. This solvation leads to the stabilisation of the cations containing N−H bonds.

Hydrogen bonds are introduced in Section 1.1

In organic solvents (which cannot solvate the cation) the order of pK_a's is expected to be as follows.

tertiary   *secondary*   *primary*
amine   *amine*   *amine*   *ammonia*

$$R_3\overset{\cdot\cdot}{N} \; > \; R_2\overset{\cdot\cdot}{N}H \; > \; R\overset{\cdot\cdot}{N}H_2 \; > \; \overset{\cdot\cdot}{N}H_3 \qquad (R = \text{+I alkyl group})$$

most basic   *least basic*

The presence of −I and/or −M groups on nitrogen reduces the basicity and so, for example, primary amides ($RCONH_2$) are poor bases.

Secondary amides (RCONHR) and tertiary amides ($RCONR_2$) are also very weak bases because the nitrogen lone pairs are stabilised by resonance

Ethanamide

The C=O group stabilises the lone pair on nitrogen by resonance – this reduces the electron density on nitrogen

−M, −I

If ethanamide was protonated on nitrogen, the positive charge could not be stabilised by delocalisation. Protonation therefore occurs on oxygen as the charge can be delocalised on to the nitrogen atom.

Reactions of amides are discussed in Section 9.8

The conjugate acid has a low pK_a of −0.5

1.7.2.2 Mesomeric effects and aryl (or aromatic) amines

For the preparation and reactions of aniline (PhNH$_2$), see Section 7.8

The lone pair of electrons on the nitrogen atom of aminobenzene (or aniline, PhNH$_2$) can be stabilised by delocalisation of the electrons onto the 2-, 4- and 6-positions of the benzene ring. Aromatic amines are therefore less basic than aliphatic amines.
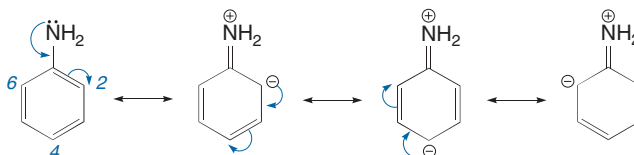

- If −M groups are introduced at the 2-, 4- and/or 6-positions (but not the 3- or 5-positions) the anion can be further stabilised by delocalisation, as the negative charge can be spread on to the −M group. This reduces the basicity of the amine.
- If −I groups are introduced on the benzene ring, the order of −I stabilisation is 2-position > 3-position > 4-position. This reduces the basicity of the amine.

| pK_a | 4.6 | 2.45 | −0.28 |

Most basic as no −I or −M groups on the ring

The NO$_2$ can stabilise the lone pair inductively

Least basic – the NO$_2$ can stabilise the lone pair inductively and by resonance

(These are pK_a values of the conjugate acids)

For the Pauling electronegativity scale see Section 1.6.1

- If +M groups (e.g. OMe) are introduced at the 2-, 4- or 6-position of aminobenzene (PhNH$_2$), then the basicity is increased. This is because the +M group donates electron density to the carbon atom bearing the amine group. Note that the nitrogen atom, not the oxygen atom, is protonated – this is because nitrogen is less electronegative than oxygen and is a better electron donor.

The OMe group is –I but +M	(These are pK_a values of the conjugate acids formed by protonation of the –NH_2 group)
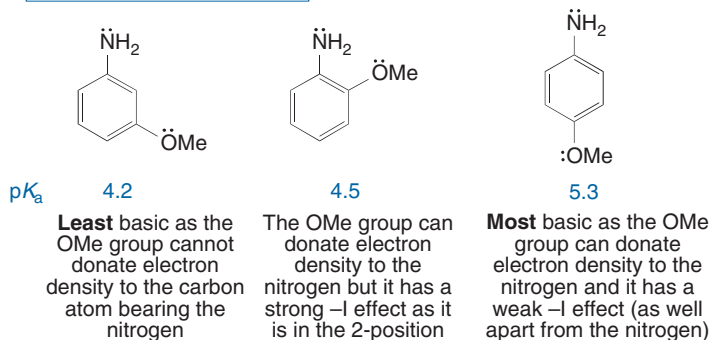
The OMe group is called a methoxy group (see Section 2.4 for naming organic compounds)

$\ddot{N}H_2$ ÖMe	$\ddot{N}H_2$ ÖMe	$\ddot{N}H_2$:OMe
pK_a 4.2	**4.5**	**5.3**
Least basic as the OMe group cannot donate electron density to the carbon atom bearing the nitrogen	The OMe group can donate electron density to the nitrogen but it has a strong –I effect as it is in the 2-position	**Most** basic as the OMe group can donate electron density to the nitrogen and it has a weak –I effect (as well apart from the nitrogen)

Curly arrows can be used to show the delocalisation of electrons on to the carbon atom bearing the nitrogen.

Curly arrows are introduced in Section 4.1

electron density adjacent to the nitrogen increases the basicity
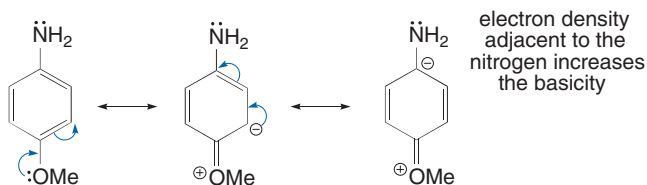
1.7.3 Lewis acids and bases

- A *Lewis acid* is any substance that accepts an electron pair in forming a coordinate bond (Section 1.1). Examples include H^+, BF_3, $AlCl_3$, $TiCl_4$, $ZnCl_2$ and $SnCl_4$. They have unfilled valence shells and so can accept electron pairs.
- A *Lewis base* is any substance that donates an electron pair in forming a coordinate bond. Examples include H_2O, ROH, RCHO, $R_2C=O$, R_3N and R_2S. They all have a lone pair(s) of electrons on the heteroatom (O, N or S).
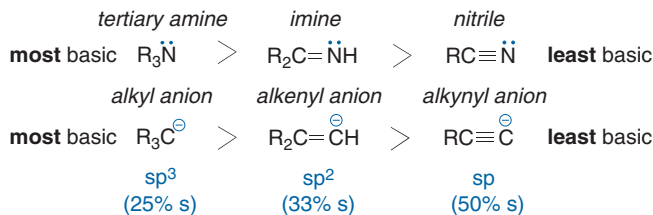
A heteroatom is any atom that is not carbon or hydrogen
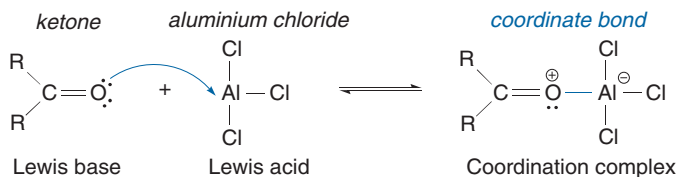
Reactions of ketones are discussed in Chapter 8
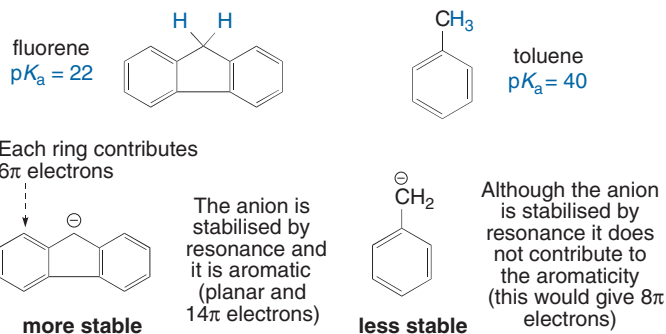
1.7.4 Basicity and hybridisation

The greater the 's' character of an orbital, the lower in energy the electrons and the more tightly the electrons are held to the nucleus. The electrons in an sp-orbital are therefore less available for protonation than those in an sp^2- or sp^3-orbital, and hence the compounds are less basic.

tertiary amine   *imine*   *nitrile*

most basic $R_3\ddot{N}$ $>$ $R_2C{=}\ddot{N}H$ $>$ $RC{\equiv}\ddot{N}$ **least** basic

alkyl anion   *alkenyl anion*   *alkynyl anion*

most basic $R_3C^{\ominus}$ $>$ $R_2C{=}\overset{\ominus}{C}H$ $>$ $RC{\equiv}\overset{\ominus}{C}$ **least** basic

sp^3 sp^2 sp
(25% s)   (33% s)   (50% s)

1.7.5   Acidity and aromaticity

Aromatic compounds are planar, conjugated systems which have $4n + 2$ electrons (Hückel's rule) (Section 7.1). If, on deprotonation, the anion is part of an aromatic π-system then the negative charge will be stabilised. Aromaticity will therefore *increase* the acidity of the compound.

Toluene is a common solvent. Oxidation of the CH_3 group is discussed in Section 7.6

Resonance stabilisation of carbanions is introduced in Section 1.6.3

fluorene
$pK_a = 22$

toluene
$pK_a = 40$

Each ring contributes 6π electrons

The anion is stabilised by resonance and it is aromatic (planar and 14π electrons)

more stable

Although the anion is stabilised by resonance it does not contribute to the aromaticity (this would give 8π electrons)

less stable

If a lone pair of electrons on a heteroatom is part of an aromatic π-system, then these electrons will not be available for protonation. Aromaticity will therefore *decrease* the basicity of the compound.

Reactions of aromatic heterocycles, including pyrrole and pyridine are discussed in Sections 7.10 and 7.11
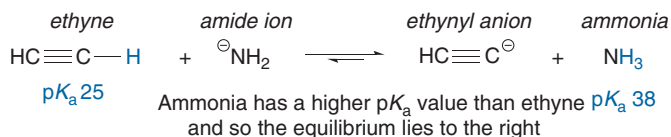
Each double bond contributes 2π electrons

Pyrrole

The lone pair of electrons contributes to the 6π-electrons in the aromatic ring. Pyrrole is therefore not basic (pK_a −4)

Each double bond contributes 2π electrons

Pyridine

The lone pair of electrons does *not* contribute to the 6π-electrons in the aromatic ring. Pyridine is therefore basic (pK_a 5)

1.7.6   Acid-base reactions
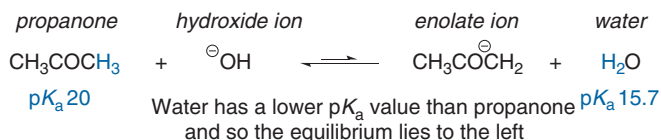
For a table of pK_a values see Appendix 3

The pK_a values can be used to predict if an acid-base reaction can take place. An acid will donate a proton to the conjugate base of any acid with a higher pK_a value.

This means that the product acid and base will be more stable than the starting acid and base.


ethyne   *amide ion*   *ethynyl anion*   *ammonia*

$HC\equiv C-H$ + $^{\ominus}NH_2$ $\rightleftharpoons$ $HC\equiv C^{\ominus}$ + NH_3

$pK_a\,25$ Ammonia has a higher pK_a value than ethyne $pK_a\,38$
and so the equilibrium lies to the right

Deprotonation of terminal alkynes is discussed in Section 6.3.2.5

propanone   *hydroxide ion*   *enolate ion*   *water*

CH_3COCH_3 + $^{\ominus}OH$ $\rightleftharpoons$ CH_3COCH_2 + H_2O

$pK_a\,20$ Water has a lower pK_a value than propanone $pK_a\,15.7$
and so the equilibrium lies to the left

For deprotonation of carbonyl compounds to form enolate ions, see Section 8.4.3

Worked Example

(a) Giving your reasons, rank the following carbanions **1–4** in order of increasing stability.
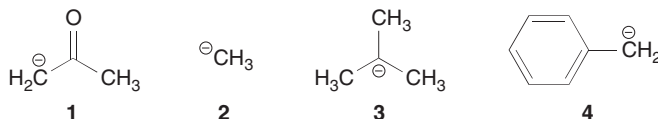
Hint: Determine whether the groups attached to the negatively charged carbons in **1–4** can stabilise the lone pair by I and/or M effects

1   **2**   **3**   **4**

(b) Identify, giving your reasons, the most acidic hydrogen atom(s) in compound **5**.
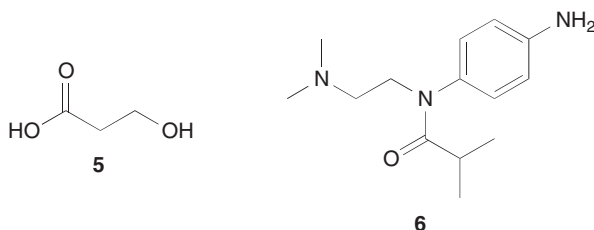
Hint: Consider a δ+ hydrogen atom bonded to an electronegative atom that, on deprotonation, gives the more stable conjugate base

5

6

Hint: Show all the lone pairs in **6** and consider their relative availability. Compare the stability of possible conjugate acids

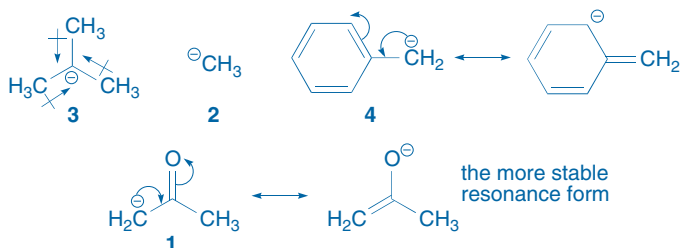(c) Identify, giving your reasons, the basic functional group in compound **6**.

Answer

(a)

3   **2**   **4**   **1**

increasing stability ⟶
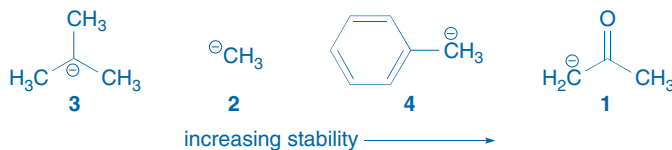
Inductive and mesomeric effects (resonance) are discussed in Sections 1.6.1 and 1.6.3

For the *tert*-butyl anion **3**, because the three CH_3 are electron-donating groups (+I), this makes **3** less stable than the methyl anion **2**.

The benzyl anion **4** is more stable than the methyl anion **2** because it is stabilised by resonance – the negative charge is delocalised on to the 2, 4 and 6 positions of the ring.

Enolate ion **1** is the most stable because the anion is stabilised by resonance and one resonance form has the negative charge on oxygen – a negative charge on oxygen is more stable than a negative charge on carbon.

(b) Hydrogen atoms bonded to oxygen are more acidic than those bonded to carbon. As oxygen is more electronegative than carbon, the conjugate base is more stable. The carboxylic acid group is more acidic than the alcohol group in **5** because deprotonation of the carboxylic acid gives a conjugate base that is stabilised by resonance.
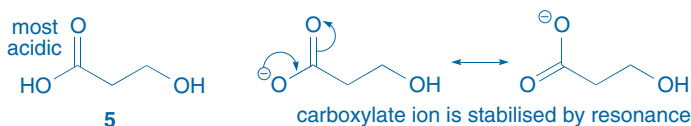
(c) The tertiary amine is the most basic group in **6**. The lone pairs on the nitrogen atoms in the tertiary amide and aniline groups are both delocalised and less available for protonation (the oxygen atom of the tertiary amide is less basic than the tertiary amine because oxygen is more electronegative than nitrogen, hence the oxygen lone pairs are less available). On protonation of the tertiary amine, the conjugate acid is stabilised by three +I effects.
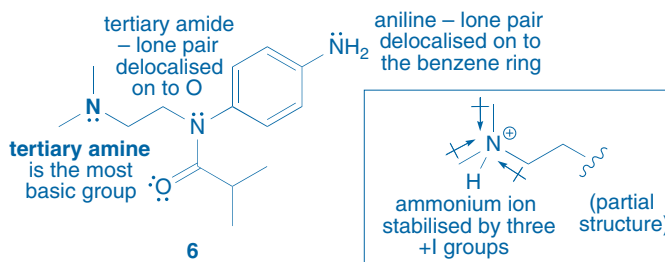
Problems

1. Using the I and M notations, identify the electronic effects of the following substituents.

(a) −Me (b) −Cl   (c) −NH$_2$ (d) −OH
(e) −Br   (f) −CO$_2$Me (g) −NO$_2$ (h) −CN

2. (a) Use curly arrows to show how cations **A**, **B** and **C** (shown below) are stabilised by resonance, and draw the alternative resonance structure(s).

A   **B**   **C**
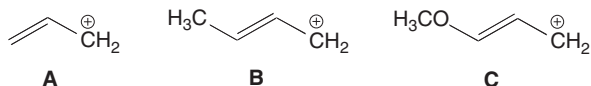
   (b) Would you expect **A**, **B** or **C** to be the more stable? Briefly explain your reasoning.

3. Provide explanations for the following statements.

   (a) The carbocation CH$_3$OCH$_2$$^+$ is more stable than CH$_3$CH$_2$$^+$.
   (b) 4-Nitrophenol is a much stronger acid than phenol (C$_6$H$_5$OH).
   (c) The pK_a of CH$_3$COCH$_3$ is much lower than that of CH$_3$CH$_3$.
   (d) The C−C single bond in CH$_3$CN is longer than that in CH$_2$=CH−CN.
   (e) The cation CH$_2$=CH−CH$_2$$^+$ is resonance stabilised whereas the cation CH$_2$=CH−NMe$_3$$^+$ is not.

4. Why is cyclopentadiene (pK_a 15.5) a stronger acid than cycloheptatriene (p$K_a \sim 36$)?

cyclopentadiene   cycloheptatriene
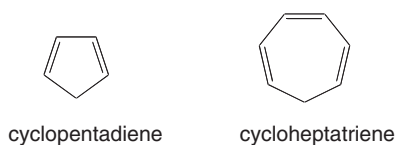
5. Which hydrogen atom would you expect to be the most acidic in each of the following compounds?

   (a) 4-Methylphenol (or *p*-cresol, 4-HOC$_6$H$_4$CH$_3$)
   (b) 4-Hydroxybenzoic acid (4-HOC$_6$H$_4$CO$_2$H)
   (c) H$_2$C=CHCH$_2$CH$_2$C≡CH
   (d) HOCH$_2$CH$_2$CH$_2$C≡CH

**6.** Arrange the following sets of compounds in order of decreasing basicity. Briefly explain your reasoning.

   (a) 1-Aminopropane, ethanamide (CH$_3$CONH$_2$), guanidine [HN=C(NH$_2$)$_2$], aniline (C$_6$H$_5$NH$_2$).
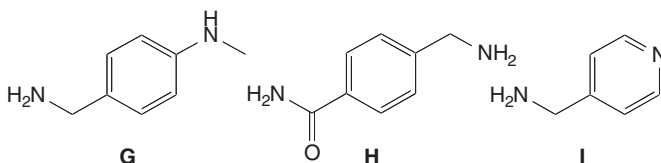   (b) Aniline (C$_6$H$_5$NH$_2$), 4-nitroaniline, 4-methoxyaniline, 4-methylaniline.

7. For each of the following compounds **D**−**F**, identify the most acidic hydrogen atom(s). Briefly explain your reasoning.

D   **E**   **F**
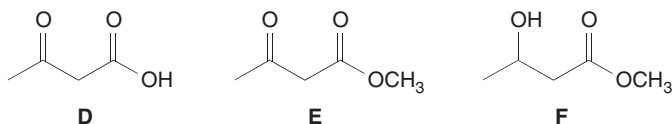
8. For each of the following compounds **G−I**, identify the most basic group. Briefly explain your reasoning.

G   **H**   **I**

9. Given the approximate pK_a values shown below, for the following acid-base reactions (a)−(e), determine whether the position of the equilibrium lies over to the reactant side or the product side.

Acid	pK_a value
PhOH	9.9
H_2O	15.7
CH_3COCH_3	20
H_2	35
NH_3	38
$H_2C=CH_2$	44

(a) NaH + PhOH $\rightleftharpoons$ $PhO^{\ominus} Na^{\oplus}$ + H_2

(b) CH_3COCH_3 + $NaOH$ $\rightleftharpoons$ $CH_3COCH_2Na^{\oplus}$ + H_2O

(c) $H_2C=CH_2$ + $NaNH_2$ $\rightleftharpoons$ $H_2C=CH\,Na^{\oplus}$ + NH_3

(d) $CH_3COCH_2\,Na^{\oplus}$ + PhOH $\rightleftharpoons$ CH_3COCH_3 + $PhO^{\ominus}Na^{\oplus}$

(e) $H_2C=CH\,Na^{\oplus}$ + H_2O $\rightleftharpoons$ $H_2C=CH_2$ + $NaOH$