

7.15 Electron spin resonance (8 points)

Outline

In this experiment you will obtain and interpret the ESR spectra of some free radicals. In the first part, the hyperfine structure of the spectra caused by the unpaired electron coupling to nearby magnetic nuclei is investigated for radicals in which coupling is to hydrogen or nitrogen nuclei. These examples serve to establish the basic coupling laws which determine the appearance of ESR spectra.

In the second half the spectrum of a more substantial radical is obtained. This is interpreted using the rules established in the first part, but now the observed coupling constants are used to determine the electron densities around the ring of the aromatic radical involved. These same electron densities are calculated using Huckel molecular orbital theory, and the experimental and theoretical results compared. A brief introduction to ESR and to the experimental method is given first, and it is essential that you read this carefully before starting the experiment.

Safety

The magnetic fields used in this experiments present no special health hazard, (except a minor risk to watches and credit cards). However, you need to work carefully with the chemicals, since they present non-trivial hazards.

1,2-dimethoxyethane (ethylene glycol dimethyl ether) and 2-propanol are flammable; prepare solutions containing them in a fume cupboard.

Concentrated sulphuric acid is extremely corrosive and reacts violently with water and many organic materials. Handle it in a fume cupboard, wear safety glasses and disposable gloves, check that all glassware is clean and dry before use, and clean up spills immediately.

Potassium hydroxide is caustic and extremely harmful to eyes; wear safety glasses when handling solutions containing it.

Benzoquinone is a severe irritant, and anthracene an irritant.

Further information on these chemicals is contained in COSHH forms available in the laboratory, and at <http://physchem.ox.ac.uk/~hmc/safetytl.html>

Relevant lecture course

Various 2nd and 3rd year courses on Spectroscopy and Magnetism, Nuclear Magnetic Resonance.

Electron Spin Resonance

ESR is exhibited only by molecules which contain unpaired electrons; we shall consider only free radicals. The electron has two possible observable values of its spin angular momentum ($m_s h/2\pi$, where $m_s = \pm \frac{1}{2}$); each of these yields a different value of its magnetic moment, defined as $\mu = \pm 2g\mu_B$. Here μ_B is the basic unit of electron magnetism, the Bohr magneton (its value is $he/2\pi m = 9.2737 \times 10^{-24}$ J Tesla⁻¹) and g is a constant. Its value is 2.0023 for a free electron, but in radicals a small amount of spin-orbit coupling changes the total angular momentum of the electron and hence the magnetic moment and the g -value. The precise value is consequently characteristic of the specific radical involved.

When a magnetic moment is placed in a magnetic field B it acquires an energy $-\mu B$, and the external field consequently removes the degeneracy of the electron spin states to give two energy levels:

$$E_{\frac{1}{2}} = -\frac{1}{2}g\mu_B B \quad E_{-\frac{1}{2}} = +\frac{1}{2}g\mu_B B$$

These two states contain different populations of electrons according to the normal Boltzmann distribution at thermal equilibrium.

The ESR experiment consists simply in inducing transitions between the two levels with radiation of frequency ν such that

$$h\nu = E_{-\frac{1}{2}} - E_{\frac{1}{2}} = g\mu_B B$$

A magnetic field of 0.33 Tesla (3300 gauss) is normally used in which transitions occur at a frequency of about 9.5 GHz; the spectrum is displayed by sweeping the field whilst keeping the frequency constant. At this high frequency normal coaxial wires have very low impedance to earth and the radiation is instead conducted to and from the sample by total internal reflection within waveguides.

The Spectrometer

The spectrometer is shown in block form in Fig. 1. Its components are identified in the separate instructions describing the spectrometer and its use.

Microwave radiation at 9.5 GHz is obtained from a solid-state source, a Gunn diode, energized from a 6V power supply. It is fed via an attenuator (which controls the intensity of the radiation) to a 3-port circulator whence it enters a waveguide arm and is delivered to the sample held within a microwave cavity. The circulator is a ferrite device which ensures the radiation entering the first port appears at the second, and then moves to the third; a negligible amount of energy flows in the reverse direction.

The cavity is designed to be resonant at the frequency of the microwave source - that is, a standing wave is set up within it. This serves to concentrate the magnetic vector of the radiation at the sample and to ensure that, as needed to induce transitions, it is perpendicular to the applied magnetic field. The cavity used here operates in the "TE₁₀₂" mode. It consists of a length of waveguide in which the end walls are two half-wavelengths apart. The accurate tuning necessary to set up the standing wave is accomplished by mechanically inserting a small dielectric rod into the cavity; this essential adjustment controls the overall signal-to-noise ratio of the experiment.

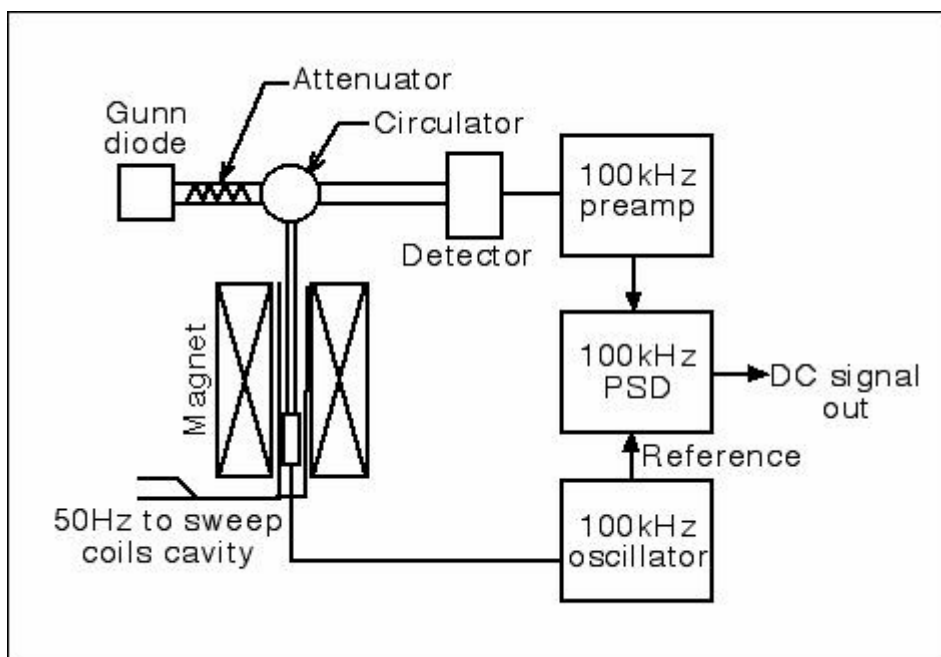


Fig. 1. The ESR spectrometer

When the cavity is properly tuned, and the magnetic field is "off-resonance" (i.e. is not set to produce transitions), it acts as an infinite impedance. All the microwave radiation entering it is trapped and none is reflected back to the circulator to appear out of its third port and be detected. Thus monitoring this output 'off-resonance',

and minimizing it, provides the means of tuning the cavity. As the magnetic field is changed to display the spectrum, the condition to induce transitions is reached and energy is absorbed by the sample, disturbing the tuned state. Some microwave energy is then reflected back up the circulator, enters the third arm and falls upon the detector crystal. This rectifies the microwave radiation incident upon it to give a direct current (DC) output proportional to the amplitude of the radiation. This is the ESR signal.

This output is small in magnitude and could easily be lost in the random noise present in any electrical system. In consequence we use a standard method to improve the signal-to-noise ratio (S/N) of the apparatus. It depends upon the fact that the normal electrical noise contains components of all frequencies; if we could limit this range we should immediately increase the S/N ratio by diminishing the noise level. This is accomplished by varying the magnetic field systematically in time ('field modulation') so that the signal itself also varies at the modulation frequency. We then detect at this frequency using a 'phase sensitive detector', PSD, which responds only to frequencies very close to the modulation frequency. This technique has a profound effect on the shape of the observed signal and must be considered in more detail.

The electrical noise of detector crystals varies with frequency and is high at low frequencies. We choose to modulate the magnetic field at 100 kHz by passing a sinusoidally-varying current through coils wound directly onto the cavity. This means that whatever the absolute value of the main magnetic field as it is swept, it varies by a small amount - the variation is chosen to be much smaller than the width of the ESR line. Under these conditions the modulation in the field produces a modulation in the output signal, also at 100 kHz, by an amount proportional to the modulation amplitude and to the slope of the resonance curve. This is shown in Fig. 2. When the external field is swept to a value where the normal signal has a high slope, positions 2 and 4 in the figure, the field modulation causes large variations in the output signal. In positions of small or zero slope, positions 1, 3 and 5, no modulated output signal is obtained. The output signal varies sinusoidally only if the region accessed during the field modulation approximates to a straight line. This is why the amplitude modulation should be as low as possible. If this condition is not satisfied, distortion of the line shape, known as 'modulation broadening' occurs.

Not only does the amplitude of the modulated signal vary as the line is swept but also its phase, since the slope of the absorption line has opposite signs on either side of the centre. This modulated signal from the detector crystal is amplified and applied to the phase sensitive detector, which yields a DC output proportional to the amplitude and to the phase of its input signal. In consequence the observed signal is the derivative of the original ESR absorption signal, and the centre of the line is where it passes through zero intensity. The PSD acts like a very sharp filter: it picks out of its input any component which varies at a frequency close to its reference frequency (here, our modulation frequency of 100 kHz), and rejects all others to give the desired improvement in S/N.

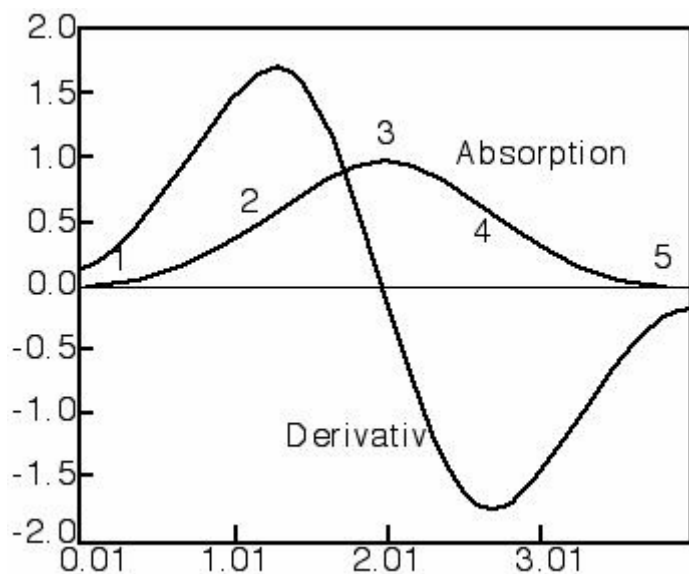


Fig. 2. The ESR absorption signal

The signal is finally displayed either on an oscilloscope, or after smoothing to lessen the noise further, on a microcomputer. In the latter case, the field is swept comparatively slowly through resonance by varying the current applied to the electromagnet. In the former, the field must be swept quickly and this is done by applying a mains 50 Hz current to separate coils wound onto the magnet. This allows the amount by which the field is swept to be controlled by adjusting the current, and is typically in the 0-150 gauss region. The field increases and then decreases as the current swings from one phase to another.

Instructions on use of the spectrometer should be available beside it.

Procedure

Hyperfine structure illustrated by coupling in a nitroxide radical

The theory given above suggests all ESR spectra should consist of a single transition centred at a field position which depends upon the g -value of the radical, at the precise frequency of the radiation. In practice this is observed only in species in which the nuclei have zero spin. In all other cases extra lines are observed which arise from the through-bond coupling between the electron and nuclear spins. The extra lines observed are termed 'hyperfine structure', and they are separated by the 'hyperfine coupling constant'. The first experiment shows that this structure obeys exactly the same rules as do 'first-order' NMR spectra - we should expect this since the electron and the proton are both spin $\frac{1}{2}$ particles.

There are many stable free radicals which contain nitroxide groups. Here we use 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), which is widely used as a 'spin label' in

biological studies. Dissolve about a dozen crystals of TEMPO in a few cm^3 of dry 1,2-dimethoxyethane, then pipette some solution into an NMR tube. You will need to fill the tube roughly half full. Cap the tube and record the ESR spectrum. Adjust the measurement conditions, and the concentration of the solution, to obtain the best possible separation between the lines in the spectrum. If the spectrum shows a single strong line, your solution is probably too concentrated; prepare a fresh solution at about one fifth of the original concentration. You will find that the lines are well-defined, but broad.

Hyperfine structure illustrated by coupling to equivalent H-nuclei: the benzoquinone radical anion

Most free radicals are reactive species, but some radical anions are comparatively stable. Next you will make a sample of the radical anion of p-benzoquinone by reduction with hydroxyl ions. The radical is stabilized by the presence of 1,2-dimethoxyethane.

In a beaker make up approximately 10 cm^3 of a 50/50 mixture of dry propan-2-ol and dry 1,2-dimethoxyethane (the solvents should be drying over molecular sieve - see the technician if they are not). Add a single pellet of potassium hydroxide and stir.

Deoxygenate the solution by passing a gentle stream of bubbles of nitrogen or argon through the solution for two minutes; a nitrogen cylinder fitted with a rubber tube and glass pipette is available near to the fume cupboard.

Add about half a microspatula full of benzoquinone; a green-black solution should develop immediately. Mix gently, then use a Pasteur pipette to introduce the solution into a clean, dry nmr tube.

Record the spectrum of the benzoquinone radical anion which should be a simple 5-line pattern.

As time passes, a secondary radical may appear (possibly an adduct of the radical with ground state benzoquinone). Shaking the tube may restore the original spectrum.

Conclusion

We see that a radical in which an electron couples to n spin $\frac{1}{2}$ H nuclei exhibits a spectrum of $(n+1)$ lines. These lines are equally spaced and have relative intensities given by the coefficients of the terms in the expansion of $(1+x)^n$. A radical in which the electron couples to a nucleus of spin I has a spectrum split into $(2I+1)$ equally-spaced lines of equal intensity. In each case the hyperfine coupling constant is measured directly from the observed splittings between the lines.

The origin of the hyperfine coupling is the 'Fermi contact interaction' and the energy of the interaction is given by $A \cdot I \cdot S$ where I is the nuclear spin vector and S is the electron spin vector. A is the hyperfine coupling constant and depends upon the electron density at the nucleus, which is proportional to the square of the electron wave function at the nucleus $|\Psi(0)|^2$. Since only electrons in 's' orbitals have any probability of being at the nucleus, it is expected that only electrons in orbitals which possess some 's' character will exhibit hyperfine coupling (but see below).

The coupling rules stem directly from a consideration of the number of ways in which nuclear spins can be arranged. I can take $(2I+1)$ values of m_I , the observable component of I , in the presence of a field and there are consequently $(2I+1)$ different values of the interaction energy. The total energy of the electron consists of a combination of these values with the energy it possesses from being in an external field. With selection rules $\Delta m_s = \pm 1$ and $\Delta m_I = 0$, this implies that a radical in which an electron couples to a single proton will have a 2-line spectrum. Similarly, a spin 1 ^{14}N nucleus will lead to a 3-line spectrum.

When equivalent nuclei are present, the value of I used must be the vector combination of the individual spins: for 2 equivalent spin $\frac{1}{2}$ nuclei these are $\{+\frac{1}{2} +\frac{1}{2}\}$, $\{+\frac{1}{2} -\frac{1}{2}\}$, $\{-\frac{1}{2} +\frac{1}{2}\}$ and $\{-\frac{1}{2} -\frac{1}{2}\}$, giving resultant values of +1, 0, -1 with statistical weights of 1, 2 and 1 respectively. The ESR spectrum is consequently a 1:2:1 triplet. If coupling occurs to two non-equivalent spin $\frac{1}{2}$ nuclei each splits the ESR line independently in turn: the 'first' yields a doublet and the 'second' then splits each component of the doublet into a further doublet of different splitting (the designation of nuclei as 'first' or 'second' is entirely arbitrary, and does not affect interpretation of the spectrum in any way). The spectrum consists of a quartet inside which each coupling constant can be measured twice. Note that if the nuclei are made equivalent the splittings due to each are equal and the two central lines of the quartet become degenerate - the 1:2:1 triplet is generated once more.

Indirect coupling and the McConnell Equation

In aromatic radicals, the odd electron occupies a molecular orbital which is delocalised over the atomic framework of the radical. Being in a π orbital, it has zero probability of being in the plane of the ring where the H atoms lie - the π orbital has a node there. However, despite our conclusion above on 's' character, hyperfine interactions with the H-atoms are observed. We conclude that a mechanism exists by which the 1s hydrogen orbitals acquire some unpaired spin density.

This occurs via a 'spin polarization' mechanism (Fig 3) and originates in the exchange interaction between the σ electrons in the C-H bond and the π electrons in the ring. Consider a single C-H fragment. We can draw the electronic structure in two ways, which differ in the electron spin orientations in the sp^2 C and s H orbitals.

In terms of the normal 'pairing' approximation each arrangement would be equally likely. However the exchange interaction causes the arrangement in which the electron spins in the two carbon atoms are parallel to be slightly preferred (cf. Hund's rules which require electrons in degenerate orbitals to have parallel spins). As a result the electrons in the C-H bond are polarized slightly so that one electron spin is favoured over the other, leading to a corresponding predominance of one spin state of the electron in the hydrogen s orbital over the other. This provides the unpaired spin density at the nucleus required for coupling.

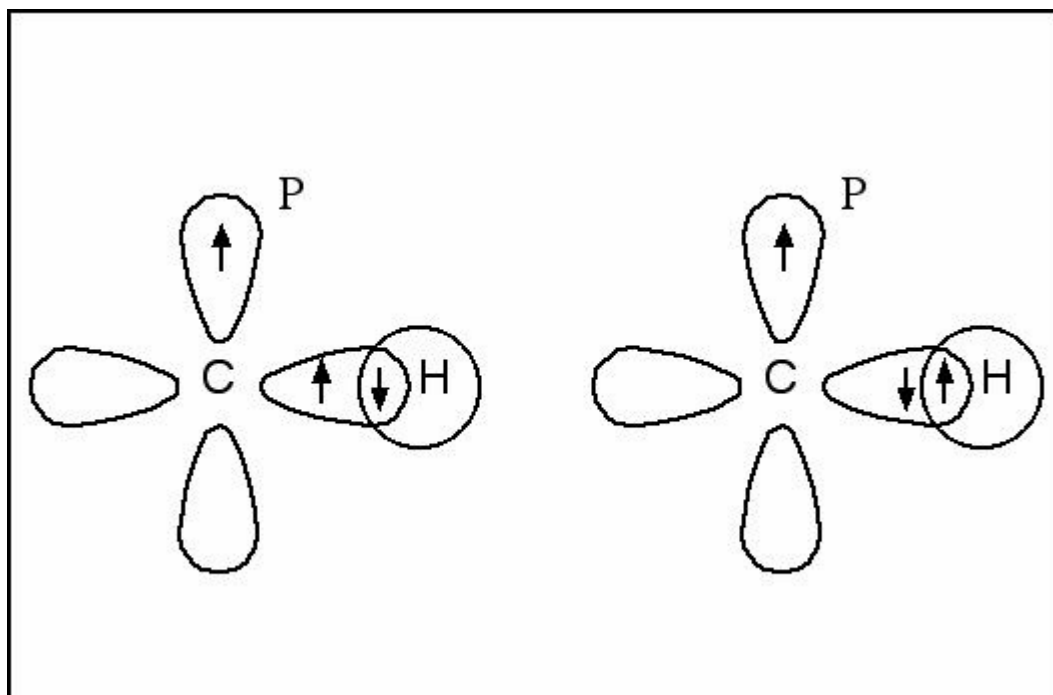


Fig. 3. Spin polarisation

In aromatic radicals delocalisation causes the average unpaired spin population of a particular carbon $2p_z$ orbital to be <1 , and the amount of spin polarization it causes in the C-H bond depends upon its precise value. This is termed the ' π -electron spin density, ρ '. The McConnell equation states that the hyperfine coupling constant A is proportional to ρ :

$$A = Q \cdot \rho$$

where Q is a constant for the type of atom with the unpaired spin density. This important relationship allows a direct link between experiment and theory, for ρ can often be calculated quite simply by Huckel MO methods. The constant Q can be determined experimentally and for carbon atoms this is performed conveniently by observing the ESR spectrum of the benzene radical anion, $C_6H_6^-$. This spectrum has

seven lines, equally spaced and with intensity ratios which disclose that the electron couples to six equivalent protons. This confirms that it occupies a molecular orbital delocalised over the ring - a nice demonstration of basic orbital theory. Symmetry requires all the carbon atoms to be equivalent so that the observed splitting of 3.75 gauss (0.375 mT) represents the value of A when $\rho = 1/6$.

Evaluate Q_c ; it will be needed to obtain ρ_c from the observed splittings in the anthracene cation.

The anthracene cation

The spectrum of anthracene is more difficult to obtain than those of TEMPO and benzoquinone. In order to record a good spectrum, it is important you follow these instructions carefully.

Check the settings on the ESR control unit of the phase, scan range and centre field. These settings will provide a useful guide to where to start looking for the anthracene resonances. Typical - though not necessarily optimum - values are:

Centre field 530
Range 455
Speed 390
100 Hz Mod middle setting
Attenuator 0
Phase 160
Scan time 60 seconds.

Prepare a solution of anthracene of concentration approximately 0.02M as follows. First put on safety glasses! Now add about a microspatula-full of anthracene to a clean 100ml Erlenmeyer flask - there should be perhaps 50-100 tiny crystals in total. Carefully add about 25ml concentrated sulphuric acid, and mix by swirling for thirty seconds. Be careful to avoid spills. Try to maintain a smooth liquid surface, since the more you break up the liquid into droplets the more you will introduce oxygen and water vapour into the solution, both of which will reduce the concentration of free radical.

The solution should be green and then quite rapidly turn very dark green or black. If the colour remains light the solution is much too dilute - you need a solution in which there is extensive charring (production of carbon, giving the black colour) to have a chance of seeing the spectrum. Transfer a portion of the sample to a CLEAN AND DRY nmr tube. Check that no acid whatsoever remains on the outside of the tube, then place in the sample area between the magnet poles.

The sample is difficult to tune, (because of the high dielectric constant of sulphuric acid) so rapidly carry the normal tuning procedure as far as possible, then attempt to

find the spectrum. If the spectrum - once found - shows excessive noise, you may tune the cavity while a spectrum is being gathered.

The radicals should be detectable for no more than 5 minutes, so you are unlikely to obtain a good spectrum from your first sample. Once you have found where the spectrum lies, immediately save a spectrum, then concentrate on zeroing in on the lines, adjusting the scan range, centre field and scan time so that the spectrum is as well defined as possible. The quality of the spectrum is particularly dependent upon the speed at which the field is scanned and the setting of the 100 Hz field. A well-resolved spectrum on this instrument shows 21 lines. (This is far fewer than the theoretical number - construction of the stick diagram later will help you understand why this is.)

When you have determined suitable operating parameters, prepare a fresh sample if necessary and record a final spectrum.

In Appendix 1 we consider how one can calculate quantities such as the electron density distribution in anthracene using MO theory.

Calculation

Use the McConnell equation and the values for ρ_c to calculate the coupling constants A_H . By drawing a diagram in which the effects of the different couplings are shown as causing successive splittings of a single original line, deduce the underlying coupling pattern for anthracene, and compare with your experimental spectrum.

Background reading

Magnetic resonance, K.A.McLauchlan, Clarendon Press [Hooke C16/1].

Introduction to magnetic resonance. A.Carrington and A.D.McLachlan, Chapman & Hall [RSL 96.E04227].

Electron Spin Resonance of aromatic radicals and radical ions. Quarterly reviews of the Chemical Society, 1968, 17, 67. [RSL Chem Per 3a].

Electron paramagnetic resonance: elementary theory and practical applications. J.A.Weil, J.R.Bolton and J.E.Wertz, Wiley [RSL Phys Ww18].

Appendix A. Some Simple Molecular Orbital Theory

In order to generate a set of MOs for anthracene, we could apply the variation principle to a trial wavefunction of the form

$$\Phi = c_1\chi_1 + c_2\chi_2 + c_3\chi_3 + \dots + c_{14}\chi_{14}$$

and use Huckel MO theory to set up a 14x14 determinant, but this would then require solution of a 14th degree polynomial, which would clearly be a challenging task.

Instead, we shall set up symmetry adapted linear combinations of atomic orbitals (SALCs) taking account of the D_{2h} symmetry of anthracene. It is convenient to use the lower symmetry C_{2v} character table to create four different types of molecular orbital, corresponding to the four irreducible representations in the table; these are:

- A_1 : totally symmetric
- A_2 : symmetric with respect to rotation about the principal axis, antisymmetric with respect to a C_2 axis perpendicular to this.
- B_1 : antisymmetric with respect to rotation but symmetric with respect to the perpendicular C_2 axis.
- B_2 : antisymmetric with respect to both rotation and the perpendicular C_2 axis.

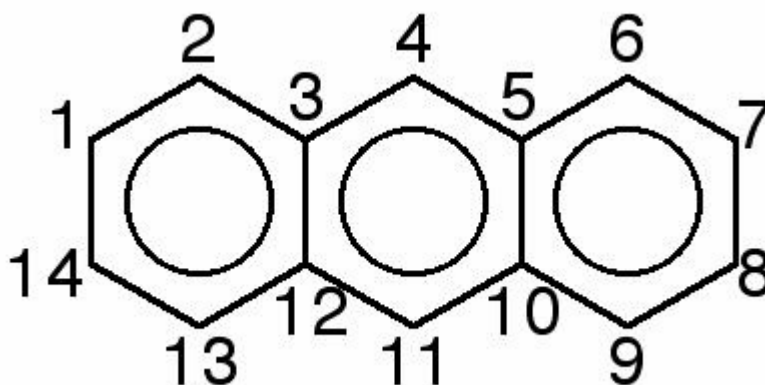


Fig. 4. Atom numbering in anthracene.

We apply each of the operations in the C_{2v} character table to the molecule, using the atom numbering scheme shown in the figure.

Carbon	Position after symmetry operation			
	E	C_2	σ_{xz}	σ_{yz}
1	1	8	7	14
2	2	9	6	13
3	3	10	5	12
4	4	11	4	11

We note that carbons (1, 8, 7, and 14) are equivalent but distinct from the other carbons, as are the groups (2, 9, 6, 13), (3, 10, 5, 12) and (4, 11).

The molecular orbitals are now built up by multiplying the appropriate atomic orbitals by the corresponding characters for each irreducible representation:

$$\frac{c_1}{2}(\chi_1 + \chi_8 + \chi_7 + \chi_{14}) + \frac{c_2}{2}(\chi_2 + \chi_9 + \chi_6 + \chi_{13}) + \frac{c_3}{2}(\chi_3 + \chi_{10} + \chi_5 + \chi_{12}) + \frac{c_4}{\sqrt{2}}(\chi_4 + \chi_{11})$$

There are four different coefficients in this MO, and so it must be quadruply degenerate, i.e. equal to Φ_1, Φ_2, Φ_3 and Φ_4 , and of symmetry A_1 . We can similarly derive expressions for the orbitals of symmetries A_2, B_1 and B_2 to give two 3x3 sub-determinants (from the A_2 and B_2 MOs) and two 4x4 sub-determinants (from the A_1 and B_1 MOs) of the following form:

$$\begin{array}{ccc} H_{11-\varepsilon} & H_{12} & H_{13} \\ H_{12} & H_{22-\varepsilon} & H_{23} \\ H_{13} & H_{23} & H_{33-\varepsilon} \end{array} \quad \text{and} \quad \begin{array}{cccc} H_{11-\varepsilon} & H_{12} & H_{13} & H_{14} \\ H_{21} & H_{22-\varepsilon} & H_{23} & H_{24} \\ H_{31} & H_{32} & H_{33-\varepsilon} & H_{34} \\ H_{41} & H_{42} & H_{43} & H_{44-\varepsilon} \end{array}$$

where

$$H_{ij} = \int \frac{1}{2}(\chi_i + \chi_8 + \chi_7 + \chi_{14})\hat{H}(\chi_j + \chi_8 + \chi_7 + \chi_{14})\delta\tau$$

$H_{ij}=0$ if i and j are not next to each other in the molecule, otherwise it is given by a similar expression to that for H_{11}

Thus the determinant corresponding to $\Phi_{1,2,3,4}$ (A_1 symmetry) is

$$\begin{array}{cccc} a+\beta-\varepsilon & \beta & 0 & 0 \\ \beta & a-\varepsilon & \beta & 0 \\ 0 & \beta & a+\beta-\varepsilon & \sqrt{2}\beta \\ 0 & 0 & \sqrt{2}\beta & a-\varepsilon \end{array}$$

To solve this, we need to expand it. After dividing by β , we can make the substitution $x = (a-\varepsilon)/\beta$ to give

$$\begin{array}{cccc} x+1 & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x+1 & \sqrt{2} \\ 0 & 0 & \sqrt{2} & x \end{array} = 0$$

from which we can calculate that the four energy levels have energies $\alpha - 1.414\beta, \alpha - 0.414\beta, \alpha + 1.414\beta, \alpha + 2.414\beta$

Continuing in this fashion we can derive the complete set of energy levels; these are given in order of decreasing energy (remembering that β is negative)

Φ_{14}	$\alpha - 2.414\beta$
Φ_{13}	$\alpha - 2\beta$
Φ_{12}, Φ_{11}	$\alpha - 1.414\beta$
Φ_{10}, Φ_9	$\alpha - \beta$
Φ_8	$\alpha - 0.414\beta$
Φ_7	$\alpha + 0.414\beta$
Φ_6, Φ_5	$\alpha + \beta$
Φ_4, Φ_3	$\alpha + 1.414\beta$
Φ_2	$\alpha + 2\beta$
Φ_1	$\alpha + 2.414\beta$

Normal anthracene has 14 π electrons, sufficient to fill the bonding orbitals completely. When a single electron is removed to form the cation, it is taken from the highest occupied molecular orbital (HOMO); this is Φ_7 , which can be shown to have the analytical form

$$\Phi_7 = 0.220(\chi_1 + \chi_7 + \chi_8 + \chi_{14}) - 0.311(\chi_2 + \chi_6 + \chi_9 + \chi_{13}) - 0.091(\chi_3 + \chi_5 + \chi_{10} + \chi_{12}) + 0.440(\chi_4 + \chi_{11})$$

Electron Densities

We recall that for real wavefunctions the probability of finding an electron in a volume of space $\delta\tau$ is given by $\Phi^2\delta\tau$. For our molecular wavefunction we obtain

$$\begin{aligned} \int \Phi^2 dt &= \int (\sum_n c_n \chi_n)^2 dt = \int \sum_n c_n^2 \chi_n^2 dt + \int \sum_n \sum_m c_n c_m \chi_n \chi_m dt \\ &= \sum_n c_n^2 \int \chi_n^2 dt \end{aligned}$$

since χ_m and χ_n are orthogonal. The integral of $\chi_n^2 dt$ we have defined as the probability of finding an electron in the region of space associated with the atomic orbital χ_n and this integral is unity since χ_n is normalised. However, each integral is multiplied by c_n^2 . Hence c_n^2 represents the probability that an electron in a molecular orbital is associated with an atomic orbital χ_n , i.e. c_n^2 is the electron density at atom n in the molecular orbital.

The total electron density at an atom is the sum of the electron densities contributed by each electron in each molecular orbital.