Solutions to End-of-Chapter Exercises
Chapter 4

Fundamental constants & properties of nuclei

$c = 2.997 \times 10^{8}$ m s^{-1}
$e = 1.602 \times 10^{-19}$ C
$k = 1.381 \times 10^{-23}$ J K^{-1}
$h = 6.626 \times 10^{-34}$ J s

Mass

Electron = $9.109\,390 \times 10^{-31}$ kg
Proton = $1.672\,622 \times 10^{-27}$ kg

$\mu_0 = 4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1} (= T^{2} J^{-1} m^{3})
$\mu_B = 9.274 \times 10^{-24}$ J T^{-1}
$\mu_N = 5.050\,784 \times 10^{-27}$ J T^{-1}
$g_e = 2.0023\,193$ (electron g factor)
$g_p = 5.585\,694\,7$ (proton g factor)
$\gamma_e = 1.761 \times 10^{11}$ s^{-1} T^{-1}

Properties for other common nuclei

	g_N	ν_N / MHz	γ / 10^{7} s^{-1} T^{-1}
^{1}H	5.5857	14.9021	26.752
^{2}H	0.8574	2.2876	4.107
^{13}C	1.4048	3.7479	6.728
^{14}N	0.4038	1.0772	1.934
^{31}P	2.2632	6.0380	10.839

ν_L (in units of MHz) for $B = 0.35$ T

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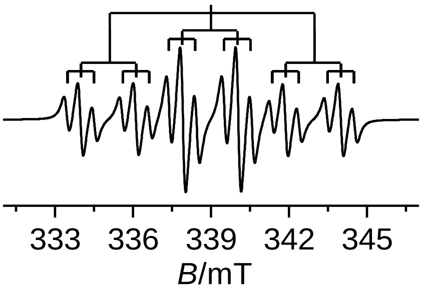
Exercise 4.1) Draw a splitting diagram for the cyclohexyl radical (Fig. 4.20) and assign the hyperfine pattern to the α- and β-protons

ANSWER

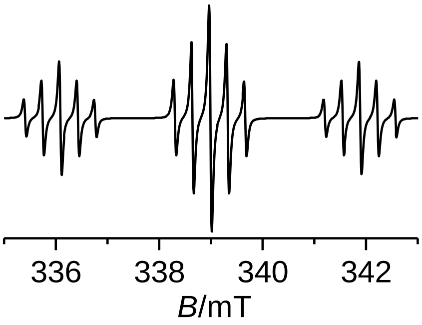
The cyclohexyl radical is expected to show splitting from one H_α, two equatorial H_β and two axial H_β protons, i.e., a doublet of triplet of triplets. Following the routine described in section 4.4, the corresponding splitting diagram is drawn. The doublet corresponds to the H_α proton, and the smaller and larger triplets to the equatorial and axial H_β protons, respectively.



Exercise 4.2) Sketch an EPR spectrum of the deuterated propyl radical $CH_3CH_2CD_2^\bullet$ paying particular attention to the number of hyperfine lines, their relative intensity and the separation between the lines. The EPR spectrum of propyl radical is in Fig. 4.8.

ANSWER

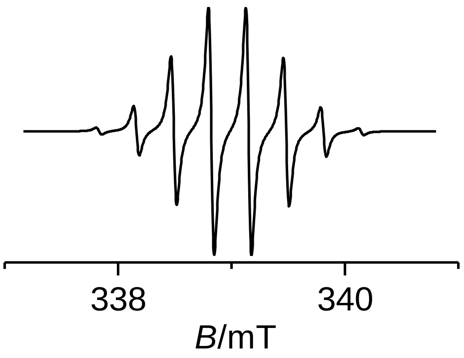
While the propyl radical shows a 1:2:1 triplet due to the splitting from the α-CH_2 group, the deuterated analogue shows a 1:2:3:2:1 quintet due to the splitting from the α-CD_2 group. As the hyperfine constants are proportional to the nuclear g_N factors, the hyperfine value for the α-CD_2 protons will be ca. 6.51 smaller than that for the α-CH_2 protons. The hyperfine value for the α-CH_2 protons can be measured from the spectrum in Fig. 4.8 as ca. 2.2 mT. Hence, the corresponding value for the α-CD_2 protons will be 2.2/6.51 = 0.34 mT. The EPR spectrum for the radical is shown below.



Exercise 4.3) Predict the number of lines and their relative intensity in the EPR spectrum of the cycloheptatrienyl radical ($C_7H_7^\bullet$). Estimate the hyperfine value for this radical and sketch the appearance of its EPR spectrum.

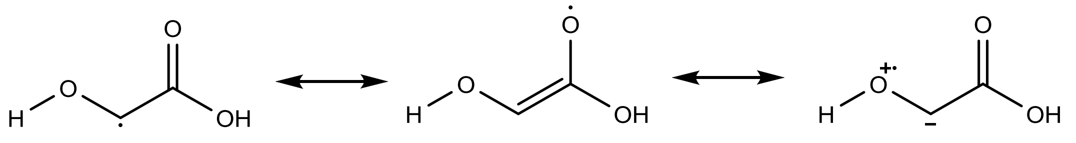
ANSWER

In cycloheptatrienyl radical, the unpaired electron density is delocalised over the whole molecule. All hydrogen atoms in the radical are thus equivalent, and the spin density at each carbon atom is therefore 1/7. The EPR spectrum of a radical with 7 equivalent hydrogen atoms will show an 8-line pattern, with the ratio of line intensities 1:7:21:35:35:21:7:1. Using McConnell equation (section 4.5), the hyperfine value for the radical can be calculated as $a = Q\rho = 2.3/7 = 0.33$ mT. The spectrum is shown below.



Exercise 4.4) The EPR spectrum of the radical of glycolic acid ($HOOC\text{-}CH^{\bullet}\text{-}OH$) shows four lines with two hyperfine constants of 17 and 2.5 G. The unpaired electron is mostly localized on the carbon atom with some unpaired electron density found on the oxygen. Deduce which hydrogen atom has the larger hyperfine constant (17 G) and estimate the spin density on the carbon and oxygen atoms. Suggest the geometry of the glycolic acid radical consistent with the given hyperfine values.

ANSWER
The unpaired electron in glycolic acid radical 1 is delocalised as shown below.

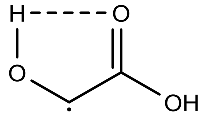


1 2 3

As most of the spin density in the glycolic acid radical is localised on the carbon atom (i.e., $\rho > 50\%$), the hyperfine value for the CH hydrogen should be greater than 1.15 mT (using McConnell equation in section 4.5). Hence the larger hyperfine value (17 G = 1.7 mT) must correspond to the CH hydrogen. The spin density on the CH carbon atom can then be estimated using McConnell equation as $\rho = a/Q = 1.7\ \text{mT}/2.3\ \text{mT} = 0.74$. The smaller hyperfine constant (2.5 G = 0.25 mT) is therefore due to the OH hydrogen.

If we disregard resonance structure 3, the OH hydrogen is in a β-position with respect to the radical centre, and the hyperfine value is related to the dihedral angle between the OH bond and the p-orbital with the unpaired electron (eqn 4.2). This angle can be calculated as $\theta = \cos^{-1}\left(\sqrt{\frac{a}{B\rho}}\right) = \cos^{-1}\left(\sqrt{\frac{0.25}{5.4 \times 0.74}}\right) = 75.5°$. This is fairly close to 90° corresponding to the OH bond almost perpendicular to the p-orbital with the unpaired electron.

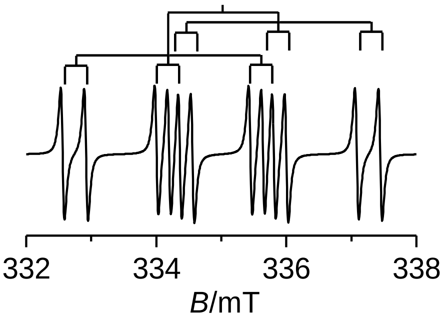
In resonance structure 3, OH hydrogen is in an α-position with respect to the radical centre. Hence, the contribution to the hyperfine value defined by eqn 4.2 is even smaller, and the diherdral angle θ is even closer to 90°. The whole radical is thus nearly planar, which can be tentatively explained by an intramolecular hydrogen bond as shown below.



Exercise 4.5) Fig. 4.32 shows an EPR spectrum recorded when a solution of diphenylphosphine (PPh_2H) and PBN spin trap was treated with lead dioxide (PbO_2). Assign the EPR spectrum and deduce the structure of the intermediate radical formed.

ANSWER

The splitting diagram is shown below.



The spectrum is a 1:1 doublet of 1:1:1 triplets of 1:1 doublets. PBN adducts usually show a triplet of doublets (cf. Fig. 4.29), due to coupling to nitrogen (*I* = 1) and hydrogen atoms (circled in Fig. 4.29a). The large additional doublet splitting is thus due to coupling with the phosphorous atom (*I* = ½) in the vicinity of the radical centre, and the structure of the radical can be assigned to PPh_2-PBN adduct.