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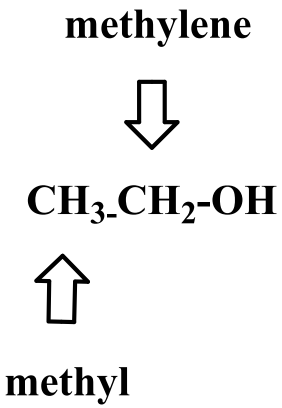
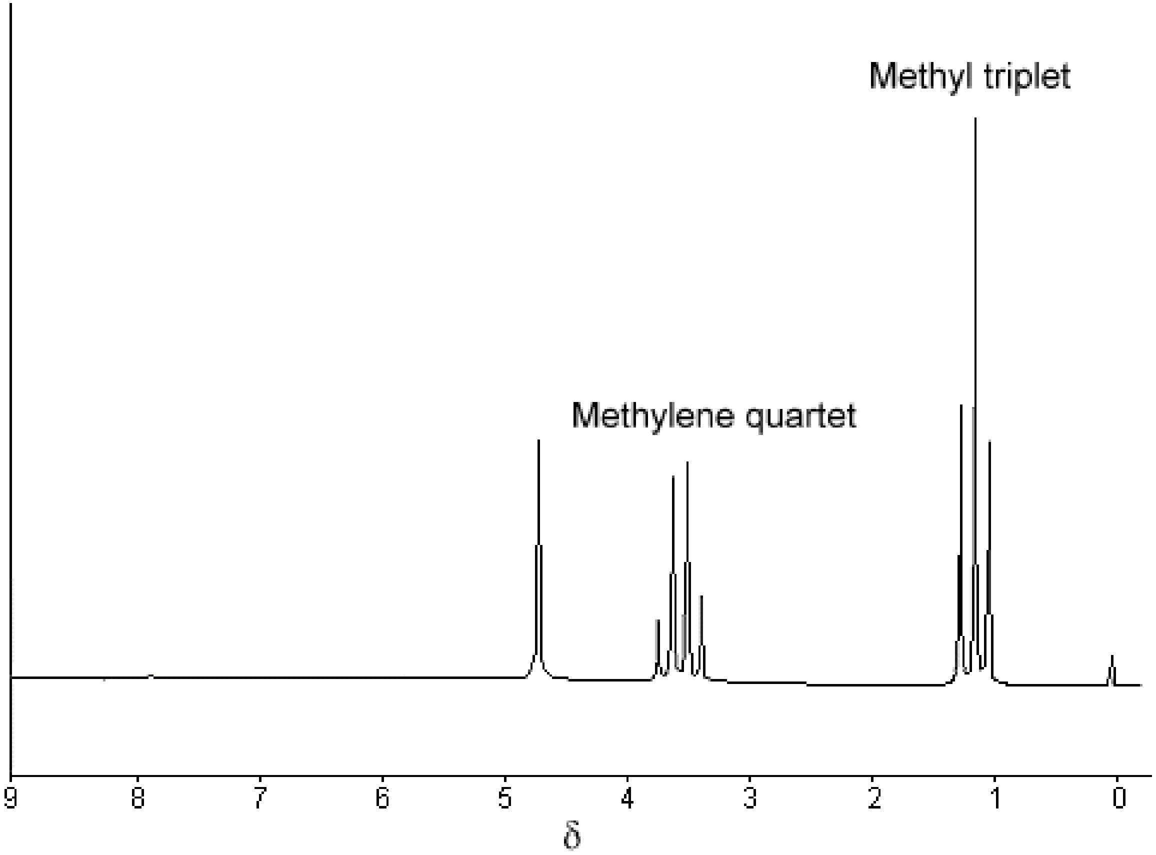
Nuclear Magnetic Resonance (NMR) Spectroscopy



methylene

$CH_3\text{-}CH_2\text{-}OH$

methyl



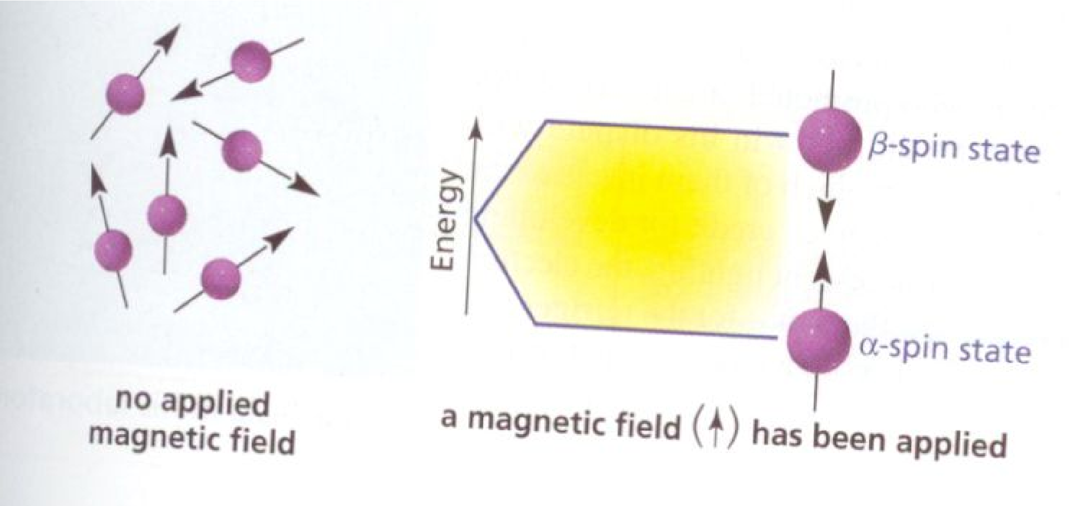
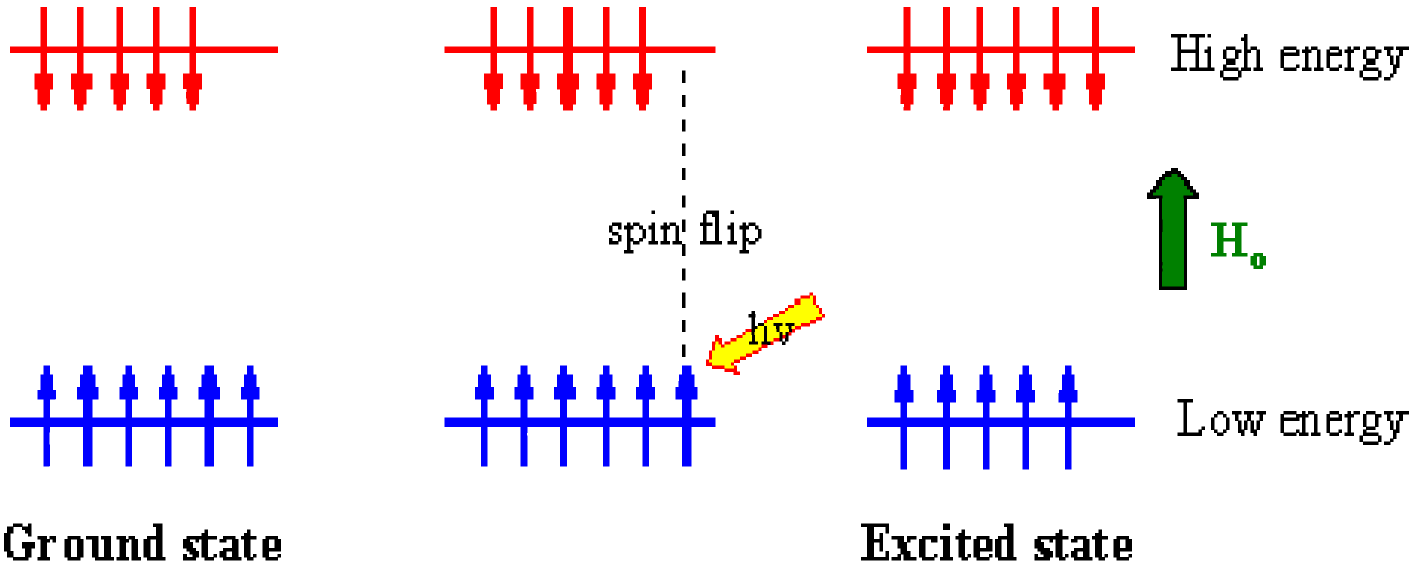
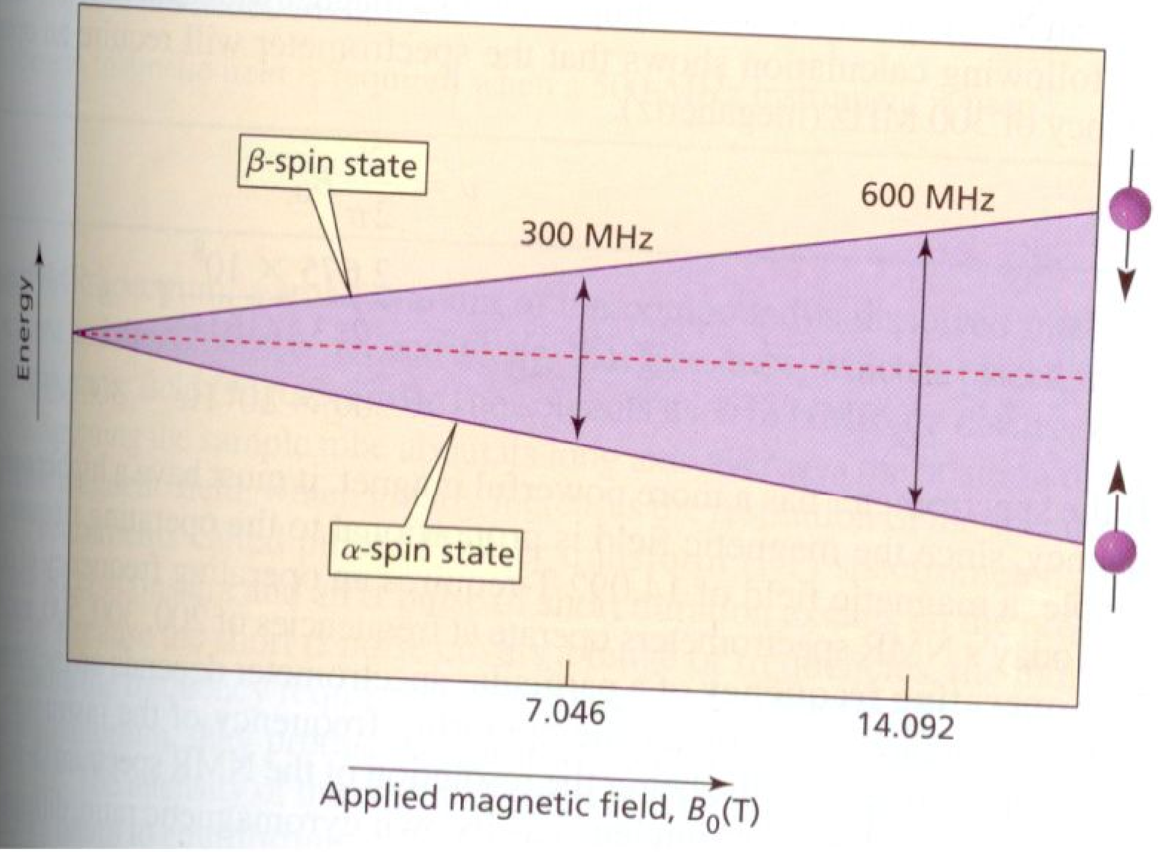
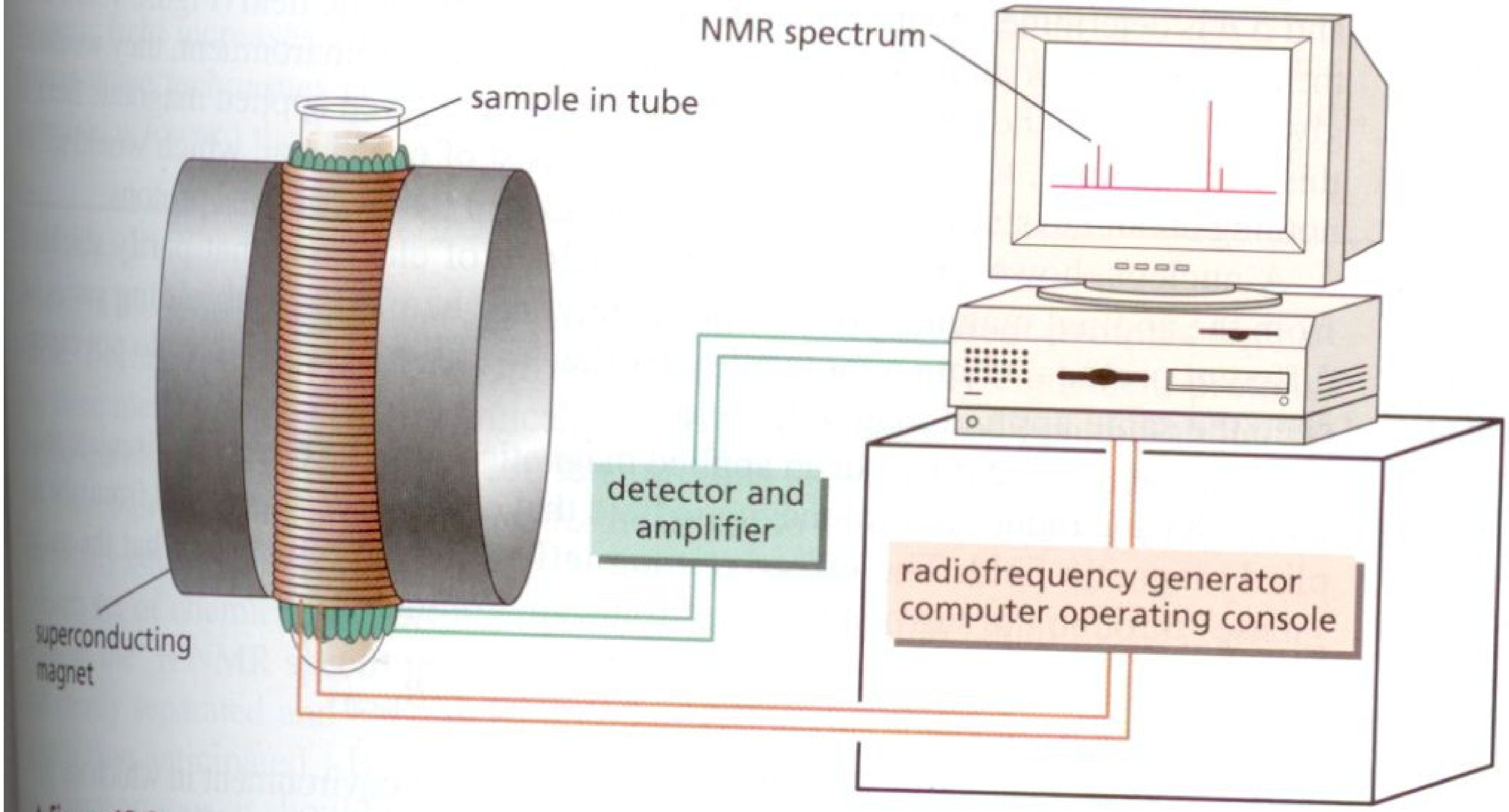


Figure 13.1 In the absence of an applied magnetic field, the spins of the nuclei are randomly oriented. In the presence of an applied magnetic field, the spins of the nuclei line up with or against the field.



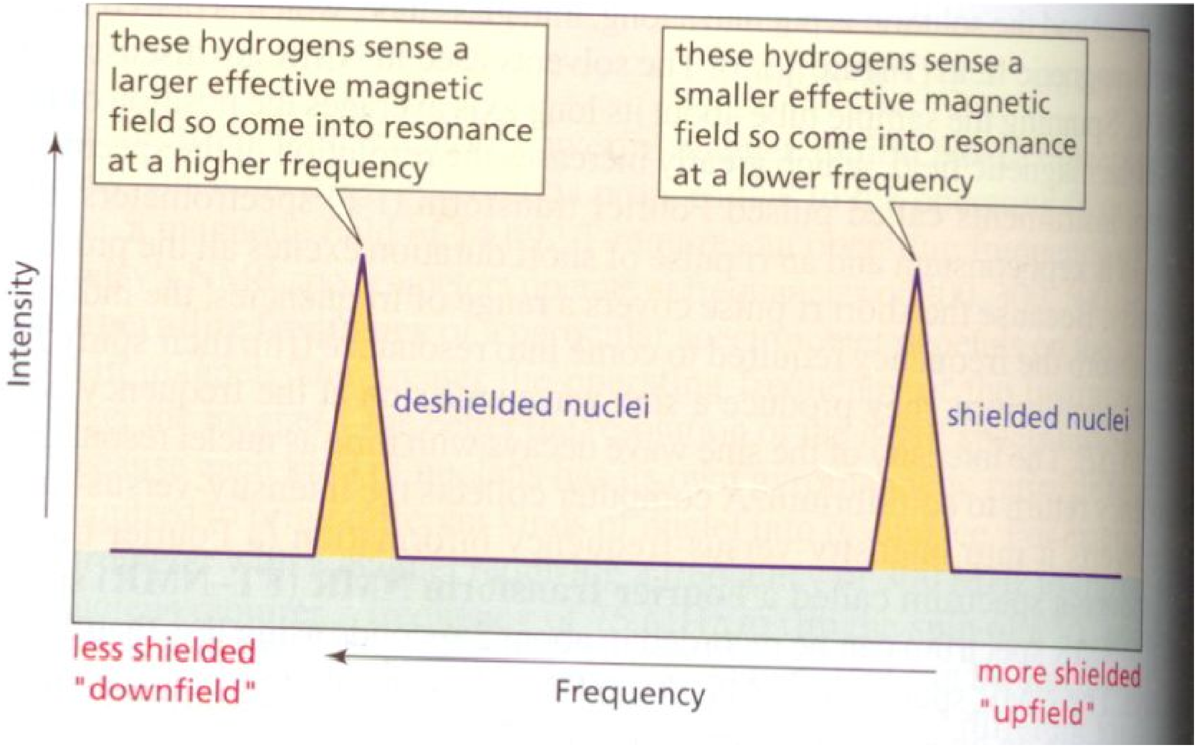


◀ **Figure 13.2**
The greater the strength of the applied magnetic field, the greater the difference in energy between the α- and β-spin states.



▲ Figure 13.3
Schematic of an NMR spectrometer.

Figure 13.4 ▶
Shielded nuclei come into resonance at lower frequencies than deshielded nuclei.


these hydrogens sense a larger effective magnetic field so come into resonance at a higher frequency

these hydrogens sense a smaller effective magnetic field so come into resonance at a lower frequency

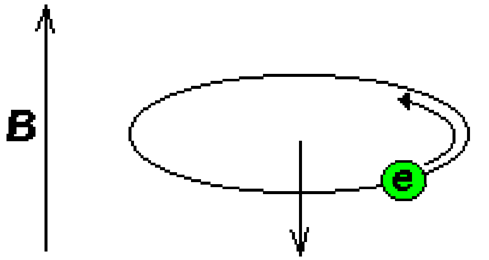
right-hand side of the spectrum:

protons in electron-dense environments
low frequency
upfield
shielded

Chemical shift

The magnetic field at the nucleus is **not** equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic field and the field at the nucleus is termed the *nuclear shielding*.

Consider the s-electrons in a molecule. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased for the nucleus to absorb at its transition frequency. This *upfield shift* is also termed *diamagnetic shift*.



Magnetic field produced
by circulating electron

Electrons in p-orbitals have **no** spherical symmetry. They produce comparatively large magnetic fields at the nucleus, which give a *low field shift*. This "deshielding" is termed *paramagnetic shift*.

Diamagnetic Anisotropy

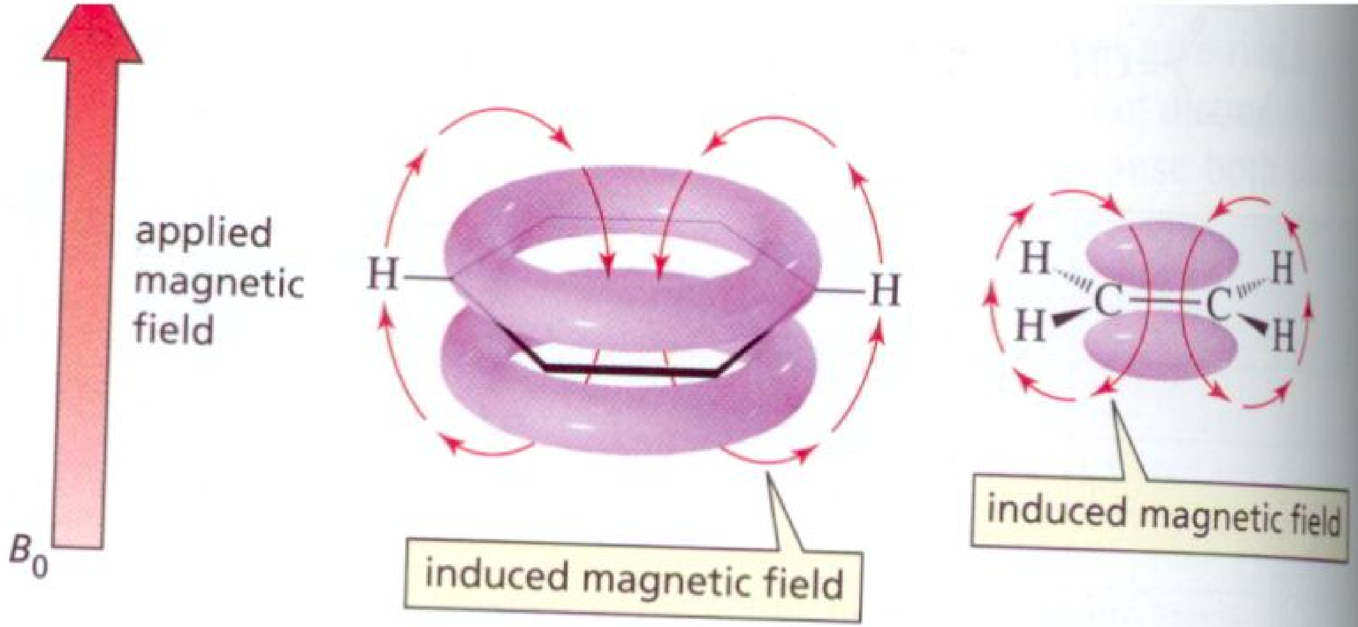
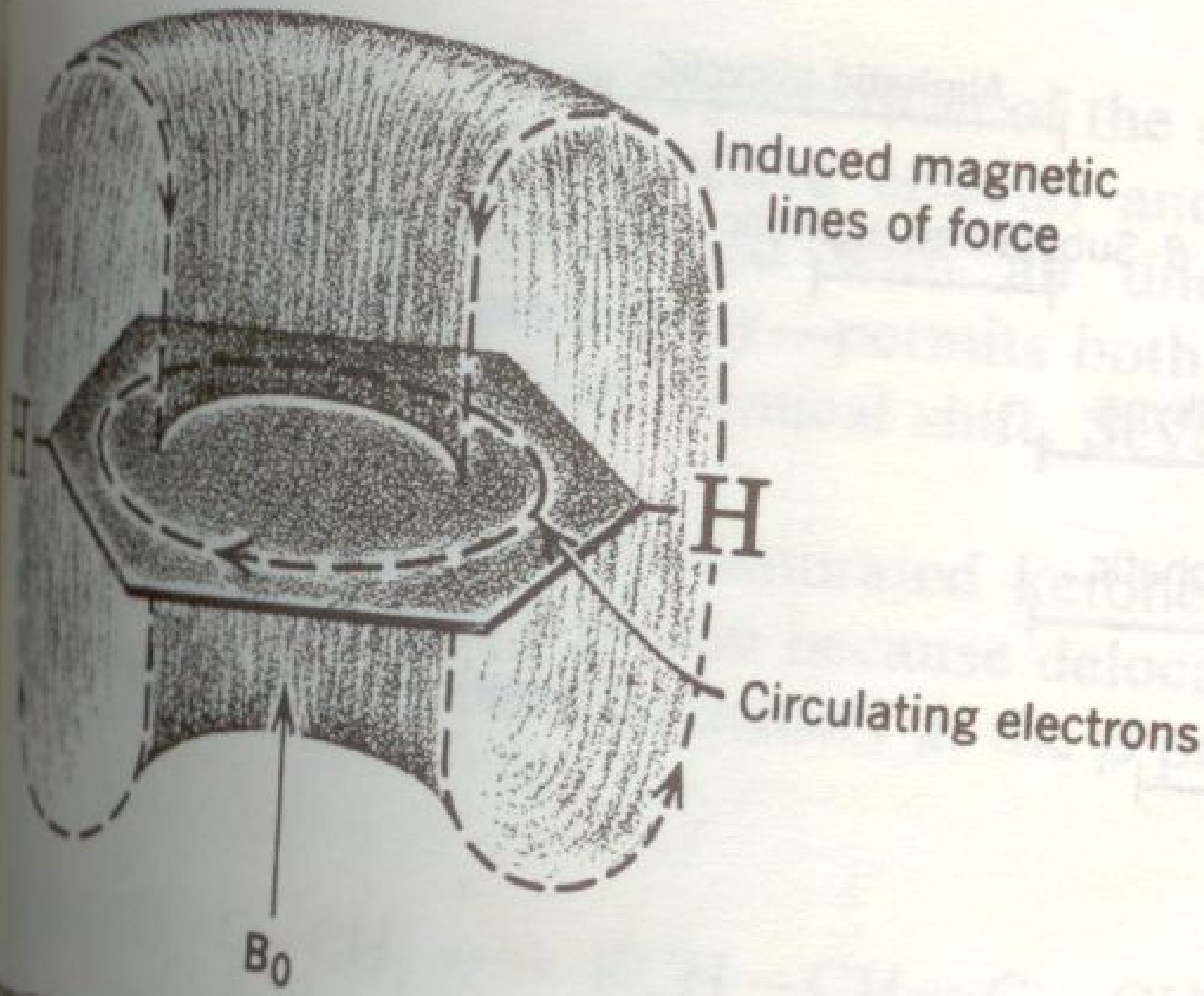
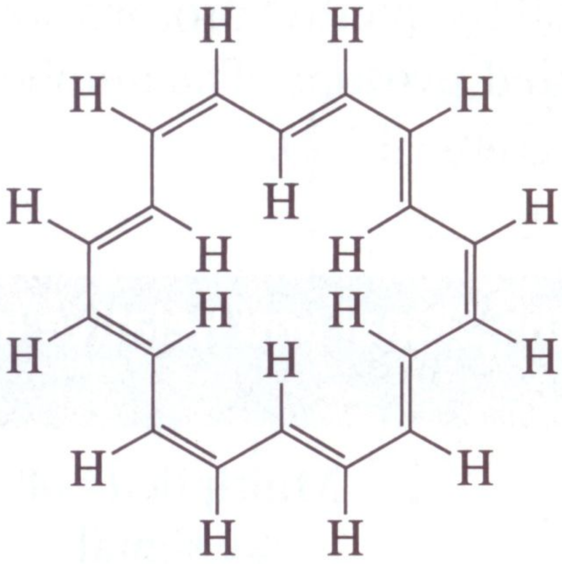


Figure 13.8
The magnetic field induced by the π electrons of a benzene ring and the magnetic fie
induced by the π electrons of an alkene, in the area of space where the aromatic or
vinylic protons are located, are in the same direction as the applied magnetic field.



URE 4.17. Ring current effects in benzene.

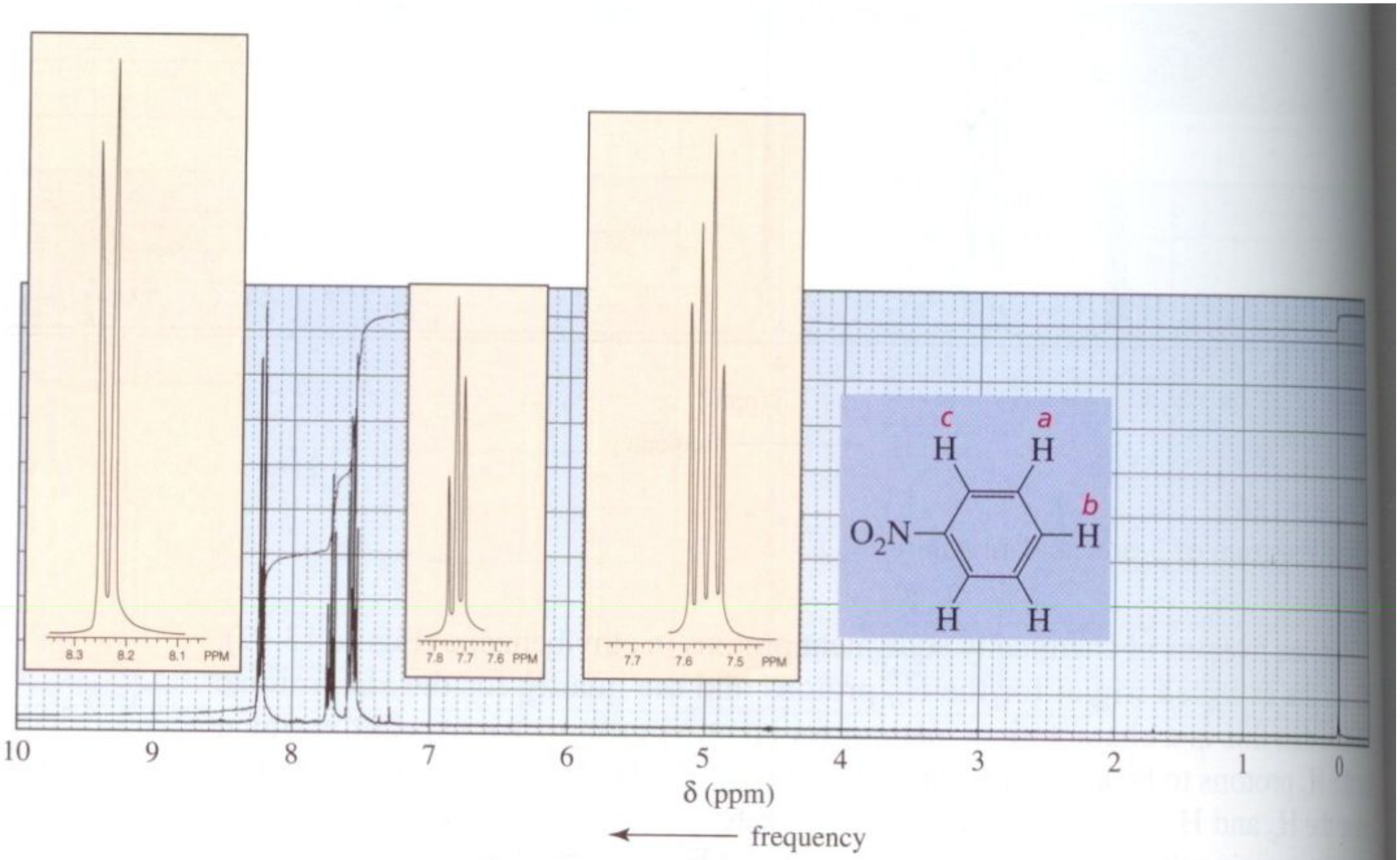
[18] annulene (4n + 2 electrons with n = 4)



12 outer protons δ 9.3

6 inner protons δ -3.0 ppm

X-ray structure of [18] annulene shows that it is very nearly planar – no bond alternation (double / single) supports delocalisation



▲ Figure 13.18
^1H NMR spectrum of nitrobenzene.