Hydrogen bonding results in downfield shifts of proton resonances from their positions in the unbonded state. The low-field values of phenols or carboxylic acids are attributed to hydrogen bonding. Increase of temperature or dilution with carbon tetrachloride can often break up hydrogen bonds and cause an upfield shift (in the hydroxyl resonance of ethanol, for instance).

1.3.1.8 Organometallic Compounds

Protons directly bonded to metals, as in transition metal hydrides, are strongly shielded and their resonances may appear as far upfield as −30 ppm. The shielding is due to the asymmetrical distribution of charge in the valence orbitals, which results in a strong diamagnetic shift of the proton resonances (Figure 1.24).

1.3.1.9 Contact Shifts

Organometallic compounds in which the metal is paramagnetic exhibit chemical shifts covering a range of 200 ppm for protons, and an even greater range for other nuclei. These shifts can occur by a *contact* or a *pseudocontact* interaction. In the contact interaction, some unpaired electron density is transferred from the metal to the organic ligand, which can cause shielding or deshielding effects, depending on electron spin correlation effects and electron distribution. Thus in the nickel complex depicted in Figure 1.25 the α-, β-, and

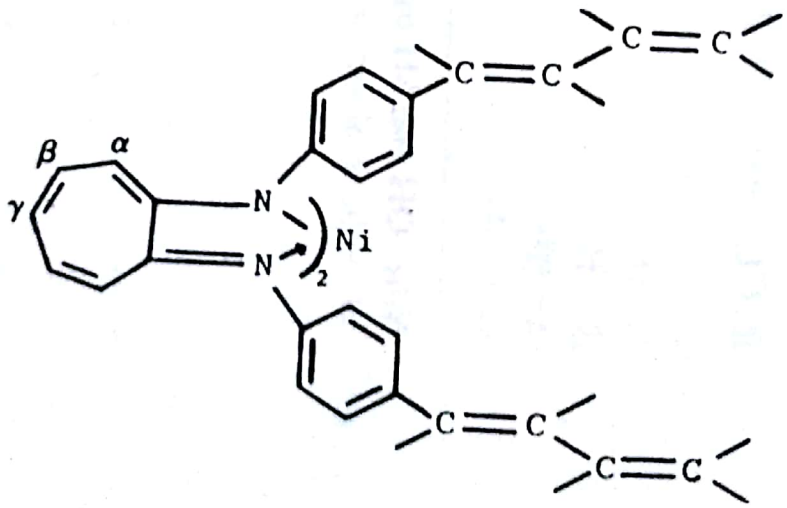
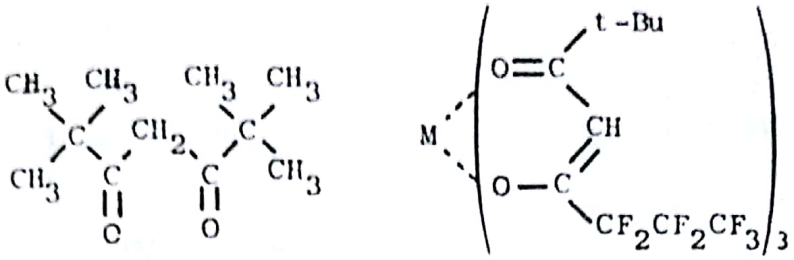


Figure 1.25. Complexation with the paramagnetic nickel ion results in the α, β, and γ protons indicated having chemical shifts of −42, +47, and −64 ppm, respectively.



(a) (b)

Figure 1.26. Complexation of diketones such as (a) with europium or praseodymium afford lanthanide shift reagents; (b) shows a heptafluorodimethyloctanedionato complex, M representing the complexing metal ion.

γ-protons resonate at $\delta -42$, $\delta +47$, and $\delta -64$, respectively. These large shifts are thought to arise because of donation of unpaired electrons from the paramagnetic ion (nickel in the complex cited) through the bonding atom (nitrogen) to the rest of the molecule. In order for such a shift to occur, a finite electron density at the nucleus has to be postulated. This type of electron–nucleus "contact" interaction was first described by Fermi.*

1.3.1.10 Lanthanide Shift Reagents

Another related interaction, known as the *pseudocontact interaction*, is observed when alcohols or amines, for example, are allowed to interact with certain rare earth metal complexes possessing unpaired electrons in their valence orbitals. The direction of the shift caused by interaction with the rare earth metal complex depends on the anisotropy of the magnetic susceptibility, X, and on the angle between the main axis of susceptibility and the vector R to the nucleus. If the proton is at a distance R from the center of the anisotropic group, and if the direction in which the proton lies makes an angle θ with the direction of the magnetic susceptibility, then the change in shielding, $\Delta\sigma$, is given by equation (1.7):

$$\Delta\sigma = \frac{1}{3R^3}(1 - 3\cos^2\theta)(X^{\parallel} - X^{\perp}) \tag{1.7}$$

(the signs $\parallel$ and $\perp$ indicate the direction of the proton–metal axis with respect to the applied field B_0, i.e., parallel or perpendicular).

The complex formed from the diketone shown in Figure 1.26(a) and europium(III), i.e., the tris(dipivaloylmethanato)europium(III) complex [Eu(DPM)$_3$], is one such reagent which interacts with alcohols or amines to

* E. Fermi, *Z. Physik* **60**, 320 (1930); D.R. Eaton and W.D. Phillips, *Advan. Magn. Resonance* **1**, 103 (1965).

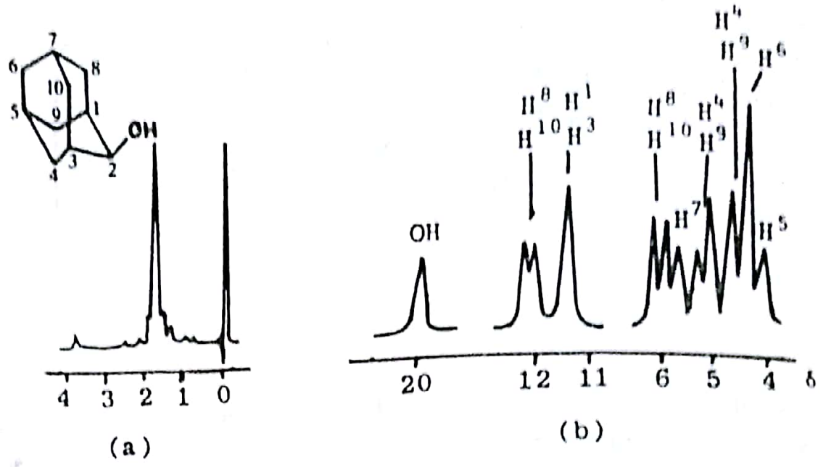


Figure 1.27. ^{1}H-NMR spectrum of 2-adamantanol: (a) normal spectrum; (b) spectrum in the presence of tris(dipivaloylmethanato)europium(III).

afford large downfield shifts resulting in great simplification in the interpretation of overlapping proton resonances. The ^{1}H-NMR spectra of 2-adamantanol before addition of the $Eu(DPM)_3$ complex [Figure 1.27(a)] and after addition of the complex [Figure 1.27(b)] can serve as an example.[1] The heptafluorodimethyloctanedionato complexes (FOD) of europium or praseodymium [Figure 1.26(b)] are also often used.

In general, the closer the proton is to the OH or NR_2 group interacting with the europium complex, the greater will be the downfield shift. With praseodymium complexes, shifts in the opposite direction are observed. Occasionally the nuclei may lie at an angle $\theta > 55°$ so that the sign of the factor $1 - 3\cos^2\theta$ changes, and shifts in the opposite direction are observed.

1.3.1.11 Charged Species

As chemical shifts are significantly affected by electron density, the presence of negative and positive charges in compounds causes shielding and deshielding, respectively, of protons attached to carbon atoms on which such charges are located. This is illustrated by comparison of chemical shift values of the cyclopentadienyl anion [Figure 1.28(a)] and the cycloheptatrienyl cation [Figure 1.28(b)]. Since all the protons in both species are equivalent, only one peak is observed in each case; in the spectrum of the cyclopentadienyl anion this singlet appears at δ 5.42 (about δ 1.85 *upfield* from benzene protons which resonate at δ 7.27) while in that of the cycloheptatrienyl cation the singlet appears at δ 9.17 (about δ 1.90 *downfield* from the benzene resonance), as shown in Figure 1.28. Similarly, the methine proton in the isopropyl cation [Figure 1.29(a)] is shifted downfield to δ 13.50 while the methyl protons on the adjacent carbon are also affected (δ 5.06). The effect of charges is dramatically illustrated when the NMR spectra of allyl cations and anions are compared [Figure 1.29(b), (c)]. In the case of the allyl cation the terminal methylenes are

[1] *Technical Bulletin*, No. 4, Varian Associates, Palo Alto, Californ...

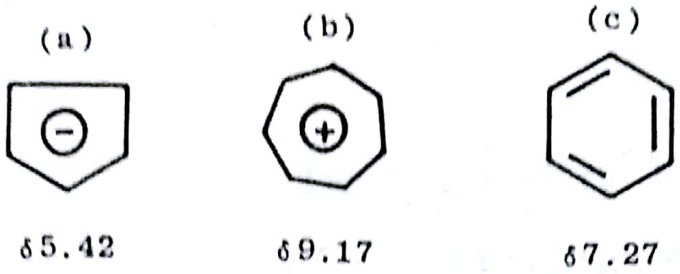


Figure 1.28. Upfield shift of aromatic proton resonances in anionic compounds and downfield shift of aromatic proton resonances in cationic compounds.

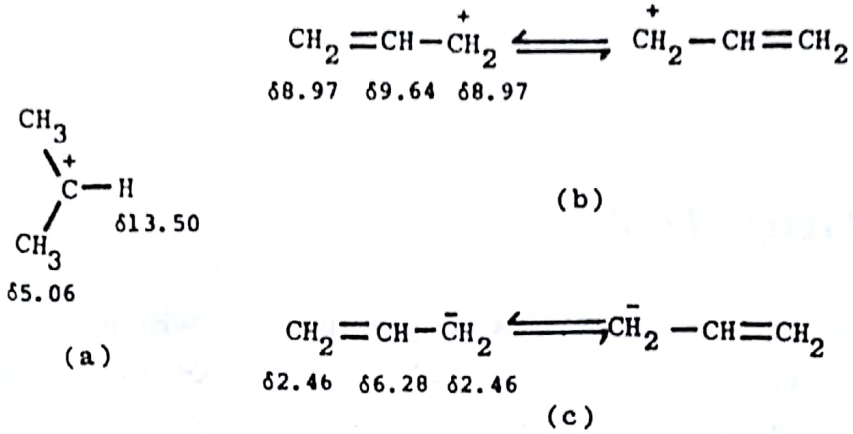


Figure 1.29. Effect of charges on the chemical shifts of some cations and anions.

deshielded by the positive charge and shifted downfield to δ 8.97 while in the anion they are shielded and therefore shifted upfield to δ 2.46. Both terminal methylenes are identical on account of the delocalization of charges.

RECOMMENDED READING

1. H. Günther, *NMR Spectroscopy*, John Wiley and Sons, New York (1980).
2. L.M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, International Series in Organic Chemistry, Vol. 10, Pergamon Press, Oxford (1969).
3. F.A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York (1969).
4. E.D. Becker, *High Resolution NMR*, Academic Press, New York (1980).
5. M.L. Martin and G.J. Martin, *Practical NMR Spectroscopy*, Heyden and Son Ltd., London (1980).
6. T. Clerc and E. Pretsch, *Kernresonanz Spektroskopie*, Akademische Verlagsgesellschaft, Frankfurt (1973).
7. A. Carrington and A.D. McLachlan, *Introduction to Magnetic Resonance*, Chapman and Hall, London (1979).