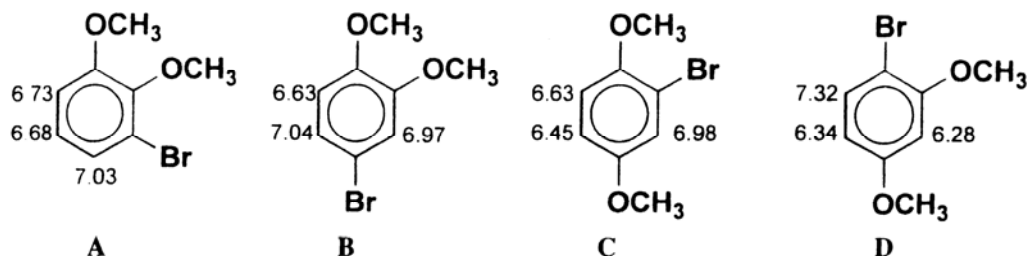# Chapter 3

The Chemical Shift

3-1 There are six possible trisubstituted isomers with two groups the same. Two are eliminated because they would give only two resonances by symmetry (2-bromo-1,3-dimethoxybenzene and 5-bromo-1,3-dimethoxybenzene). The calculated shifts for the remaining four isomers (**A-D**) are given below.

1-Bromo-2,4-dimethoxybenzene (**D**) is in good accord with the observed chemical shifts, even without analysis of splitting patterns. The δ 7.32 value, shifted to high frequency (downfield) by the effect of an ortho bromine, coupled with the small effect of meta methoxyl, is particularly diagnostic.

3-2 Ramsey's equation for paramagnetic shielding is dominant for nuclei other than hydrogen:

$$\sigma^{\mathrm{p}} \propto -(\Delta E)^{-1} <r^{-3}> \sum Q_{ij}$$

The π bonding and radial terms probably are not important here. The $t_{2g} \to e_g$ transition apparently is dominant and determines ΔE in the equation. The energy of an electronic transition is equal to $h\nu$ or hc/λ (in which c is the speed of light). Since the cobalt chemical shift is dominated by σ^{P}, which is inversely proportional to ΔE, and since ΔE is inversely proportional to λ, it follows that the chemical shift is directly proportional to λ. In this case, λ corresponds to the $t_{2g} \to e_g$ transition. Although this result is general for paramagnetic shielding, it often is not apparent. For ^{14}N, Richards demonstrated a similar relationship between the chemical shift and the longest wavelength transition, usually n $\to \pi^{*}$. See *Proc. Roy. Soc.*, **A242**, 455 (1955).

3-3 **(a)**

$$CH_3-CH_2-CH(CH_3)-CH(CH_3)_2$$
11.0   29.5   53.0 16.8   41.1 20.4

(b)

$$CH_3-CH_2-CH(NO_2)-CH_3$$
13.5   29.1   82.1   17.5

(c)

$$ICH_2-CH_2-CH_2Br$$
7.0   37.7   35.0

(d)

$$(CH_3)_3C-CN$$
28.4   28.8 145.4

These calculations ignored the δ effect and corrections for branching. A base of δ 117.2 from CH_3CN is used in eq. 3-11 in place of -2.5 to calculate the nitrile carbon position $(117.2 + (3 \times 9.4))$.

3-4 Both H_α and H_β are deshielded the same amount by the ring to which they are attached. They are shielded differentially, however, by the remote ring. Both are deshielded with respect to benzene (δ 7.3), but H_α (8.4) more so than H_β (7.7), since H_α is closer to the remote ring.
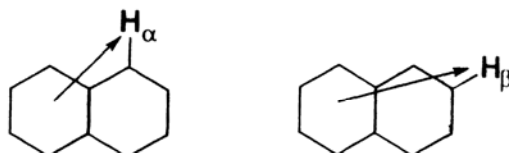
3-5 The hydroxyl of phenol is intermolecularly hydrogen bonded. In dilute $CDCl_3$ many of the hydrogen bonds are broken, so the resonance is shifted to lower frequency (higher field). In 2-nitrophenol the hydroxyl is intramolecularly hydrogen bonded, so even in dilute $CDCl_3$ the anisotropy of the lone pair in the hydrogen bond maintains the resonance at a high frequency position.

3-6 **(a)** crotonic acid, *trans*-$CH_3CH=CHCO_2H$ (the trans stereochemistry is deduced from coupling constant analysis, as described in Chapter 4)

(b) 1,3-dichlorobutane, $CH_3CHClCH_2CH_2Cl$ (the chiral center causes nonequivalence in methylene groups, as explained in Section 4-2)

(c) 1-chloro-3-pentanone, $ClCH_2CH_2(C=O)CH_2CH_3$

(d) propyl formate, $H(C=O)OCH_2CH_2CH_3$

(e) methyl 3-(4-hydroxyphenyl)propionate **(A)**

(f) 2-bromo-5-methoxybenzoic acid **(B)**

(g) l-methyl-2-pyrrolecarboxaldehyde **(C)**