TABLE 1-1

Usefulness of Common Nuclei in Natural Abundances in NMR Studies

Most useful	H^1	F^{19}	P^{31}		
Useful	B^{11}	N^{14}	Si^{29}		
Usable	H^2	C^{13}	N^{15}	O^{17}	S^{33}
Not usable	C^{12}	O^{16}	Si^{28}	Si^{30}	S^{32}
	Cl^{35}	Cl^{37}	Br^{79}	Br^{81}	I^{127}

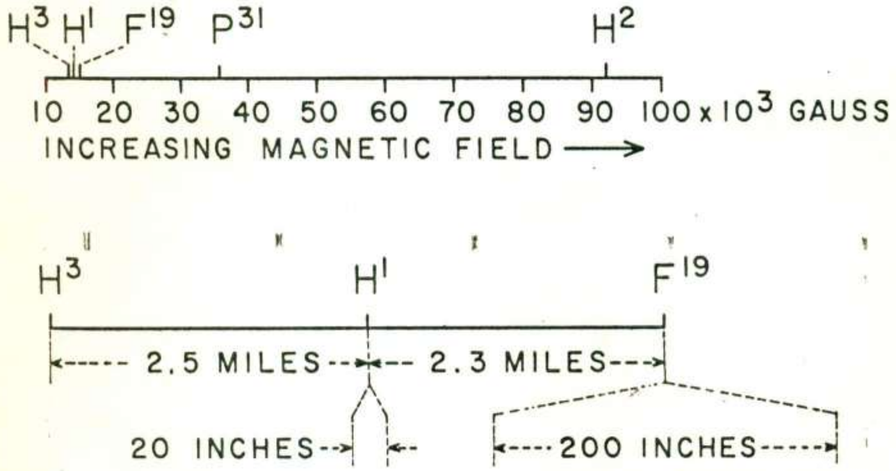


Fig. 1-1. Magnetic field strength at which common nuclei would absorb energy from a 60-Mcps signal. The lower chart indicates the relatively small region over which individual nuclear signals occur compared to the differences among different nuclei.

TABLE 1-2

Types and Origin of Information Obtainable from High-Resolution Spectra

Information obtainable	How obtained
Number of groups of nuclei in different molecular (electronic) environments	From number of absorption bands
Relative number of nuclei in each different environment	From relative areas under the absorption curve for the various bands
Relationship of one group of nuclei to other nearby groups of nuclei	From finer details in the absorption bands
Some rates at which nuclear environments are being changed	From number and shapes of absorption bands; often studied by causing changes in the rate

TABLE 1-3

Approximate Limitations for Proton Spectra Using a Single Scan on the Varian A-60 Instrument

(The HR-100 is four times as sensitive.)

Compound Requirements	
Amount	2.5 to 30 mg
State	Must be in a nonviscous liquid state
Solubility requirement	5 to 20%

TABLE 2-1

Common NMR Solvents

The dark areas are not usable under the conditions normally employed. Some of the absorption bands are due to impurities which vary in concentration.

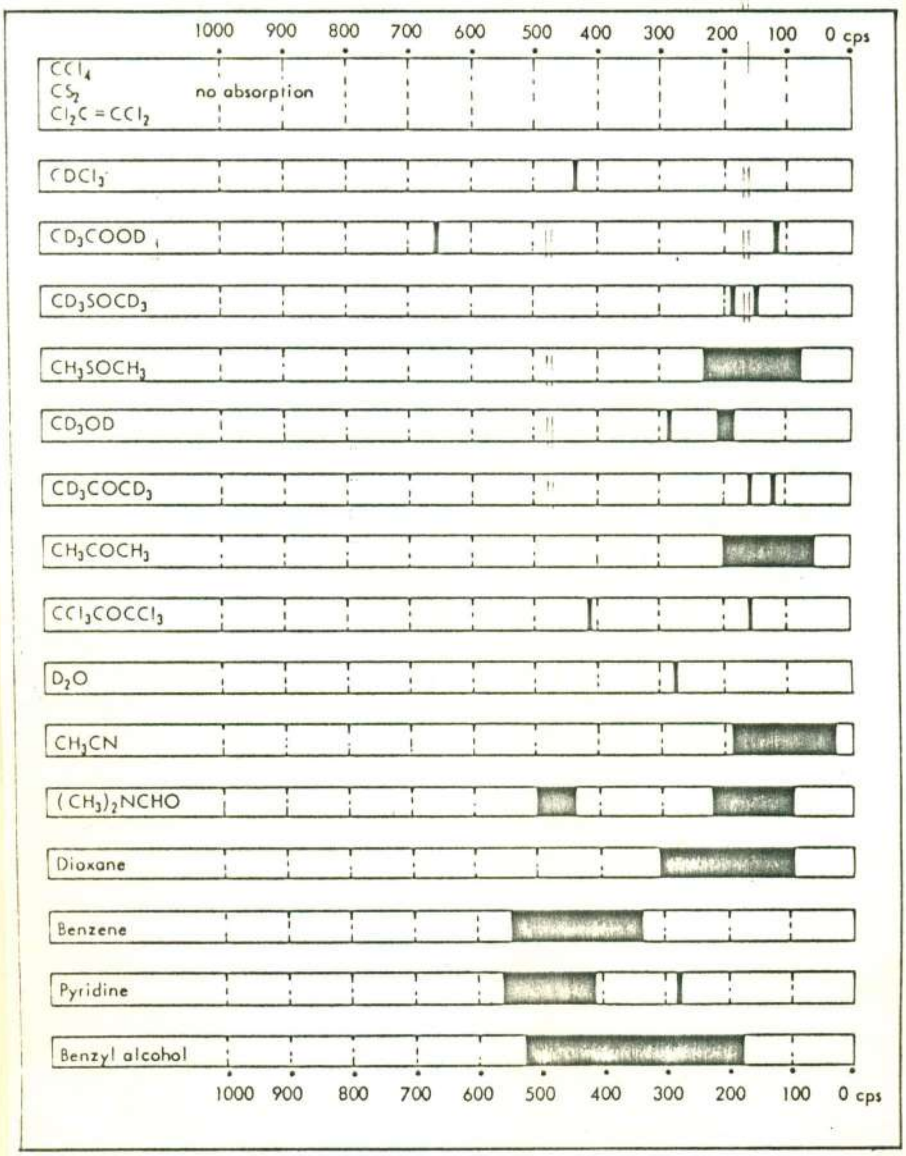


TABLE 2-2

Special Methods of Obtaining Usable Spectra with a Small Amount of Compound or an Insoluble Compound

For an insoluble compound	Use more sensitive instrument	For a small amount of compound
	Use C.A.T.	
	Change solvent	
	Increase temperature	

Un desplazamiento de izq a derecha Bo ⇉
se denomina DIAMAGNETICO.
Un desplazamiento de derecha a izq ⇇ Bo
se denomina PARAMAGNETICO.

TABLE 2-3

Arguments for Each of the Three Scales Used in Expressing Magnetic Field Strength

	Scale	Arguments for the use of the scale
ν	(cps)	(1) All instruments are calibrated in cps. (2) Coupling constants must be reported in cps. (3) Unless the actual chemical shifts are known, positions of peaks should be reported in cps. (4) Most laboratories have only one frequency available, and thus they are not greatly concerned with the frequency-dependence of chemical shifts. (5) Double resonance experiments are set up in terms of cps.
δ	(ppm) (ν divided by the frequency used)	True chemical shifts expressed in ppm are independent of the frequency used.
τ	(ppm) (for TMS: $10-\delta$)	(1) True chemical shifts expressed in ppm are independent of the frequency used. (2) The scale numbers increase from left to right. (3) There are fewer negative numbers.

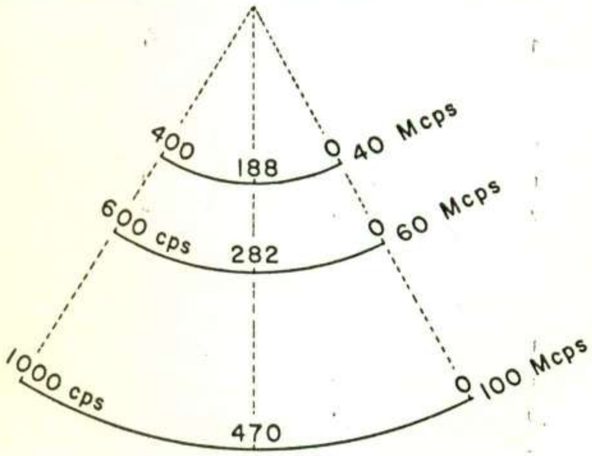


Fig. 2-3. Separation of single, sharp peaks as a function of the frequency used.

TABLE 2-4

Conversion of Literature Values to Chemical Shifts in Cycles per Second at 60 Mcps Using TMS as Internal Reference

I.	Convert to cps at 60 Mcps:	
A.	cps · (60 divided by the frequency used)	
B.	δ (ppm) · 60	
C.	$(10-\tau)\cdot 60$	
II.	Correct for reference used:	
	cyclohexane	86 cps
	water	282 cps
	benzene (internal)	438 cps
	benzene (external)	384 cps

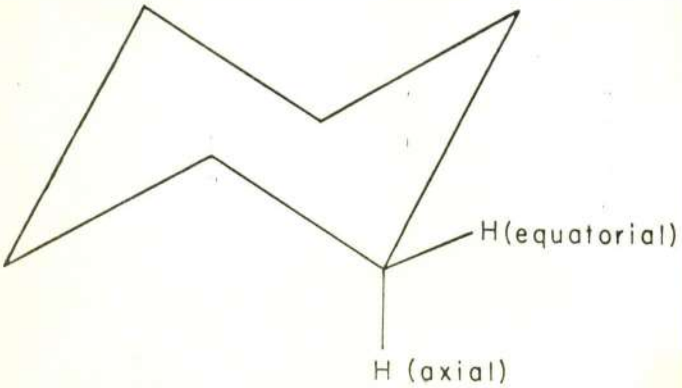


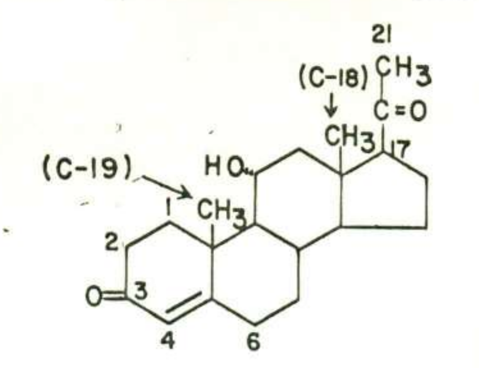
Fig. 2-7. The axial proton in an α,α'-unsubstituted, rigid cyclohexane system often appears at higher fields (to the right) than the corresponding equatorial proton. This results from the spatial effect of the carbon–carbon bonds.

TABLE 2-5

Shoolery's Additive Constants [23,24]

The position in cps of the signal due to an aliphatic methylene group in XCH_2Y in CCl_4 is equal to the sum of the constants (cps) for the two substituents plus 14 cps. The position in ppm is equal to the constants (ppm) plus 0.233 ppm. The constants may be used, but with much less success, for methine proton positions. Data is for 60 Mcps with TMS as internal reference.

Group	σ (cps)	σ (ppm)
Cl	152	2.53
Br	140	2.33
I	109	1.82
C_6H_6	110	1.83
NR^1R^2	94	1.57
OAlkyl	142	2.36
SR	98	1.64
CR=O	102	1.70
$CR^1=CR^2R^3$	79	1.32
C≡CH	86	1.44
C≡N	102	1.70
CH_3	28	0.47



	C−19	C−18
5α, 14α-androstane (used as reference)	47.5	41.5
3-oxo-Δ^4 system	25.0	4.5
11α-hydroxyl	7.0	1.5
17β − $COCH_3$	−0.5	−5.0
Calculated	79.0 cps	42.5 cps
Found	79.8	42.5

Fig. 2-8. Example of the use of Zürcher's additive constants [25] for the C-19 and C-18 methyl protons of steroids. See also Ref. 19.

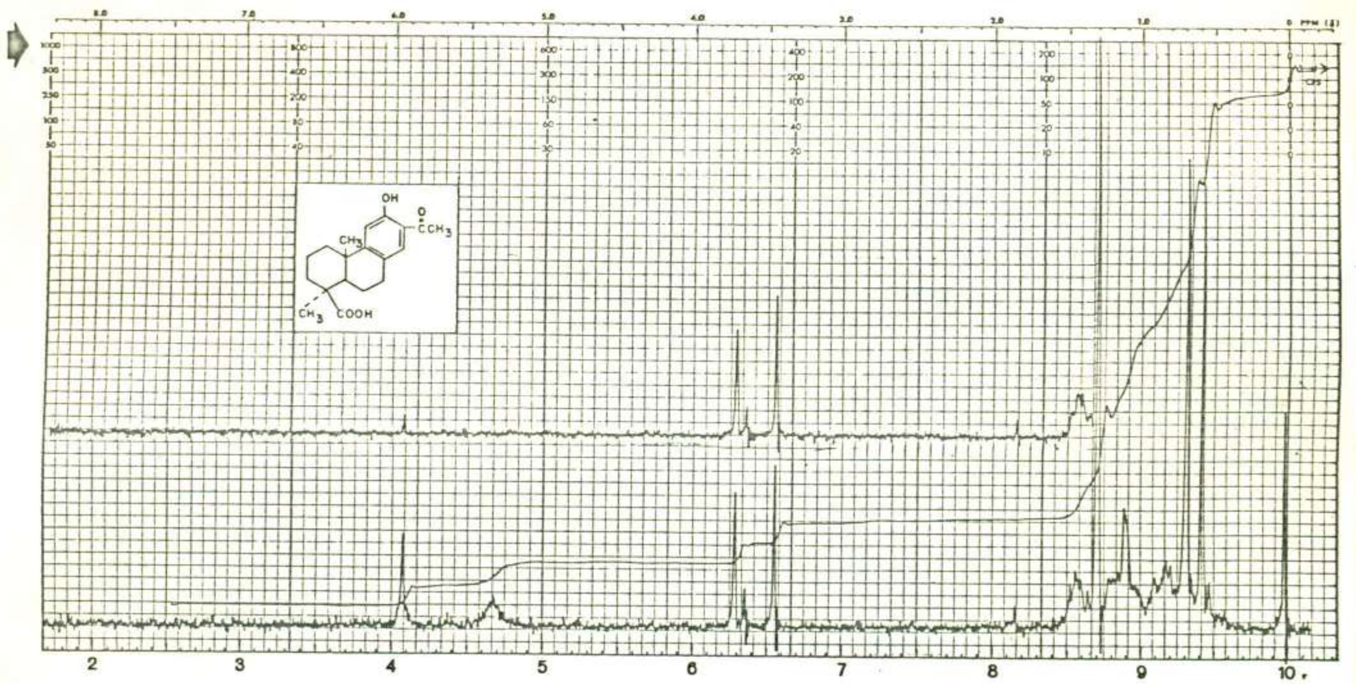


Fig. 2-10. Example of D_2O exchange. This spectrum was run from 1000 cps to 0 cps. Note the absence of the two exchangeable proton signals in the upper spectrum.

TABLE 2-6

Summary of Methods of Predicting Chemical Shifts and the General Rules Governing These Shifts

Chemical shifts can be predicted by the use of:

I. Correlation charts such as Figure 2-4 and those given by Stothers [15] and by Mohacsi [67].

II. Shoolery's additive constants (Table 2-5).

III. Tables of additive constants such as those of Zürcher [25].

IV. Reference to catalogs of spectra [7,8] or published spectra [9].

V. Closely related compounds.

In general, a shift to the left (to lower field) is caused by:

I. Increasing the electronegativity (electron-withdrawing effect) of a substituent.

II. Going from methyl ($-CH_3$) to methylene ($-CH_2-$) to methine ($-\overset{|}{\underset{|}{C}}H$).

III. Placing the proton (1) in the plane of a phenyl ring, carbonyl group, or olefinic bond, or (2) in line with a carbon—carbon or carbon—oxygen bond, or (3) above an acetylenic bond. [The signal of a proton placed (1) above the plane of a phenyl ring, carbonyl group, or olefinic bond, or (2) above a carbon—carbon or carbon—oxygen single bond, or (3) in line with an acetylenic bond is shifted to the right.]

IV. Increasing the hydrogen bonding to a proton.

The positions of signals due to protons attached to oxygen, nitrogen, and sulfur are difficult to predict because of variations in the degree of hydrogen bonding. These signals are easily identified by the D_2O exchange technique.

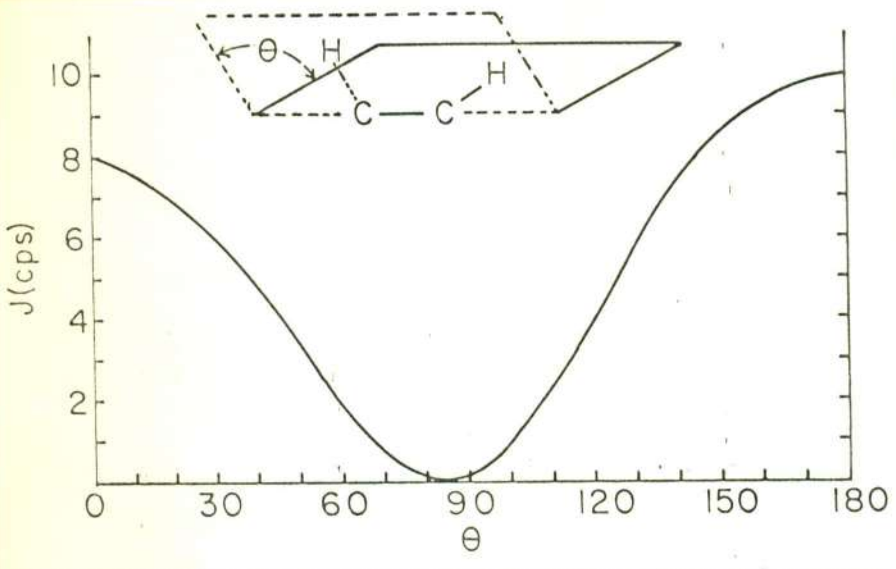


Fig. 2-17. Relationship of the coupling constant of protons on adjacent carbon atoms to the dihedral angle [33]. This angular relationship is only one of the factors which must be considered [34].

TABLE 2-7a

Spin–Spin Coupling Constants for Protons on Saturated Systems

Most of the values in this chart and in Tables 2-7b and 2-7c are from the collections of (1) Jackman [27], (2) Pople, Schneider, and Bernstein [28], and (3) Hollis [29]. A survey of couplings between vicinal protons in cyclohexane systems is given by Huitric, Carr, Trager, and Nist [30]. The effect of a carbonyl on the coupling between geminal protons is discussed by Takahashi [31], and the effect of ring size on coupling in 1,3-dioxolans by Crabb and Cookson [32]. Many leading references are given by Bishop [13].

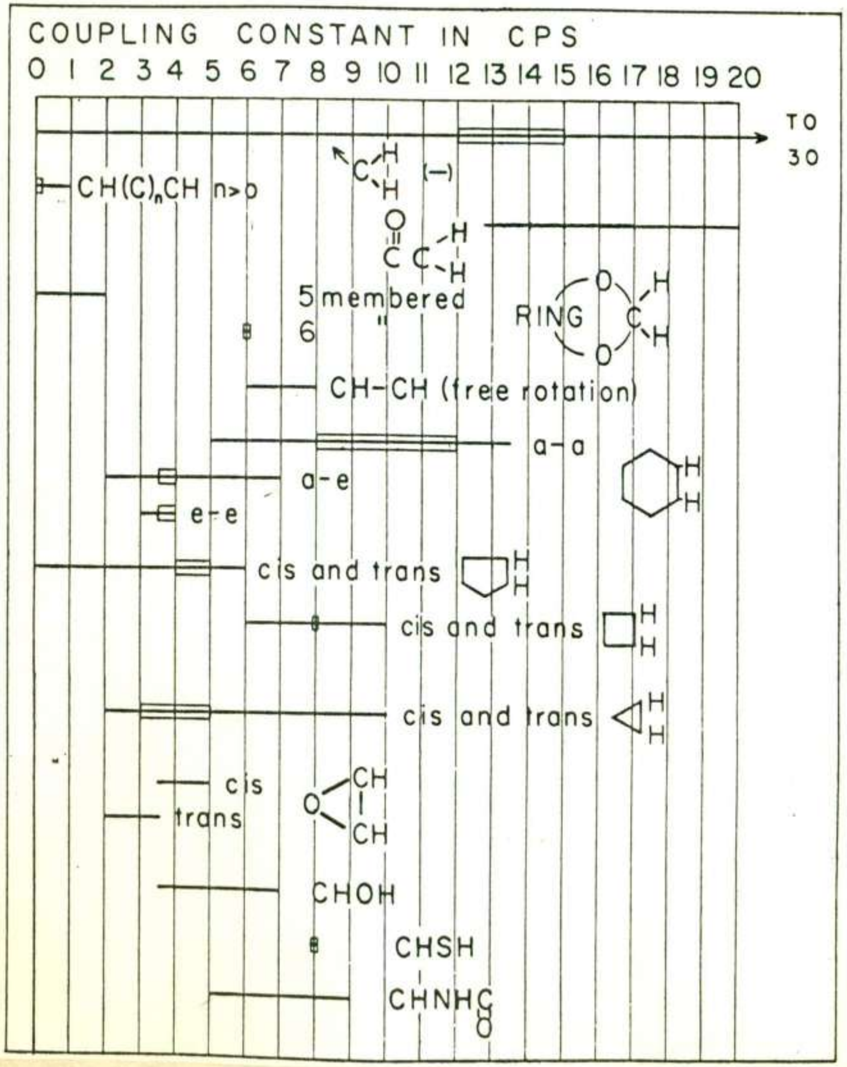


TABLE 2-7b

Spin–Spin Coupling Constants for Aldehydic Protons and Protons on Multiple Bonds

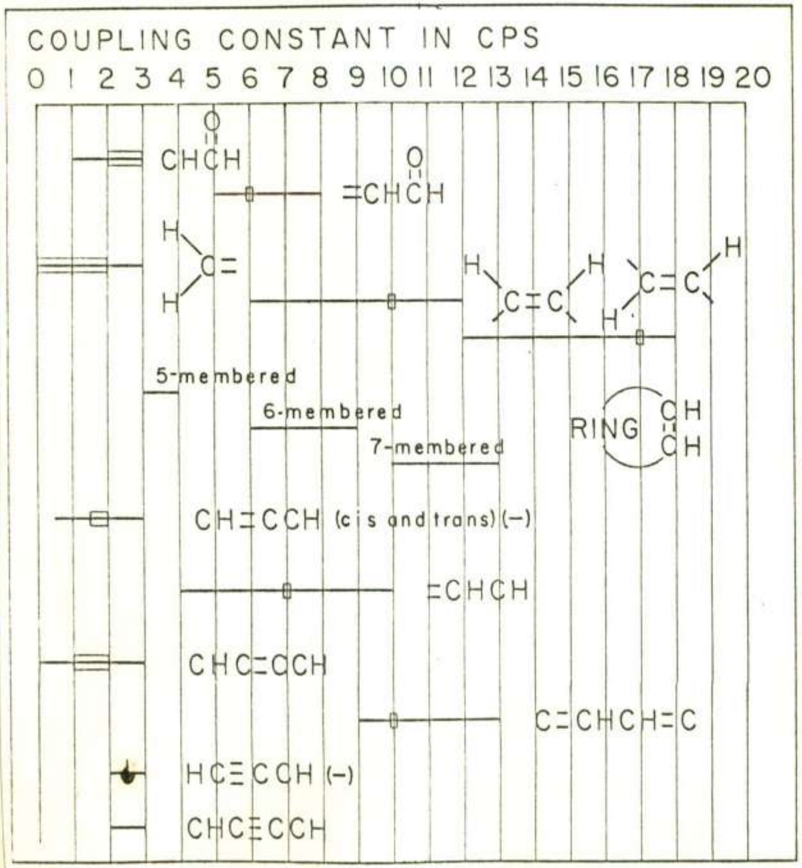


TABLE 2-7c

Spin–Spin Couplings for Protons on Aromatic Systems

A review of the NMR of heterocyclic compounds is given by R. F. M. White [16]. Other leading references are given by Sternhell [40a].

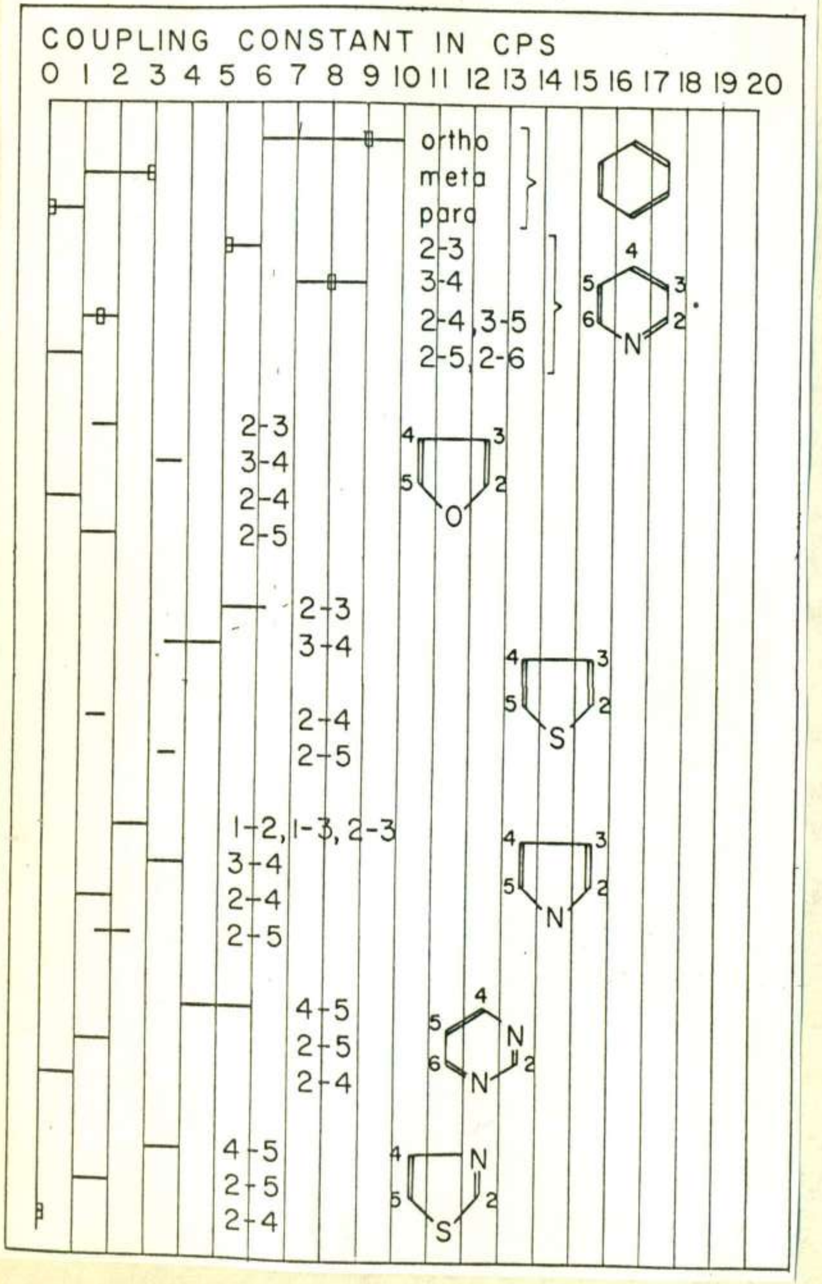
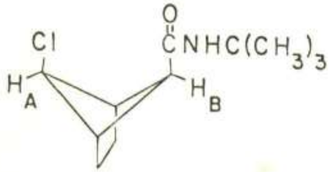
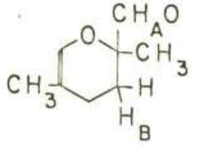
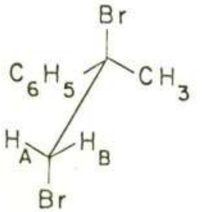


TABLE 2-7d

Some Examples of Long-Range Spin–Spin Interactions

The bonds linking the coupled protons in (b) form a figure W. This appears to be a general requirement for four-bond proton–proton coupling in saturated systems. See the review by Sternhell [40a].

(a)	$CH_3C\equiv C-C\equiv C-C\equiv C-CH_2OH$	$J_{C\underline{H}_3,C\underline{H}_2}$ = 0.4 cps[38]
(b)		J_{AB} = 7 cps[39]
(c)		J_{AB} = 1.3 cps[41]
(d)		$J_{C\underline{H}_3,\underline{H}_B}$ = 0 cps[42] $J_{C\underline{H}_3,\underline{H}_A}$ = 0.65 cps[42]

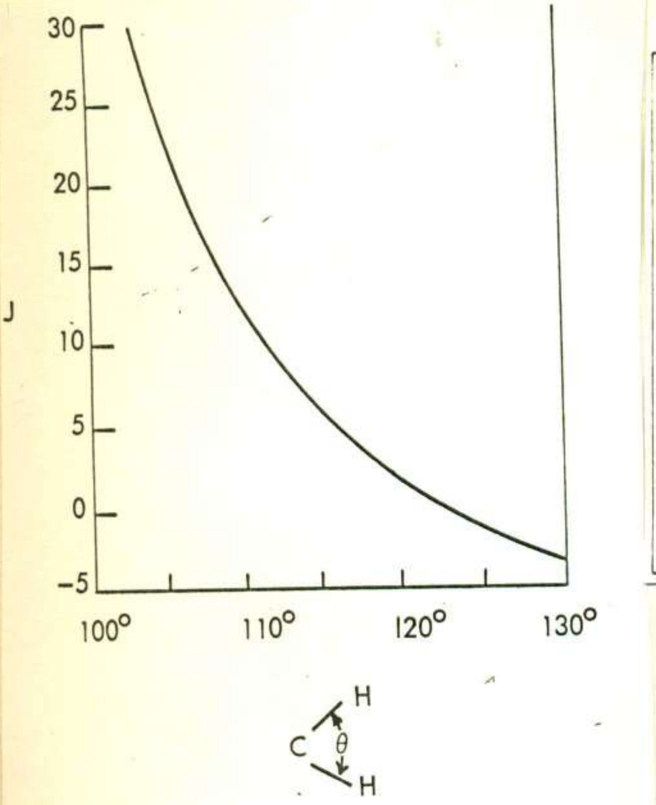


Fig. 2-18. A theoretical curve [35], no longer considered as valid [36], previously used for predicting the effect of a change in the angle between the bonds to protons attached to the same carbon atom.

TABLE 2-9

Summary of Facts About First-Order Systems and Their Patterns

First-Order Conditions

I. $\Delta\nu > 6J$.

II. Each proton in one group must be coupled equally to each and every proton in the second group.

First-Order Rules

I. Equivalent protons give only single peaks regardless of the strength of the coupling between the protons.

II. Multiplicity of a group of equivalent protons is caused by the number of neighboring protons, not by the number of equivalent protons.

III. The number of peaks is equal to the number of neighboring protons plus one.

IV. The peaks are symmetrical about the center of the chemical-shift position of the group and are separated by J.

V. The ratio of intensities of the peaks is 1:1, 1:2:1, 1:3:3:1, 1:4:6:4:1, etc.

TABLE 3-1

Proton–Proton Coupling Constants for Protons Attached to Oxygen, Nitrogen, and Sulfur

	J_{AB}(cps) (no exchange)
CH_AOH_B	4-7
CH_ASH_B	8
CH_ANH_B	not usually observed
$CH_ANH_B\overset{O}{\overset{\|}{C}}-$	5-9

TABLE 3-2

Effect of Conditions on Observed Coupling of Exchangeable Protons with Neighboring Protons

Y = oxygen, nitrogen, or sulfur

$-CH_A-YH_B$ (position of $-Y\underline{H}$ very sensitive to hydrogen bonding; dependent on solvent, temperature, and concentration).

Whether or not coupling is observed depends on J_{AB} and exchange rate; when rate in exchanges per second equals J_{AB} in cps, no coupling is observed.

Exchange with D_2O removes observable coupling; H_2O which is formed may appear near 282 cps.

TABLE 3-3

Nuclei of Interest in Organic Chemistry with Which Protons Can Couple

Nuclei which obey a modified multiplicity rule also cause broadening of the proton signals. The ranges of coupling constants listed for various arrangements are approximate. The data are taken from the Varian table [44], review by Lauterbur [10], and lecture by T. J. Flautt.

Nucleus (Y)	Natural abundance (%)	Modified multiplicity rule	J_{YH}, cps		
			Y—H	Y—C—H	Y—C—CH
H^1	99.98		280	0 to − 30	0 to + 15
H^2	0.02	$2N+1$	40	0 to − 4	0 to + 2
B^{11}	81.17	$3N+1$	30-190		
C^{13}	1.1		120-200	3-25	6
N^{14}	99.63	$2N+1$	50	0	
O^{17}	0.04	$5N+1$			
F^{19}	100		615	40-80	11-20
Si^{29}	4.70		120-250	6	6
P^{31}	100		180-700	5-15	5-15

TABLE 3-4

Influence of Various Factors on Appearance of Signal Due to Proton Attached to Nitrogen

Note that primary amides can give two broad peaks (see Table 3-5).

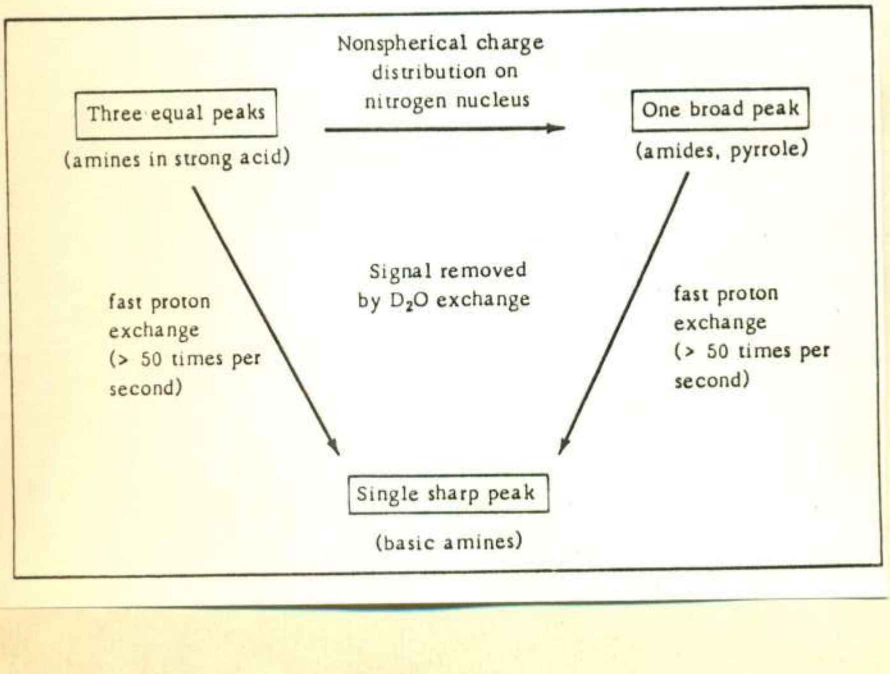


TABLE 3-5

Characteristic Appearance of Signals Due to Protons Attached to Nitrogen in Various Functional Groups

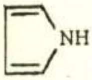
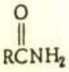
	Basic Amines
$-CH_A-NH_B$	Usually produce single, sharp peak due to rapid exchange.
$R_3\overset{\oplus}{N}H\overset{\ominus}{X}$	In strong acid, amines may give three rather broad, equally intense peaks due to coupling with the nitrogen nucleus.
	Pyrrole
	Proton on the nitrogen appears as extremely broad band.
	Amides
 $R\overset{O}{\overset{\parallel}{C}}NH_2$	Often give two broad bands because of restricted rotation about the C−N bond. The broadness is due, in part, to coupling with nitrogen.
 $R\overset{O}{\overset{\parallel}{C}}NH_ACH_B$	J_{AB} is usually in the range of 5 to 9 cps. This coupling is often observed, which means that the exchange rate is much less than 5 to 9 times per second. Splitting may be confused with nonequivalence due to restricted rotation.

TABLE 3-7

Conditions Which May Produce Unexpected Nonequivalence of Protons

I. Restricted (or prohibited) internal rotation about a
    A. double bond
    B. partial double bond
    C. single bond:
        1. because of bulky substituents
        2. because of rigid ring systems
II. Restricted inversion of a nitrogen atom
III. Asymmetry when a nearby carbon atom carries three different substituents (possible that the carbon atom may not be an optically active asymmetric center)

TABLE 3-8

Some Features of Concern in the Interpretation of Spin–Spin Patterns

I. Many spin system designations are only approximations. The best description is the simplest one which gives the desired agreement with the observed pattern.

II. First-order patterns and the relative intensities of the peaks can be pictured by the use of first-order splitting diagrams.

III. Methylene protons which are chemically equivalent may be magnetically nonequivalent because of restricted rotation, restricted inversion about a nitrogen atom, or because of molecular asymmetry.

IV. Differences in chemical shifts among protons is averaged out if the environments of the protons are interchanged at a rate equal, in times per second, to the difference in chemical shift in cycles per second.

V. Coupling can, and does, occur with other magnetic nuclei. Of particular concern are H^2, N^{14}, F^{19}, and P^{31}.

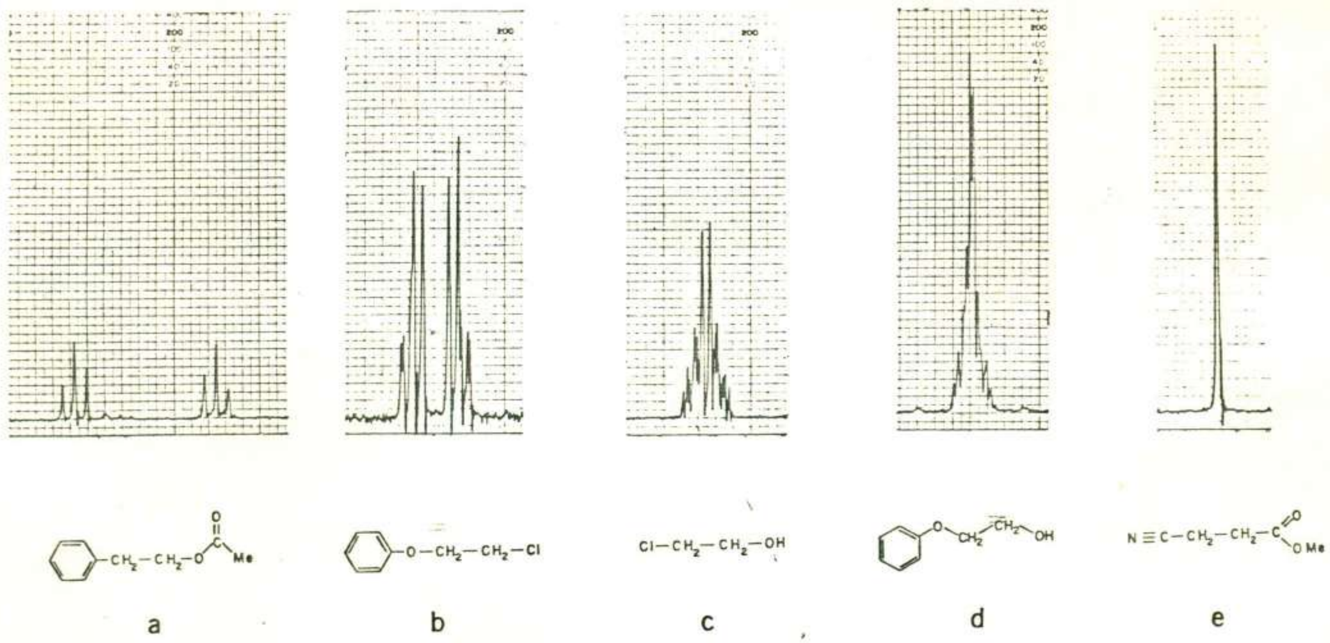


Fig. 4-1. Effect of decreasing $\Delta\nu_{AB}/J_{AB}$ on the spin multiplet due to an A_2X_2 system. These patterns range from A_2X_2 in (a) to A_4 in (e). Although patterns b, c, and d are approximately of the A_2B_2 type, detailed study would be required to determine whether or not these are actually A_2B_2 or $A_2'B_2'$ patterns. See the discussion on p. 80. The chemical shifts can be determined by inspection only in the first-order patterns, (a) and (e). The coupling constant can also be measured in (a). However, neither $\Delta\nu_{AB}$ nor J_{AB} can be determined by inspection of the higher-order patterns, b, c, and d. All of these patterns are reprinted fron the Varian Catalogs [7,8] by permission of the copyright holder, Varian Associates.

Sequence of Changes in Spin Pattern Brought About by Decreasing the Ratio of the Difference in Chemical Shifts ($\Delta\nu$) to the Coupling Constant

1. Relative intensities of peaks toward other part of pattern increases at expense of peaks away from the other part of the pattern.
2. Some single peaks break up into multiplets.
3. Weaker outer peaks are lost in the noise.
4. Center peaks merge.
5. Center peak sharpens.
6. All outer peaks are lost in the noise.

TABLE 4-2

Commonly Occurring Spin Systems

The primed systems are those in which each proton in one group is not coupled equally to each and every proton in the second group. The higher-order systems are in bold type. All of the other systems in this table are first-order.

A					
A_2	AB	AX			
A_3	A_2B	A_2X	ABC	ABX	AMX
	A'_2B'	A'_2X'			
A_4	A_3B	A_3X	A_2B_2	A_2X_2	
	A'_3B'	A'_3X'	$A'_2B'_2$	$A'_2X'_2$	
A_5	A_2B_3	A_2X_3	ABC_3	ABX_3	
	$A'_2B'_3$	$A'_2X'_3$			

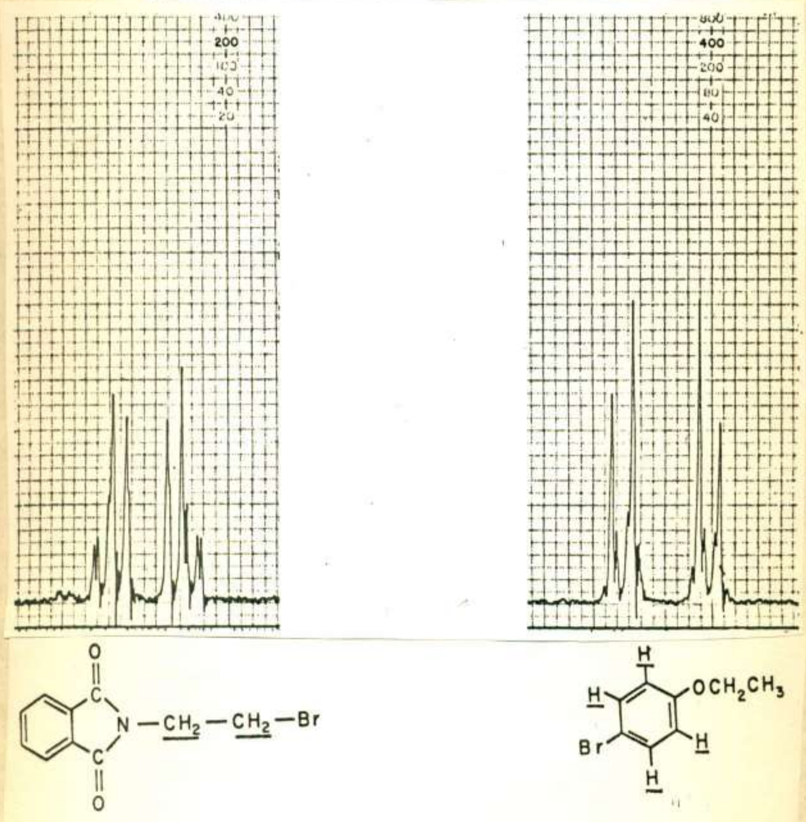


Fig. 4-2. Comparison of an A_2B_2 (left) and $A_2'B_2'$ (right) system. Reproduced by permission of the copyright holder, Varian Associates.

TABLE 4-3

Prediction of Spin Patterns for Common Systems [6,45,46]

The determination of the spin system from the pattern is given in Table 6-1

System *	Maximum number of lines†	Comments
A_N	1	Equivalent nuclei give a single peak even though they are strongly coupled.
A_NX_P	For A: $P+1$; for X: $N+1$	Each band is symmetrical and has peaks separated by J_{AX}; peaks have relative binomial intensities.‡
AMX	12	Each band has two or four equally intense peaks. Also see ABX below.
AB	4	$\frac{\text{Intensities of weaker outer peaks}}{\text{Intensities of inner peaks}} = \frac{\text{Separation of inner peaks}}{\text{Separation of outer peaks}}$; $\Delta\nu^2_{AB}$ = (separation of peaks 1 and 3)$^2 - J^2_{AB}$
A_2B A'_2B'	8 + 1	B: slanting** quartet. A: pair of doublets; outer doublet has greater separation. For A'_2B', pattern is a function of $\Delta\nu_{AB}/J_{AB_{\text{average}}}$
ABC	15	No good generalizations.
ABX	12 + 2	X: two (or three) doublets symmetrical about center of X band. Separation of strongest doublet is equal to $J_{AX} + J_{BX}$ Becomes a triplet if: $J_{AX} = J_{BX}$ or $J_{AB} \gg \Delta\nu_{AB} + \frac{1}{2}(J_{AX} - J_{BX})$. AB: two typical AB patterns (may be superimposed) J_{AB} occurs 4 times.
A_2B_2 $A'_2B'_2$	14 24	Band symmetrical about center but not about center of each half.
$A'_2X'_2$	20	Band symmetrical about center and also about center of each half. Each half: strong doublet plus two symmetrical quartets each having more intense inner lines.
A_3B	14 + 2	A: two bands, outer one weaker. Separation of these two bands is less than J_{AB}

*The primed systems are those in which each A is not coupled equally to each B or X.
†The second number given indicates the number of lines which in nearly all cases are very weak or absent.
‡"Relative binomial intensities": 1:1, 1:2:1, 1:3:3:1, 1:4:6:4:1, etc.
**"Slanting": intensities increase in direction of other portion of the pattern.

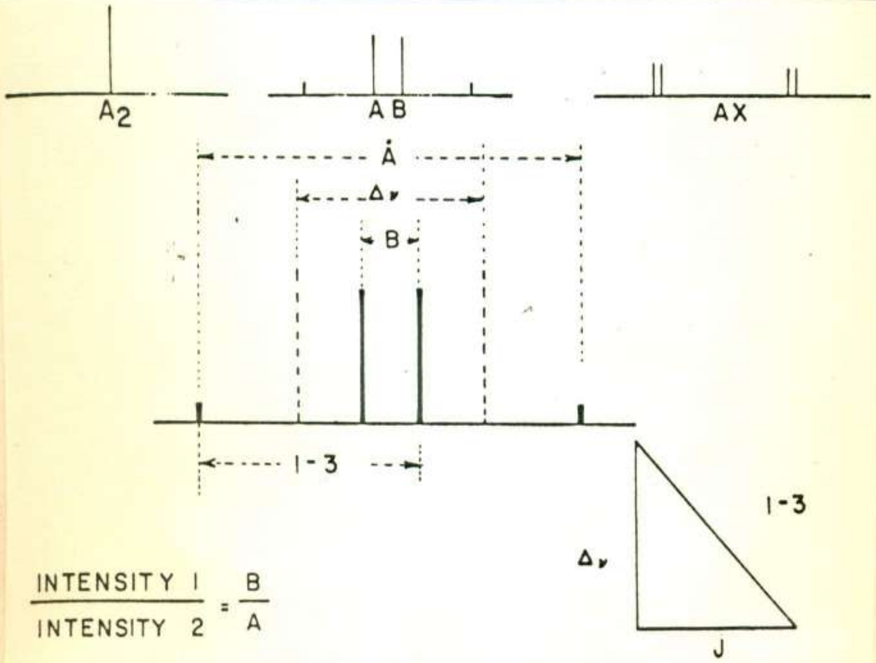


Fig. 4-3. Analysis of an AB system.

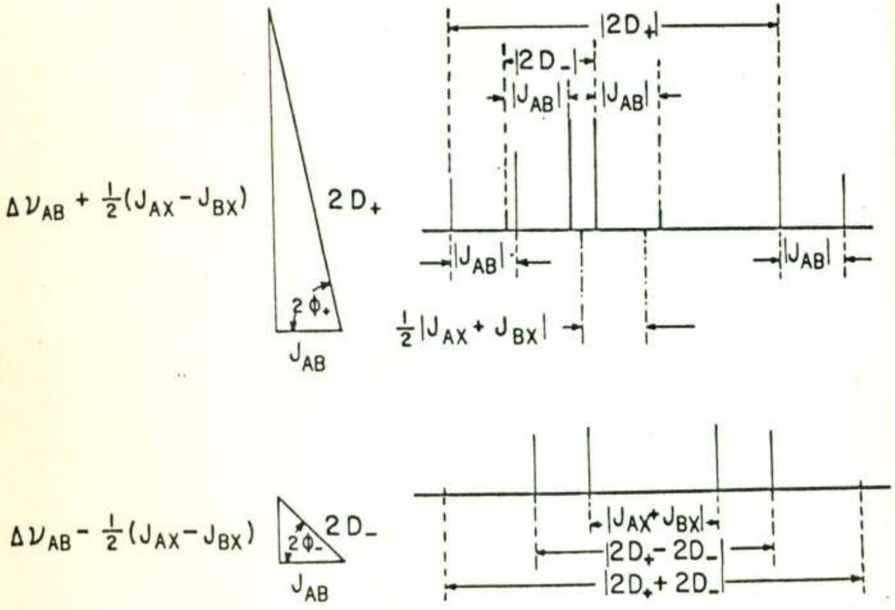


Fig. 4-5. Graphical representation of an ABX system in which $\Delta\nu_{AB} = -6$, $J_{AB} = 2$, $J_{AX} = -6$, and $J_{BX} = 2$. The AB pattern is shown in the upper section and the X pattern in the lower section. The notation follows that used by Pople, Schneider, and Bernstein [47]. Data from Wiberg and Nist [64].

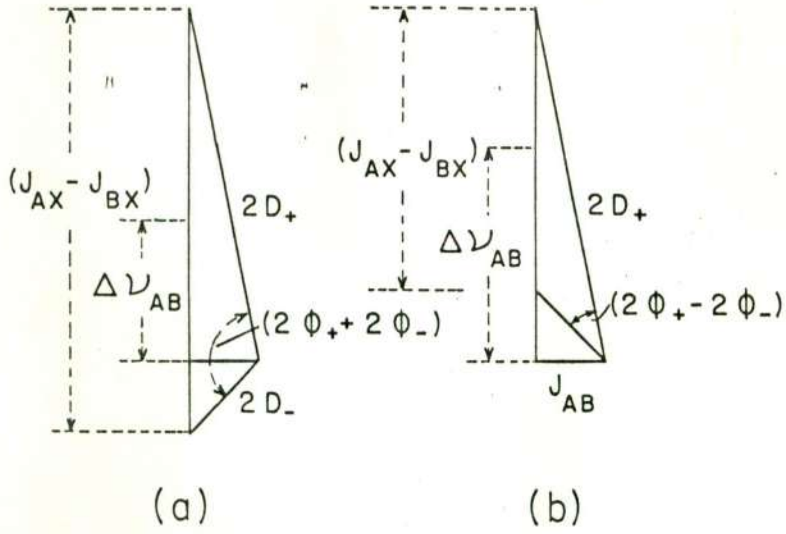
TABLE 4-4

Analysis of an ABX Pattern

I. Determine J_{AB} from the AB pattern. This separation occurs four times.

II. Determine $2D_+$ and $2D_-$ These cannot be distinguished from each other. Assume that the larger value is $2D_+$ The relative, but not the absolute, signs can be established later.

III. Construct two triangles having J_{AB} as bases and $2D_+$ as the hypotenuse of one and $2D_-$ as the hypotenuse of the other triangle.



(a) (b)

IV. Determine the angles $\frac{1}{2}(2\phi_+ + 2\phi_-)$ and $\frac{1}{2}(2\phi_+ - 2\phi_-)$. The ratio of the intensities of the medium to the strong peaks in the X pattern is equal to the square of the cosine of one of these angles. Select the correct angle. If the sum $\frac{1}{2}(2\phi_+ + 2\phi_-)$ gives the correct angle, then the two triangles are related as in (a). Otherwise they are related as in (b). It is not always possible to make this decision.

V. Determine $|\Delta\nu_{AB}|$ and $|J_{AX} - J_{BX}|$ by noting that in (a) $|J_{AX} - J_{BX}|$ is equal to the sum of the two vertical sides. In (b), $|J_{AX} - J_{BX}|$ is equal to the difference between the two sides. The halfway point on the combined vertical side in (a) or the point halfway between the vertical apexes in (b) is marked. The distance from this mark to the base is $|\Delta\nu_{AB}|$.

VI. From the X pattern find $|J_{AX} + J_{BX}|$, which is the separation between the two strongest peaks. The centers of the two AB patterns should be separated by $\frac{1}{2}|J_{AX} + J_{BX}|$ The medium peaks in the X pattern should be separated by $|2D_+ - 2D_-|$ The weakest peaks should be separated by $|2D_+ + 2D_-|$.

VII. From the values obtained in V and VI, $|J_{AX}| = \frac{1}{2}(|J_{AX} + J_{BX}| + |J_{AX} - J_{BX}|)$ and $|J_{BX}| = |J_{AX} + J_{BX}| - |J_{AX}|$.

VIII. The relative intensities of the peaks in the AB pattern may be calculated as indicated for the AB case in Figure 4-3.

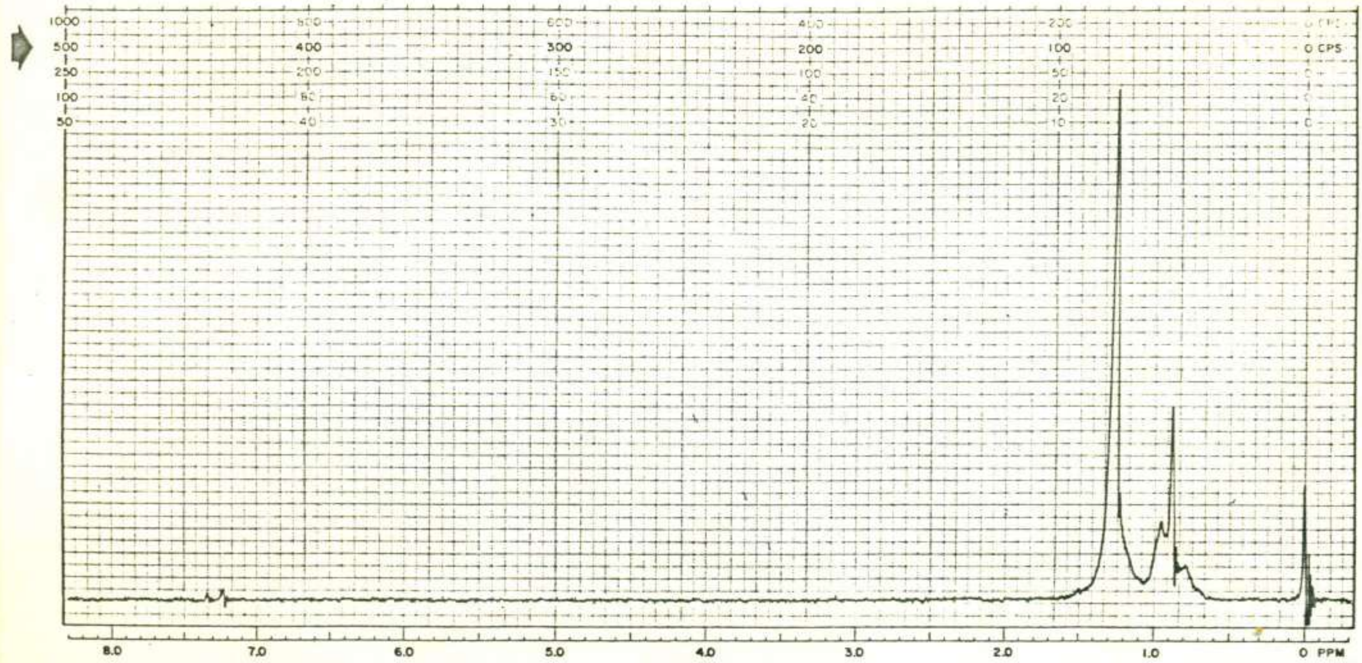


Fig. 4-9. Spectrum of N-octane illustrating the usual extreme in distortion seen in the methyl triplet of an ethyl group. Reproduced by permission of the copyright holder, Varian Associates.

TABLE 4-5

Summary of Points Which Must be Remembered in Working with Higher-Order Systems

I. Departure from one or both of the two first-order conditions causes (1) distortion of intensities (slanting towards other band), (2) appearance of extra peaks, and (3) unequal separations.

II. Intuitive analysis of higher-order patterns is not possible.

III. Chemical shifts and coupling constants cannot be extracted from higher-order patterns by simple inspection.

IV. Unequal coupling constants are of concern in all higher-order systems except in $A_2'B'$, and $A_2'X'$.

V. A change in relative signs of coupling constants may cause changes in the patterns of higher-order systems involving three or more nuclei.

VI. For a system of the type $A_M B_N X_P$, the X_P group can be considered as part of a $B_N X_P$ system only if $\Delta\nu_{AB}$ is at least three times J_{AB}. Otherwise the entire system must be dealt with.

VII. If the difference in chemical shifts among a group of nonequivalent nuclei is small compared to the coupling constants among the nuclei, the nonequivalent nuclei may behave like a group of equivalent nuclei which are equally coupled to neighboring nuclei.

TABLE 4-6

Some Conditions Required to Decouple Nucleus X (Lower Field Signal) from Nucleus A (Higher Field Signal) for an AX System by Double Resonance

I. The two radio frequencies used must differ approximately by the difference in chemical shifts (X frequency higher).

II. Power in the radio-frequency signal used for:

- A. nucleus X must be large,
- B. nucleus A must be small.

TABLE 5-1

Problems Which Hamper the Interpretation of Spectra

I. Presence of several components:

- A. impurities: solvents, etc.
- B. molecular complexes
- C. slowly interconverting forms
  - 1. restricted rotation
  - 2. enol—keto

II. Overlapping bands.

III. Low resolution.

IV. Unpredictable variations in coupling constants.

V. Different possible interpretations.

TABLE 5-2

Aids for Identifying Signals Due to Protons in Impurities

I. Presence of unexplainable single peaks or multiplets.

II. Use of integration curve.

III. Investigation of purity:

- A. history of sample and spectrum
- B. other physical methods (IR, UV, chromatography, etc.)
- C. spectra of different lots
- D. spectra of precursors and derivatives

This analysis is followed by

8. Correlation of the NMR spectrum with other data
9. Overall review

The step-by-step program is given on the following pages.

OUTLINE OF PROCEDURE FOR INTERPRETING SPECTRA

1. Check the TMS signal for position, symmetry, and ringing. Correct the entire spectum for any error in the position of the TMS signal. Repeat the spectrum if the signal is not symmetrical or if inadequate ringing is observed.

Establish which regions are covered in the spectra; note the solvent employed.

Mark known impurities such as $CHCl_3$, CHD_2COOD, and HOD in exchange spectrum.

2. Calculate the relative numbers of protons represented by each band using one of the methods presented in Chapter 2. Make allowances for impurities.

3. Mark signals due to exchangeable protons by comparing the spectra obtained before and after the D_2O exchange. Make tentative identification from number, position, peak shape, multiplicity, elemental analysis and IR spectrum.

4. Identify single sharp peaks such as those due to CH_3O-, $CH_3-\overset{|}{N}-$, $CH_3\overset{|}{\underset{|}{C}}-$, and $-\overset{|}{\underset{|}{C}}-C\equiv CH$. Remember the possibility of accidental equivalence of protons. Check for proper relative numbers from the integration.

5. Pick out first-order multiplets by (1) their symmetry about the center of each portion of the pattern, (2) the relative intensities of the peaks (1 : 1, 1 : 2 : 1, etc.), and (3) the equal separations of the peaks. All separations between peaks in each portion of the pattern must be equal to the coupling constant (mutual coupling). Closer examination should reveal that in these first-order multiplets the peaks on the side toward the other part of the pattern are more intense than the corresponding peaks on the side away from the other part of the pattern. Furthermore, each multiplet in the pattern must be distorted to the same extent.

Consider possible couplings to nuclei other than protons if N^{14}, F^{19}, or P^{31} are present (Table 3-3, p. 61).

Assign $N-1$ protons to the group causing the splitting. Check the assignment of relative numbers against those obtained using the integration curve.

Connect groups in the manner dictated by the number of protons in the groups and by the magnitudes of the coupling constants (Tables 2-7a to 2-7d, pp. 37-40).

Propose environments for the protons in the first-order multiplets using other physical measurements, correlation charts (Figure 2-4, p. 16), or spectra of known compounds (see Table 2-6, p. 25).

Recall conditions which may produce unexpected nonequivalence of protons (Table 3-7, p. 74).

Consider the possibility of slowly interconverting forms, especially if nitrogen is present (Table 3-6, p. 68).

6. Identify broad unresolved bands. If possible, compare appearance, width at half-height, and position with similar bands of closely related model compounds.

7. Proceed to identify higher-order patterns (Tables 4-3, p. 82, and 6-1, p. 116). Note any gross resemblance to first-order patterns. Look for symmetry about center of pattern or portion of pattern. Check against relative numbers of protons in groups. Compare with expected higher-order effects (Table 4-5, p. 101). Consider the possibility of overlapping bands and presence of impurities. Repeat the spectra in a different solvent, if necessary, to change the chemical shifts or to help separate bands. Use multiple resonance to simplify patterns such as the A_2BX type.

Assign the nature of the four-spin types A_2B_2, $A_2'B_2'$, and $A_2'X_2'$ from examples in Figure 4-8, p. 99.

Assign molecular environments for the protons.

Check questionable assignments using model compounds or published calculated spectra. If desirable, calculate the pattern using successive estimates of the various parameters until a fit is obtained. Previous experience must be used as a guide in the selection of reasonable coupling constants and chemical shifts. A calculated pattern may be within the experimental error and still be based on incorrect parameters.

8. Combine the groupings suggested by this analysis with the functional groups determined by IR. Correlate the UV spectrum with any olefinic or aromatic proton signals. Propose a carbon skeleton from the chemistry, elemental analysis, and types of proton signals. The number of "rings" in a compound can be calculated [63] using the formula:

"Rings" = carbons + 1 − (hydrogens + halogens − trivalent nitrogens)/2

TABLE 6-1

Analysis of Spin Patterns from Their Characteristics

Number of protons from integration	Number of peaks n	Spacing of peaks	Relative intensities of peaks*	Possible systems†
1	2 to 9	Equal	Binomial	$\underline{A}X_{n-1}$
	2		Slanting	$\underline{A}B$
	3	Equal		$AB\underline{X}$: $J_{AX} = \|J_{AX}\|$ or $J_{AB} \gg \Delta\nu_{AB} + \frac{1}{2}(J_{AX} - J_{BX})$
	4 (or 4 + 2 weak)	Symmetrical about center of band		$AB\underline{X}$
	4	Unequal	Slanting	$\underline{A}B_2$
2	2 to 9	Equal	Binomial	$\underline{A_2}X_{n-1}$
	Complex: strong doublet + 2 quartets	Symmetrical about center of band; also mirror image of another 2-proton band		$\underline{A'_2}X'_2$
	Complex: as many as 12 peaks	Not symmetrical about center of band but mirror image of another 2-proton band		$\underline{A_2}B_2$ or $\underline{A'_2}B'_2$
	2 quartets (may be superimposed)	One spacing occurs 4 times	Like 2 AB systems	$\underline{AB}X$
	2 doublets (may have one other weak peak)	One doublet separated less than other	Slanting	$\underline{A_2}B$
3	2 or 3	Equal	Binomial	$\underline{A_3}X_{n-1}$
	2 unresolved bands		Slanting	$\underline{A_3}B$
	Complex	Complex	Complex	$\underline{ABC}$
	8 to 9 (4 peaks + 2 unequally spaced doublets + possible extra peak)	Unequal	Slanting	$\underline{A_2B}$
4	Complex	Symmetrical about center of band		$\underline{A_2B_2}$ or $\underline{A'_2B'_2}$
5	Complex	Complex	Complex	$\underline{A_2B_2C}$ (monosubstituted phenyl, for example)

*Binomial Intensities: 1:1
1:2:1
1:3:3:1
1:4:6:4:1
1:5:10:10:5:1
1:6:15:20:15:6:1

"Slanting" means general increase in intensities in direction of other part of pattern.
†The primed systems are those in which each A is *not* coupled equally to each B or X.

TABLE 6-2

Characteristics That Aid in Analysis of Spin Patterns

I. Symmetry of pattern
II. Relative intensities of peaks
III. Spacings of peaks
IV. Number of protons represented
V. Number of peaks
VI. Correlation with other parts of pattern

"Ring" here is defined as any cyclic system. A double bond is counted as one ring, a triple bond as two rings. (Benzaldehyde has five "rings.") Propose structures that combine all of the data.

9. Review the spectrum for its correlation with the proposed structures. If possible, eliminate structures by using closely related models. Use multiple resonance, if available, to confirm which groups are coupled and to locate hidden protons.

It is to be noted that the first step in the analysis of any spin multiplet is the recognition of possible spin systems which could give rise to the pattern. There is no alternative to this initial identification by inspection. The characteristics which have been noted in this and previous chapters by which these identifications are made are summarized in Table 6-2. These characteristics form the basis for the correlations given in Table 6-1.

Equipped with this body of empirical facts, the student is ready to deduce a wealth of data from NMR spectra. Confidence can be derived only by the examination of many spectra. The spectra in the Varian catalogs [7,8] serve quite conveniently for this purpose. Experience with a series of closely related compounds can make the interpretation of spectra of related derivatives extremely easy. The student is also now in an excellent position to proceed with a study of the theory of NMR.