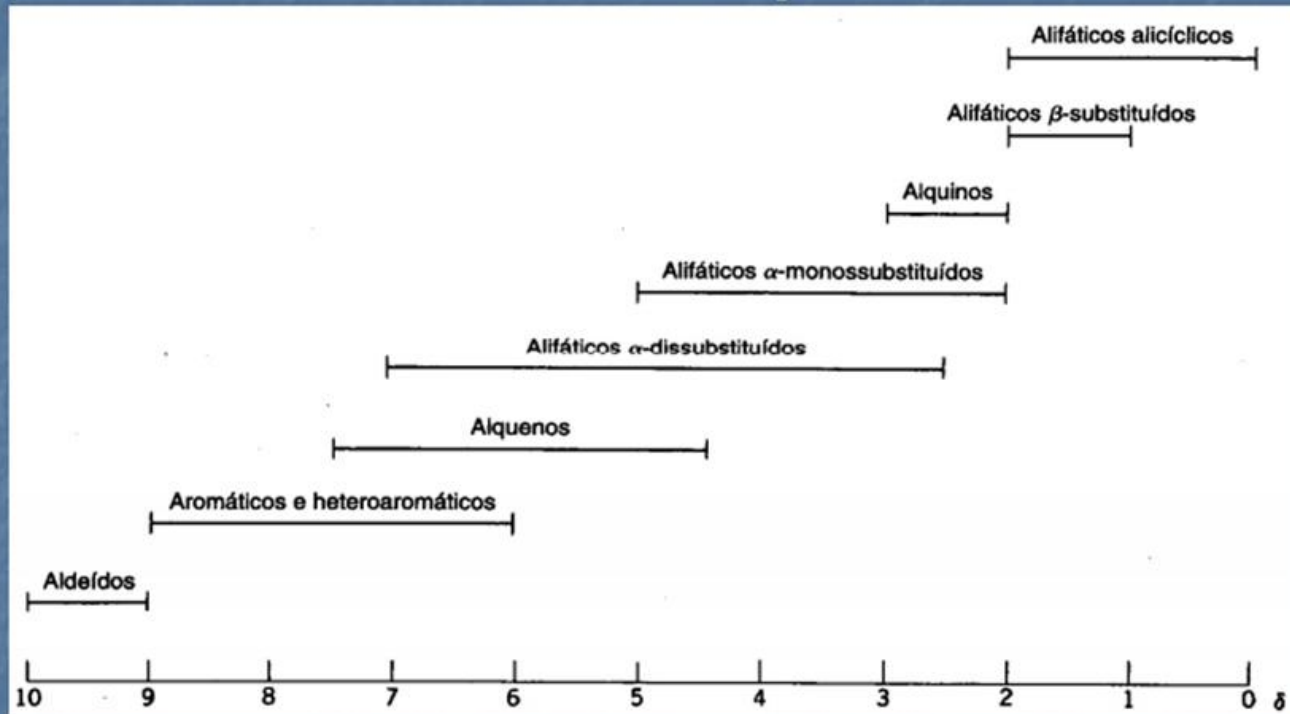


CÁLCULO DO DESLOCAMENTO QUÍMICO

Absorções características dos deslocamentos químicos

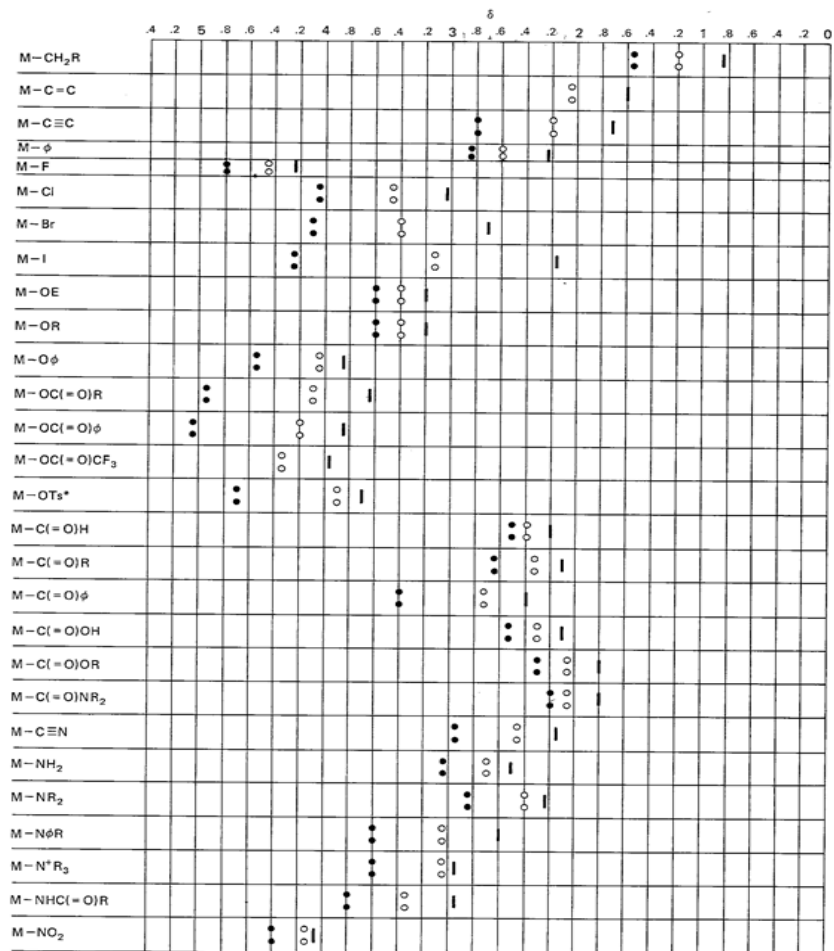


A posição de um sinal de RMN depende do ambiente eletrônico do núcleo

ALCANOS MONOSUBSTITUÍDOS EM ALFA

CHART 1. CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ADJACENT (α - POSITION) TO A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M-Y).

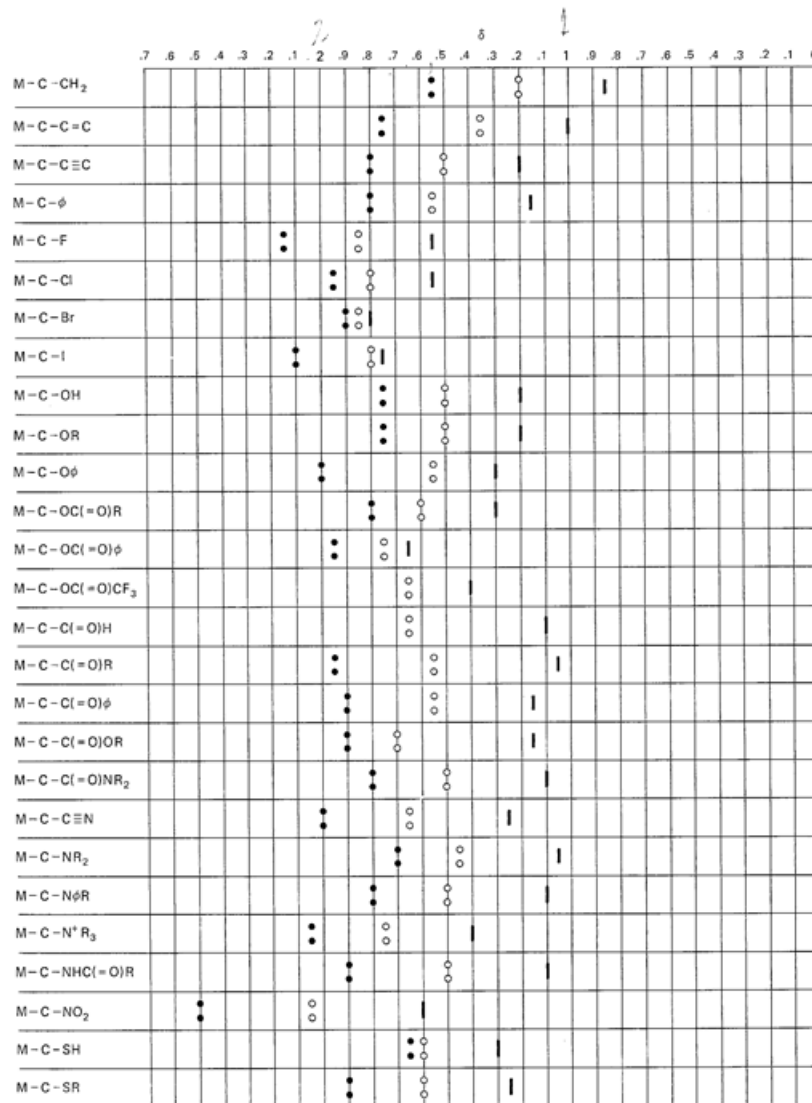
M = methyl
 M = methylene
 M = methine



ALCANOS IMONOSSUBSTITÍDOS *em* beta

CHART 2. CHEMICAL SHIFTS OF PROTONS ON A CARBON ATOM ONCE REMOVED (β - POSITION) FROM A FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M-C-Y).

| M is methyl
 ○ M is methylene
 ● M is methine



appendix b. effect on chemical shifts
of two or three functional groups
(Y-CH₂-Z , and Y - CH - Z)

$$\begin{array}{c} | \\ \text{W} \end{array}$$

Shoolery's rules (B. P. Dailey and J. W. Shoolery, *J. Am. Chem. Soc.*, 77, 3977 (1955)) permit calculation of a shift position of a methylene group attached to two functional groups by the additive effect of the shielding constants in Table 1, below. The sum of the constants is added to δ 0.23, the position for CH₄.

Thus, to calculate the shift for the -CH₂- protons of C₆H₅CH₂Br:

$$\begin{array}{r} \text{C}_6\text{H}_5 = 1.85 \quad 0.23 \\ \text{Br} = 2.33 \quad 4.18 \\ \hline 4.18 \quad 4.41 = \delta \text{ value for the } -\text{CH}_2- \text{ group.} \end{array}$$

Table I. Shielding Constants

Y or Z	Shielding Constants	Y or Z	Shielding Constants
-CH ₃	0.47	-C(=O)NR ₂	1.59
-C=C	1.32	-C≡N	1.70
-C≡C	1.44	-NR ₂	1.57
-φ	1.85	-NHC(=O)R	2.27
-CF ₂	1.21	-N ₃	1.97
-CF ₃	1.14	-SR	1.64
-Cl	2.53	-OSO ₂ R	3.13
-Br	2.33		
-I	1.82		
-OH	2.56		
-OR	2.36		
-Oφ	3.23		
-OC(=O)R	3.13		
-C(=O)R	1.70		
-C(=O)φ	1.84		
-C(=O)OR	1.55		

The shielding constants have been used to prepare the chart on page 224. Several values have been added to the original set of constants.

Alternatively, Chart 1 can be used to find the shift position of a methylene group attached to two functional groups from the δ values in the box at the intersection of the horizontal and diagonal groups ("mileage chart"). The upper number in each box is an experimental value; the lower number is calculated from Shoolery's constants.

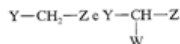
METILENOS COM DOIS SUBSTITUÍNTES

CHART 1. CHEMICAL SHIFTS FOR METHYLENE GROUPS
ATTACHED TO TWO FUNCTIONAL GROUPS (Y-CH₂-Z).

GROUP	-CH ₃	-C=C	-C≡C	-φ	-CF ₂	-CF ₃	-Cl	-Br	-I	-OH	-OR	-Oφ	-OC(=O)R	-C(=O)R	-C(=O)φ	-C(=O)OR	-C(=O)NR ₂	-C≡N	-NR ₂	-NHC(=O)R	-N ₃	-SR
-CH ₃	1.17	1.90 2.02	2.14	2.55	1.91	1.84	3.57 3.43 3.20	3.70 3.40	3.26	3.06	3.93	3.83	4.25 2.47	2.25 2.23	2.25 2.29	2.40 2.27	2.40 2.27	2.63	2.97	2.67	2.53 2.34	
-C=C	2.60 2.87	3.39 3.40	3.30	2.76	2.69	4.08 3.88	3.93 3.87	3.95	4.13	3.91	4.78	4.68	3.25	3.39	3.10	3.14	3.15 3.30	3.15 3.30	3.12 3.82	3.52	3.08 3.19	
-C≡C	3.11	3.52	2.88	2.81	4.20	4.00	3.49	4.28	4.03	4.90	4.80	3.37	3.51	3.22	3.26	3.37	3.24	3.97	3.67	3.31		
-φ	3.97	3.29	3.22	4.61	4.41	3.90	4.58	4.44	5.31	5.21	3.78	3.92	3.63	3.66	3.78	3.65	3.48	4.34	4.04	3.72		
-CF ₂	2.63	2.58	3.97	3.76	3.26	4.01	4.01	3.80	4.67	4.57	3.12	3.28	2.99	3.03	3.12	3.01	3.71	3.41	3.08			
-CF ₃	2.51	3.90	3.70	3.19	3.93	4.73	4.60	4.54	3.07	3.21	2.92	2.96	3.07	2.94	3.64	3.34	3.01	3.71	3.41	3.08		
-Cl	4.99	5.16	4.99	5.40	5.29	5.09	4.58	5.32	5.12	5.99	5.89	4.46	4.60	4.31	4.35	4.46	4.37	5.13	4.73	4.40		
-Br	4.94	4.89	4.38	5.12	4.92	5.79	5.69	4.26	3.40	4.11	4.15	4.26	4.13	4.83	4.53	4.20	4.20	4.76	4.43			
-I	3.87	4.61	4.41	5.16	5.06	3.75	3.89	3.60	3.64	3.75	3.62	4.32	4.02	3.69								
-OH	4.55	5.15	6.02	5.92	4.49	4.63	4.34	4.38	4.49	4.35	5.06	4.76	4.43									
-OR	5.55	5.82	5.72	4.29	4.43	4.22	4.18	4.29	4.15	4.94	4.64	4.23										
-Oφ	6.69	6.59	5.16	5.30	5.09	4.05	5.16	5.03	5.86	5.56	5.10											
-OC(=O)R	6.46	5.10	5.20	4.91	4.95	5.10	4.92	5.63	5.37	5.00												
-C(=O)R	3.60	3.63	3.77	3.48	3.52	3.63	3.50	4.10	3.90	3.57												
-C(=O)φ	3.91	3.62	3.66	3.77	3.64	4.34	4.02	3.71														
-C(=O)OR	3.33	3.37	3.48	3.35	4.05	3.75	3.42															
-C(=O)NR ₂	3.30	3.41	3.52	3.39	4.09	3.79	3.46															
-C≡N	3.63	3.50	4.20	3.90	3.57																	
-NR ₂	3.10	3.37	4.07	3.77	3.44																	
-NHC(=O)R	4.75	4.45	4.14																			
-N ₃	4.15	3.84																				
-SR	3.51																					

CORREÇÃO DA TABELA DE DOIS E TRÊS GRUPOS FUNCIONAIS

EFEITO SOBRE OS DESLOCAMENTOS QUÍMICOS DE DOIS OU TRÊS GRUPOS FUNCIONAIS DIRETAMENTE LIGADOS AO APÊNDICE B CARBONO



usando a constante do grupo H (0,34). Por exemplo, H—CH₂—Br é o mesmo que CH₃Br.

O deslocamento químico de um grupo metileno ligado a dois grupos funcionais pode ser calculado com o auxílio das constantes de substituição da Tabela B.1.

Tabelas B.2a, B.2b e B.2c: Correlações de Deslocamento Químico para Hidrocarbonos

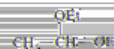
O deslocamento químico dos hidrogênios do grupo metileno de CH2Br2, por exemplo, pode ser calculado a partir dos valores de σ tirados da Tabela B.1:

$$\begin{aligned} \sigma_{\text{H}} &= 0,34 \\ \sigma_{\text{Br}} &= 2,33 \end{aligned}$$

$$\delta = 4,01 \text{ -- Encontrado } \delta = 3,43^*$$

$$\delta_{\text{CH}_2\text{OZ}} = 2,50 + \sigma_{\text{Y}} + \sigma_{\text{Z}}$$

que dá resultados satisfatórios se pelo menos dois dos grupos forem grupos que retiram elétrons. Encountre valores para os grupos que são am-grupos alquila (R). Dentre limites, o erro padrão estimado é igual a 0,20 ppm. Como exemplo, o deslocamento químico do hidrogênio do CH2



é calculado a partir da Tabela B.2a da seguinte maneira:

$$\delta = 2,50 + 1,14 + 1,14 + 0,00 = 4,78$$

O valor encontrado é 4,72.

As Tabelas B.2b e B.2c são usadas conjuntamente para hidrogênios do grupo metileno substituídos por pelo menos um

As constantes originais de Shoolery foram revisadas e seu número aumentado (Tabela B.1). Os deslocamentos químicos observados e calculados para 62 das amostras listadas estão em torno de $\pm 0,2$ ppm; 92% em torno de $\pm 0,1$ ppm; 96% em torno de $\pm 0,4$ ppm; e 99% em torno de $\pm 0,6$ ppm. A Tabela B.1 contém constantes de substituição de Friedrich e Banks (1955) para os grupos funcionais mais comuns. Observe que os deslocamentos químicos dos grupos metileno podem ser calculados

* Bell, H.M.; Bowler, D.J. *J. Org. Chem.* 1954, 19, 1030. Com permissão.

* Shoolery, J.N. (1959) *British Technical Information Bulletin*, Vol. 2, No. 3, 210. Alho, CA: Martin Associates.
 * Friedrich, E.C. and Banks, W.A. (1955) *J. Chem. Ed.* 32, 188-192.

TABELA B.2a: Constantes de Substituição de Hidrogênio de Grupos Metileno

TABELA B.1: Constantes de Substituição de Hidrogênio de Grupos Metileno e Metílicos

Y ou Z	Constantes de Substituição (σ)	Y ou Z	Constantes de Substituição (σ)
H	0,34	—OC(=O)R	3,01
—CH ₃	0,68	—OC(=O)Ph	3,27
—C—C—	1,32	—C(=O)R	1,50
—C=C—	1,34	—C(=O)Ph	1,90
—Ph—	1,83	—C(O)R	1,46
—CF ₃	1,12	—C(=O)NR ₂ (H ₂)	1,47
—Cl—	1,13	—C=N	1,59
—F—	3,30	—NR ₂ (H)	1,57
—O—	2,83	—NHPh	2,04
—Br—	2,33	—NHC(=O)R	2,27
—I—	2,19	—N ⁺	1,97
—OH	2,56	—NO ₂	3,36
—OR	2,36	—SR(H)	1,64
—OPh	2,94	—OSO ₂ R	5,13

Grupo	σ
F	3,30
Cl	1,13
Br	2,33
—NO ₂	3,36
—NH ₂	1,57
—NH ₃ ⁺	1,97
—NHCOR	2,27
—OH, —OR	2,36
—OAr	2,36
—OCOR	1,46
Ar	1,83
—C=C	1,34
—C≡C	1,59
—C=N	1,59
—COR, —COOR, —COOH	1,50
—CONH ₂	2,27
—COAr	2,36
—SH, —SR	1,64
—SOR	2,94
R	0,68

CONTINUAÇÃO

TABLE B.2b Observed Methine Proton Chemical Shifts of Isopropyl Derivatives.

(CH ₃) ₂ CHZ		(CH ₃) ₂ CHZ	
Z	δ (ppm) obs	Z	δ (ppm) obs
H	1.33	HO	3.94
H ₃ C	1.56	RO	3.55
R	1.50	C ₆ H ₅ O	4.51
XCH ₂	1.85	R(H)C(=O)O	4.94
R(H)C(=O)	2.54	C ₆ H ₅ C(=O)O	5.22
C ₆ H ₅ C(=O)	3.58	F ₃ CC(=O)O	5.20
R(H)OC(=O)	2.52	ArSO ₂ O	4.70
R ₂ (H ₂)NC(=O)	2.44		
C ₆ H ₅	2.89	R(H)S	3.16
R ₂ (H ₂)C=CR(H)	2.62	RSS	2.63
R(H)C≡C	2.59		
N≡C	2.67	F	4.50
		Cl	4.14
R ₂ (H ₂)N	3.07	Br	4.21
R(H)C(=O)NH	4.01	I	4.24
O ₂ N	4.67		

(or other groups of low polarity). Friedrich and Runkle proposed the relationship

$$\delta_{\text{CHXYZ}} = \delta_{(\text{CH}_3)_2\text{CHZ}} = \Delta_{\text{XY}}$$

in which the X and Y substituents are alkyl groups or other groups of low polarity. The Z substituent covers a range of polarities. Δ_{xy} is a correction factor. The relationship states that the chemical shift of a methine proton with at least two low-polarity groups is equivalent to the chemical shift of an isopropyl methine proton plus correction factor.

The substituent constants for a Z substituent on an isopropyl methine proton are given in Table B.2b. The Δ_{xy} correction factors are given in Table B.2c.

The following example illustrates the joint use of Tables B.2b and B.2c, with CH₃, CH=CH₂, and C₆H₅ as substituents. The most polar substituent is always designated Z.

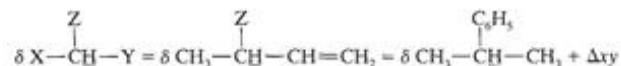


TABLE B.2c Correction Factors for Methine Substituents of Low Polarity.

Open-Chain Methine Proton Systems	Δ_{xy}	Cyclic Methine Proton Systems	Δ_{xy}
$\text{CH}_3-\overset{\text{Z}}{\underset{ }{\text{CH}}}-\text{CH}_3$	0.00		-1.0
$\text{CH}_3-\overset{\text{Z}}{\underset{ }{\text{CH}}}-\text{R}$	-0.20		+0.40
$\text{R}-\overset{\text{Z}}{\underset{ }{\text{CH}}}-\text{R}$	-0.40		+0.20
$\text{CH}_3-\overset{\text{Z}}{\underset{ }{\text{CH}}}-\text{CH}_2\text{X}$	+0.20		monosub. -0.20 axial H -0.45
$\text{CH}_3-\overset{\text{Z}}{\underset{ }{\text{CH}}}-\text{CH}=\text{CH}_2$	+0.40		equat. H +0.25
$\text{CH}_3-\overset{\text{Z}}{\underset{ }{\text{CH}}}-\text{C}_6\text{H}_5$	+1.15		0.00
$\text{R}-\overset{\text{Z}}{\underset{ }{\text{CH}}}-\text{C}_6\text{H}_5$	+0.90		0.00

From Table B.2b, $\delta = 2.89$ for $\text{CH}_3-\overset{\text{C}_6\text{H}_5}{\underset{|}{\text{CH}}}-\text{CH}_3$.

From Table B.2c, $\Delta_{\text{xy}} = 0.00$ for CH₃, $\Delta_{\text{xy}} = 0.40$ for CH=CH₂.

Therefore, $\delta \text{CH}_3-\overset{\text{C}_6\text{H}_5}{\underset{|}{\text{CH}}}-\text{CH}=\text{CH}_2 = 2.89 + 0.00 + 0.40 = 3.29$ (Found: $\delta = 3.44$).

DOIS OU MAIS SUBSTITUINTES EM *alfa* OU *beta*

Table II can be used to calculate chemical shifts of Y-CH₃, Y-CH₂-Z, or Y-CH-Z groups. Thus, the CH₂ chemical shifts in BrCH₂²CH₂¹OCH₂CH₂Br can be calculated.

1-CH ₂		2-CH ₂	
CH ₂ standard (footnote b)	1.20	CH ₂ standard	1.20
α-OR	2.35	α-Br	2.18
β-Br	0.60	β-OR	0.15
	4.15		3.53

Determined: 1-CH₂ at ~δ 3.80; 2-CH₂ at ~δ 3.40.

Table II. Substituent Effects on Chemical Shift^a



Substituent	Type of Hydrogen ^b	C-C-H	
		β	α
-C=C-	CH ₃	0.78	-
	CH ₂	0.75	0.10
	CH	-	-
-C=C-C-R X (X=C or O)	CH ₃	1.08	-
	CH ₂	-	-
Aryl	CH ₃	1.40	0.35
	CH ₂	1.45	0.53
	CH	1.33	-
-Cl	CH ₃	2.43	0.63
	CH ₂	2.30	0.53
	CH	2.55	0.03
-Br	CH ₃	1.81	1.23
	CH ₂	1.95	0.58
	CH	2.75	0.00
-OH	CH ₃	2.50	0.33
	CH ₂	2.30	0.13
	CH	2.20	-
-OR (R is saturated)	CH ₃	2.43	0.33
	CH ₂	2.35	0.15
	CH	2.00	-
-OC-R, -OC-OR, -OAr	CH ₃	2.88	0.38
	CH ₂	2.98	0.43
	CH	3.43 (esters only)	-
-CR, where R is alkyl, aryl, OH, OR', H, CO, or N	CH ₃	1.23	0.18
	CH ₂	1.05	0.31
	CH	1.05	-
-NRR'	CH ₃	1.30	0.13
	CH ₂	1.33	0.13
	CH	1.33	-

^aFrom the Ph.D. dissertation of T.J. Curphey, Harvard University, by permission.

^bStandard positions are CH₃, δ0.87; CH₂, δ1.20; CH, δ1.55.

DESLOCAMENTOS QUÍMICOS E CONSTANTES DE ACOPLAMENTO EM ALCINOS

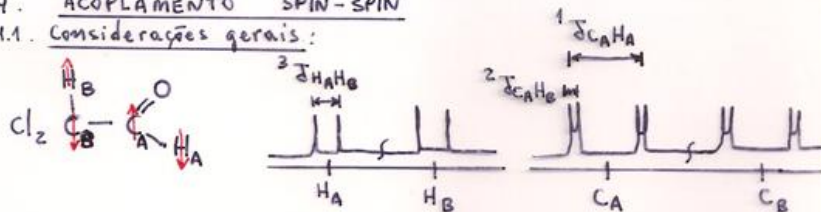
^1H -Chemical Shifts (δ in ppm relative to TMS) and Coupling Constants
(J in Hz) in Acetylene Derivatives

H-C \equiv C-H	1.80	$\overset{\text{a}}{\text{CH}_3}\text{-C}\equiv\text{C-}\overset{\text{b}}{\text{H}}$	(a) 1.80
H-C \equiv C-alkyl	1.7-1.9		(b) 1.80
H-C \equiv C-C=C	2.6-3.1	$\overset{\text{b}}{\text{CH}_3}\overset{\text{a}}{\text{CH}_2}\text{-C}\equiv\text{CH}$	(a) 2.16
H-C \equiv C-C \equiv C	1.7-2.4		(b) 1.15
H-C \equiv C- 	2.7-3.4	$\overset{\text{b}}{(\text{CH}_3)_2}\overset{\text{a}}{\text{CH}}\text{-C}\equiv\text{CH}$	(a) 2.59
			(b) 1.15
H-C \equiv C-O-alkyl	1.3	 - $\overset{\text{a}}{\text{SO}_3}\overset{\text{b}}{\text{CH}_2}\text{-C}\equiv\text{CH}$	(a) ~ 4.7
H-C \equiv C-CO	2.1-3.3		(b) 2.55
CH ₃ -C \equiv C-H	$ J = 2.9$	$\text{CH}_3\text{CONH}\overset{\text{a}}{\text{CH}_2}\text{-C}\equiv\text{CH}$	(a) 4.06
CH ₃ -C \equiv C-CH ₃	$ J = 2.7$		(b) 2.25
H-C \equiv C-C \equiv C-H	$ J = 2.2$		

CONSIDERAÇÕES GERAIS SOBRE ACOPLAMENTO SPIN-SPIN

4. ACOPLAMENTO SPIN-SPIN

4.1. Considerações gerais:



(a) Definição: é a interação entre o spin nuclear de um átomo com os spins dos núcleos vizinhos através das ligações.

(b) Constante de acoplamento (J): separação, em Hz, entre as linhas de um multiplete.

(c) Multiplicidade: # de linhas de um multiplete.
Depende do spin (I) e do # de núcleos vizinhos (n).
regra da multiplicidade: $2nI + 1$

(d) Sinal de J : (+) $\uparrow\downarrow$ (sentidos opostos)
(-) $\uparrow\uparrow$ (mesmo sentido)

(e) Representação do J : $n \begin{matrix} \text{---} \\ \text{---} \\ \text{---} \end{matrix} \begin{matrix} \text{---} \\ \text{---} \\ \text{---} \end{matrix} \begin{matrix} \text{---} \\ \text{---} \\ \text{---} \end{matrix}$ $\begin{cases} n = \# \text{ de lig. entre spins} \\ xy = \text{núcleos acoplados} \end{cases}$

(f) Espectros de 1ª ordem: $\frac{\Delta\delta}{J} \geq 10$ $\Delta\delta$

* A resolução das linhas espectrais dependem do B_0

TRIÂNGULO DE PASCAL (Multiplicidade, intens. Relativa de sinais)

ESPECTROMETRIA DE RMN DE HIDROGÊNIO

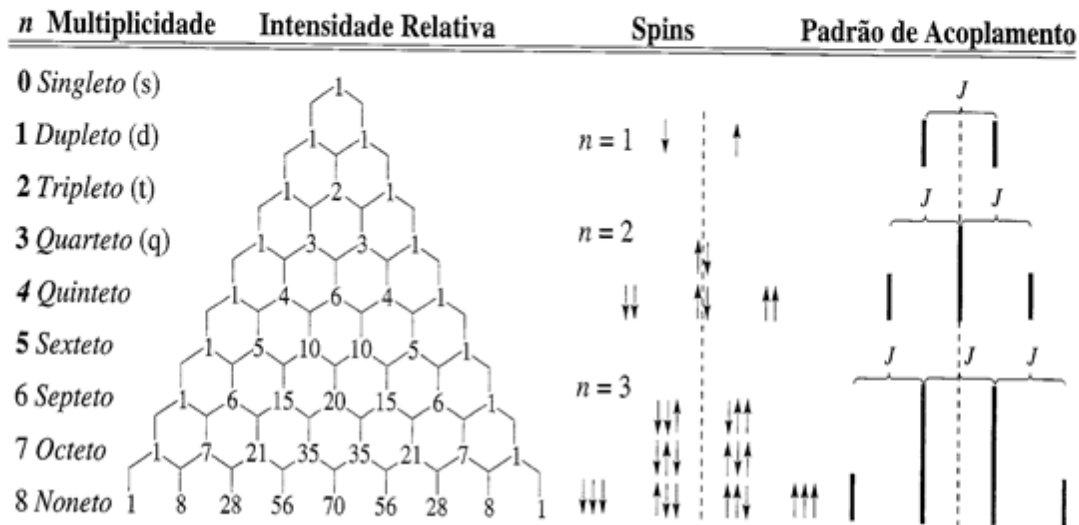





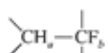

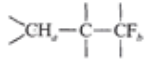

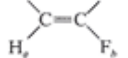
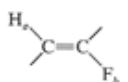
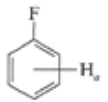

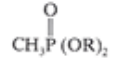
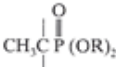
FIGURA 3.32 Triângulo de Pascal. Intensidades relativas dos multipletos de primeira ordem; n = número de núcleos equivalentes de spin $1/2$ que se acoplam (isto é, núcleos de hidrogênio).

CONSTANTES DE ACOPLAMENTO (J)

APPENDIX F PROTON SPIN-COUPLING CONSTANTS

J_{AB} (Hz)	J_{AB} Typical	Type	J_{AB} (Hz)	J_{AB} Typical	Type	
0-30	12-15		6-12	10		
6-8	7		0-3	1-2	CH ₂ -CH ₃ (free rotation)	
0-1	0		4-10	7		
			0-3	1.5		
6-14	8-10		0-3	2	ax-ax	
0-5	2-3		9-13	10	ax-eq	
0-5	2-3	C=CH ₂ -CH=CH ₂	3 member	0.5-2.0	eq-eq	
cis 5-10			4 member	2.5-4.0		
trans 5-10			5 member	5.1-7.0	(cis or trans)	
			6 member	8.8-11.0		
			7 member	9-13		
			8 member	10-13		
cis 4-12		CH ₂ -C≡CH	2-3			
trans 2-10		-CH ₂ -C≡C-CH ₂ -	2-3		(cis or trans)	
				6		
cis 7-13				4	(cis or trans)	
trans 4-9				2.5		
change	4-10	5			CH ₂ -OH ₂ (no exchange)	
			J (ortho)	6-10	9	
	1-3	2-3	J (meta)	1-3	3	C=CH ₂ -CH ₃
			J (para)	0-1	~0	
	5-8	6	J (2-3)	5-6	5	C=CH ₂ -CH ₃
			J (3-4)	7-9	8	
			J (2-4)	1-2	1.5	
			J (3-5)	1-2	1.5	
	12-18	17	J (2-5)	0-1	1	
			J (2-6)	0-1	~0	
			J (2-3)	1.3-2.0	1.8	
			J (3-4)	3.1-3.8	3.6	
	0-3	0-2	J (2-4)	0-1	~0	
			J (2-5)	1-2	1.5	

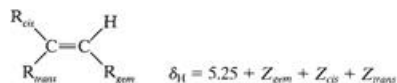
CONSTANTES DE ACOPLAMIENTO

Type	J_{ab} (Hz)	J_{ab} Typical	Type	J_{ab} (Hz)	J_{ab} Typical
	$J(2-3)$	4.9-6.2	5.4	Proton-Carbon-13 (See Tables 5.17, 5.18)	
	$J(3-4)$	3.4-5.0	4.0		
	$J(2-4)$	1.2-1.7	1.5		
	$J(2-5)$	3.2-3.7	3.4	Proton-Fluorine	
	$J(1-3)$	2-3			44-81
	$J(2-3)$	2-3			
	$J(3-4)$	3-4			
	$J(2-4)$	1-2			
	$J(2-5)$	1.5-2.5			
	$J(4-5)$	4-6			3-25
	$J(2-5)$	1-2			0-4
	$J(2-4)$	0-1			
	$J(4-6)$	2-3			
	$J(4-5)$	3-4			1-8
	$J(2-4)$	~0			
	$J(2-5)$	1-2			12-40
					o 6-10 m 5-6 p 2
				α $H_3C-C(=O)-CH_2F$ γ	$\alpha\gamma$ 4.3 $\beta\gamma$ 48
Proton-Phosphorus					
			630-707		
$(CH_3)_3P$			2.7		
$(CH_3)_3P=O$			13.4		
$(CH_3CH_2)_3P$			0.5 (HCCP) 13.7 (HCP)		
$(CH_3CH_2)_3P=O$			11.9 (HCCP) 16.3 (HCP)		
			10-13		
			15-20		
$CH_3OP(OR)_2$			10.5-12		
$P[N(CH_3)_2]_3$			8.8		
$O=P[N(CH_3)_2]_3$			9.5		

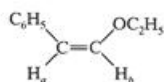
CÁLCULO DE DESLOC. QUÍMICO PARA ALCENOS

APPENDIX D CHEMICAL SHIFTS IN UNSATURATED AND AROMATIC SYSTEMS

(See Table D.1)



For example, the chemical shifts of the alkene protons in



are calculated:

H _a	C ₆ H ₅ _{gem}	1.35	5.25
	OR _{trans}	-1.28	0.07
		0.07	δ 5.32
H _b	OR _{gem}	1.18	5.25
	C ₆ H ₅ _{trans}	-0.10	1.08
		1.08	δ 6.33

TABLE D.1 Substituent Constants (Z) for Chemical Shifts of Substituted Ethylenes.

Substituent R	Z			Substituent R	Z		
	gem	cis	trans		gem	cis	trans
-H	0	0	0		1.03	0.97	1.21
-Alkyl	0.44	-0.26	-0.29		1.37	0.93	0.35
-Alkyl-ring ^a	0.71	-0.33	-0.30		1.10	1.41	0.99
-CH ₂ O, -CH ₂ I	0.67	-0.02	-0.07	-OR, R: aliph	1.18	-1.06	-1.28
-CH ₂ S	0.53	-0.15	-0.15	-OR, R: conj ^b	1.14	-0.65	-1.05
-CH ₂ Cl, -CH ₂ Br	0.72	0.12	0.07	-OCOR	2.09	-0.40	-0.67
-CH ₂ N	0.66	-0.05	-0.23	-Aromatic	1.35	0.37	-0.10
-C≡C	0.50	0.35	0.10	-Cl	1.00	0.19	0.03
-C≡N	0.23	0.78	0.58	-Br	1.04	0.40	0.55
-C=C	0.98	-0.04	-0.21		0.69	-1.19	-1.31
-C=C conj ^b	1.26	0.08	-0.01		2.30	-0.73	-0.81
-C=O	1.10	1.13	0.81	-SR	1.00	-0.24	-0.04
-C=O conj ^b	1.06	1.01	0.95	-SO ₂	1.58	1.15	0.95
-COOH	1.00	1.35	0.74				
-COOH conj ^b	0.69	0.97	0.39				
-COOR	0.84	1.15	0.56				
-COOR conj ^b	0.68	1.02	0.33				

^a Alkyl ring indicates that the double bond is part of the ring

^b The Z factor for the conjugated substituent is used when either the substituent or the double bond is further conjugated with other groups.

Source: Pascual C., Meier, J., and Simon, W. (1966) *Helv. Chim. Acta*, 49, 164.

ESPECTRO DE UM ALCENO MONOSSUBSTITUÍDO

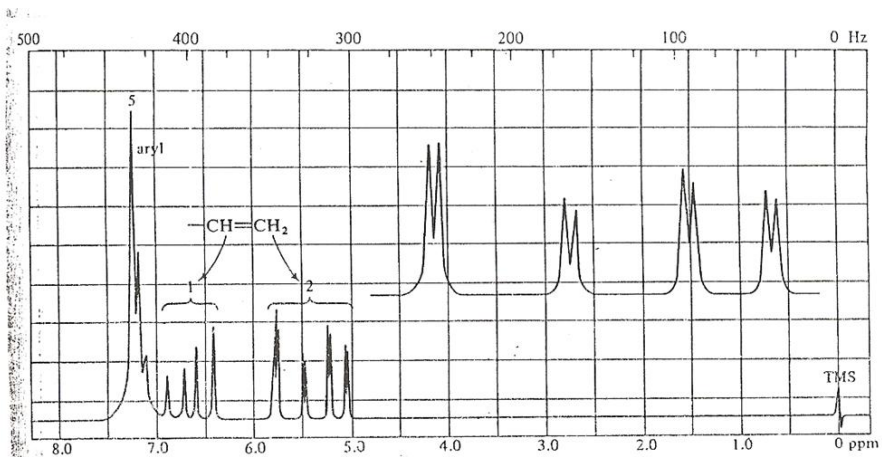


Figure 9.6. Nmr spectrum of styrene, $C_6H_5CH=CH_2$. (The superimposed line is a higher-resolution, expanded spectrum of the eight peaks between 5.0 and 6.0 ppm.)

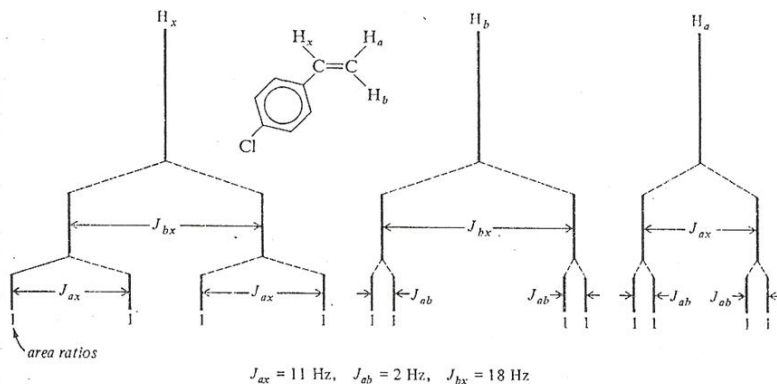
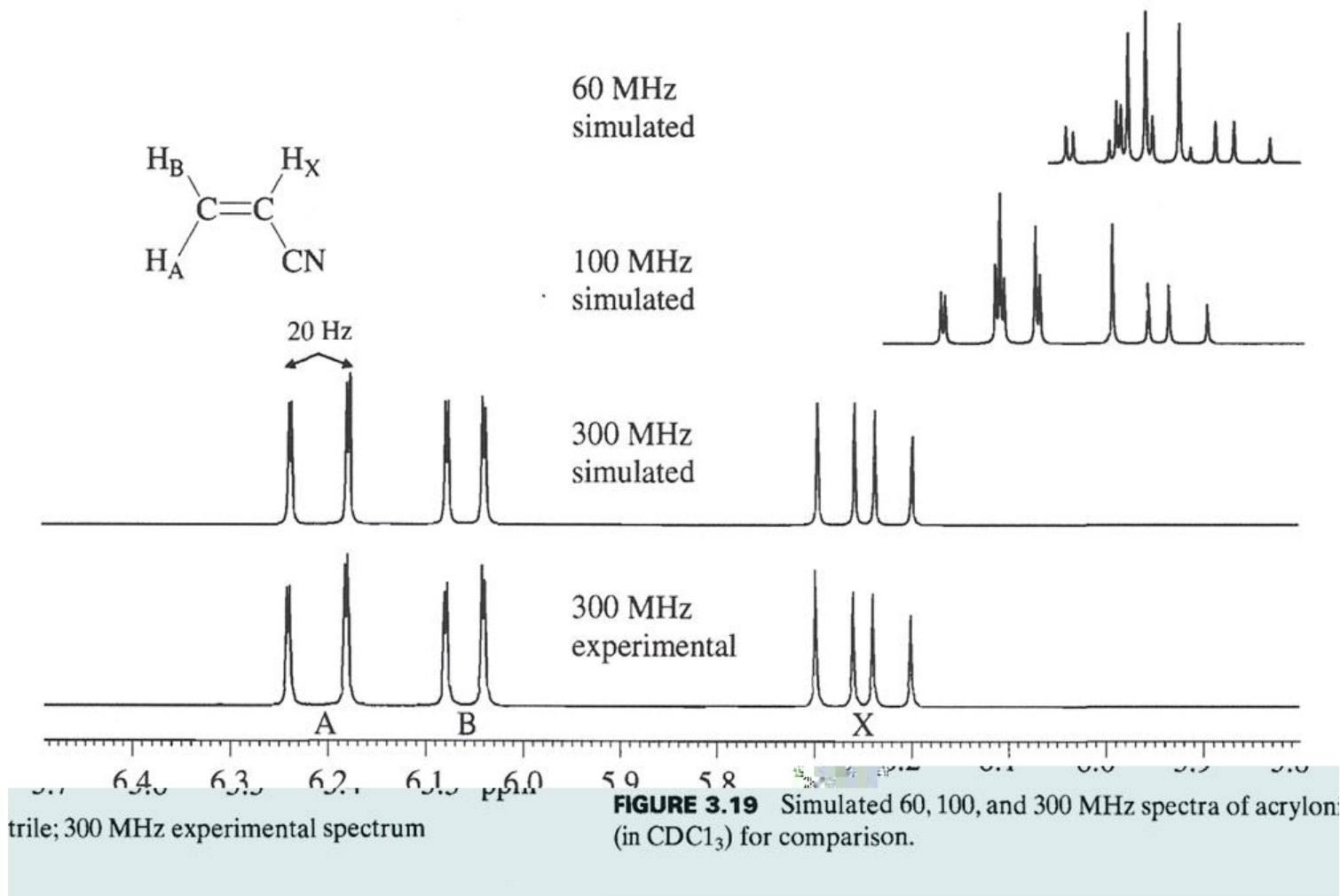


Figure 9.5. Tree diagrams for the splitting patterns of the three double-bond protons in *p*-chlorostyrene.

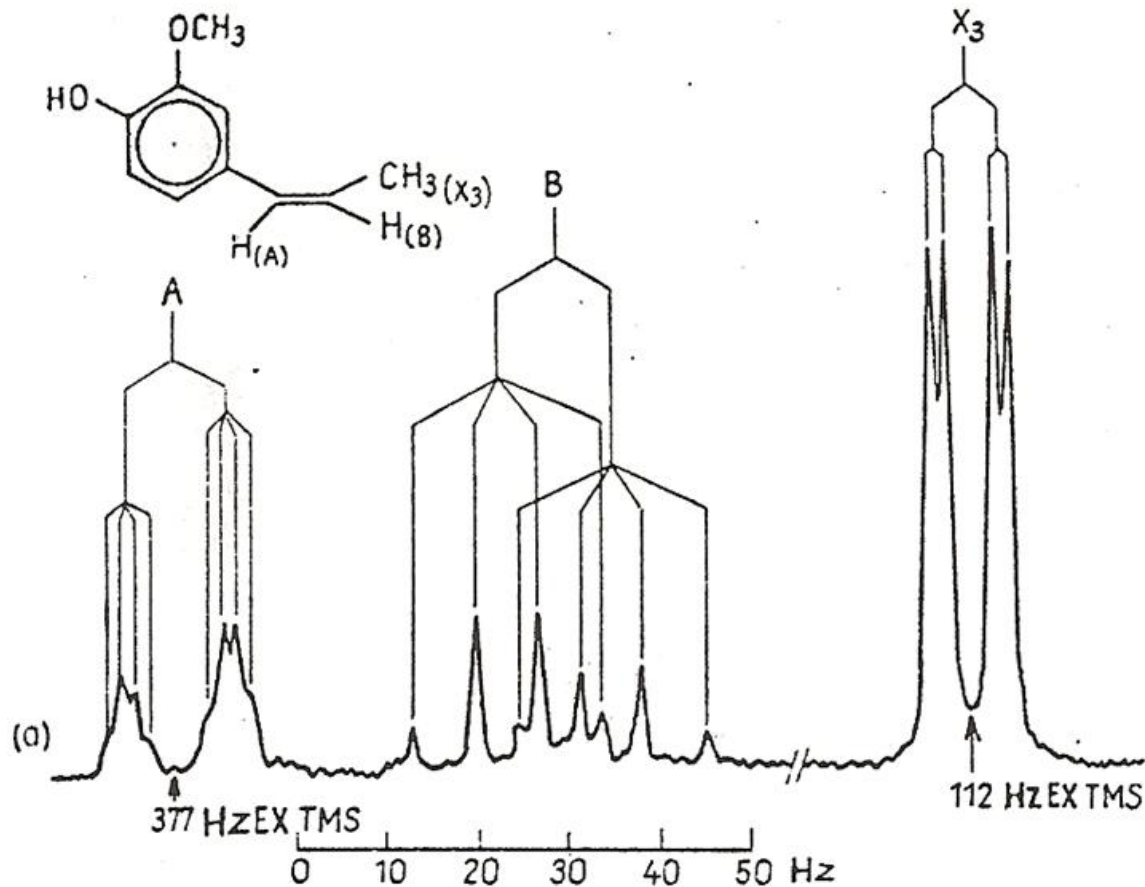
ESPECTRO DE UM ALCENO MONOSSUBSTITUÍDO



trile; 300 MHz experimental spectrum

FIGURE 3.19 Simulated 60, 100, and 300 MHz spectra of acrylonitrile; 300 MHz experimental spectrum (in CDCl_3) for comparison.

ESPECTRO TÍPICO DE UM COMPOSTO VINÍLICO DISSUBSTITUÍDO



ABX₃ Analysis

δ_A	6.28 ppm
δ_B	5.59 ppm
δ_X	1.87 ppm
J_{AB}	11.6 Hz
J_{AX}	1.6 Hz
J_{BX}	7.0 Hz

ESPECTRO DO *trans*-EUGENOL

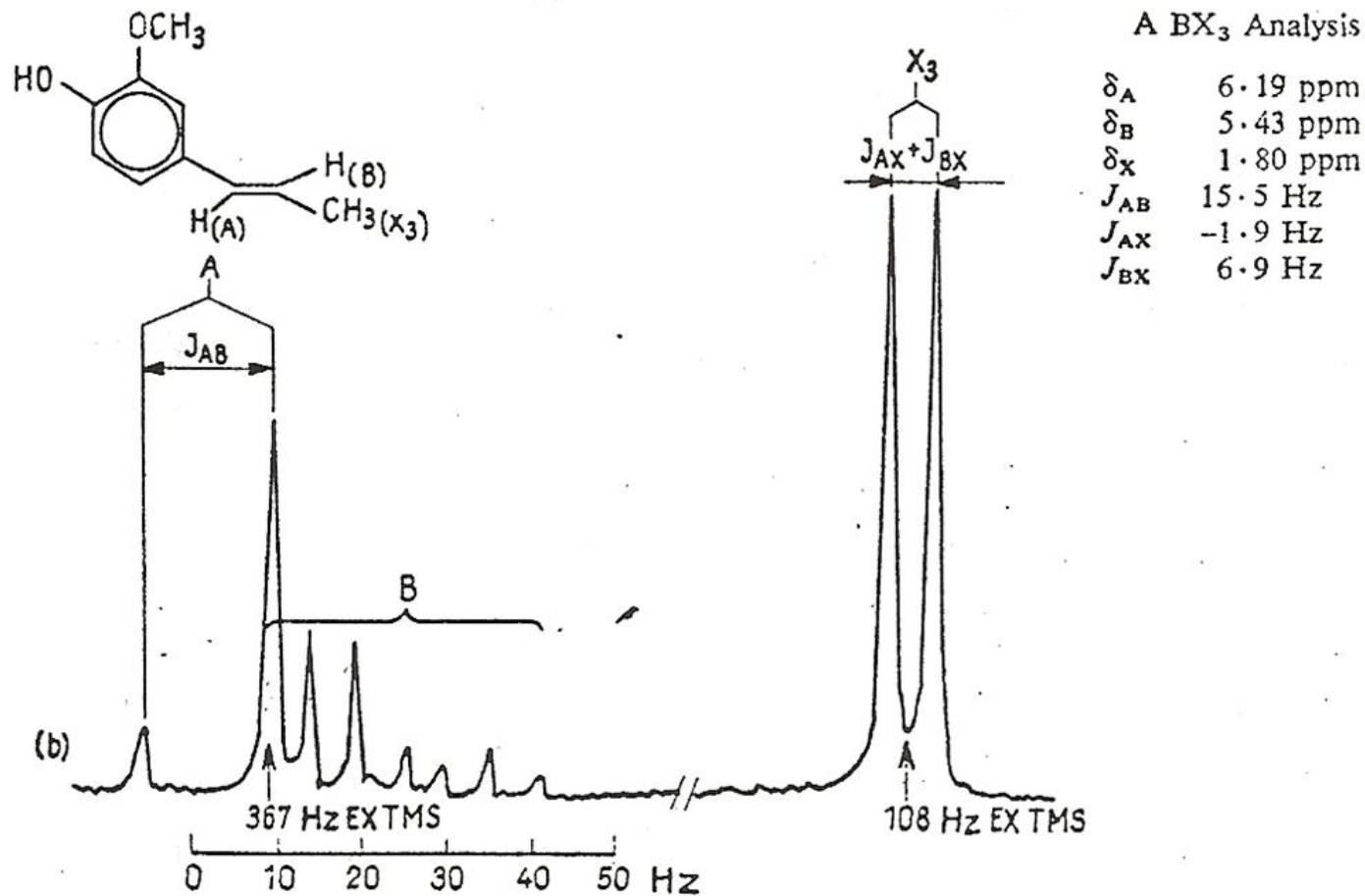


FIG. 2-3-9. 60 MHz spectra of (a) *cis* and (b) *trans*-isoeugenol (ca. 10 per cent in CDCl₃).²¹⁴⁴

CÁLCULO DE DESLOC. QUÍMICO EM BENZENO SUBSTITUÍDOS

CHART D.1 CHEMICAL SHIFTS OF PROTONS ON MONOSUBSTITUTED BENZENE RINGS

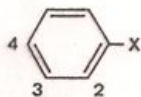
	9	.8	.6	.4	.2	8	.8	.6	.4	.2	7	.8	.6	.4	.2	6	8
Benzene ^a																	
CH ₃ (omp)											:						
CH ₂ CH ₂ (omp)											:						
(CH ₂) ₂ CH (omp)											:						
(CH ₂) ₂ C o,m,p											:	:	:				
C=CH ₂ (omp)											:						
C≡CH o, (mp)											:	:					
Phenyl o, m, p											:	:	:				
CF ₃ (omp)											:						
CH ₂ Cl (omp)											:						
CHCl ₂ (omp)											:						
CCl ₃ o, (mp)						:			:								
CH ₂ OH (omp)											:						
CH ₂ OR (omp)											:						
CH ₂ OC(=O)CH ₃ (omp)											:						
CH ₂ NH ₂ (omp)											:						
F m,p,o											:	:	:				
Cl (omp)											:						
Br o, (pm)											:	:					
I o,p,m							:		:	:							
OH m,p,o											:	:	:				
OR m, (op)											:	:					
OC(=O)CH ₃ m,p,o											:	:	:				
OTs ^b (mp), o											:	:	:				
CH(=O)o,p,m						:	:	:									
C(=O)CH ₃ o, (mp)						:	:										
C(=O)OH o, p, m						:	:	:									
C(=O)OR o, p, m						:	:	:									
C(=O)Cl o, p, m						:	:	:									
C≡N (omp)											:						
NH ₂ m,p,o											:	:	:				
N(CH ₂) ₂ m(op)											:	:	:				
NHC(=O)R o,m,p											:	:	:				
NH ₂ ⁺ o (mp)						:	:										
NO ₂ o,p,m						:	:	:									
SR (omp)											:						
N=C=O (omp)											:						

^a The benzene ring proton is at δ 7.27, from which the shift increments are calculated as shown at the end of Section 3.4.

^b OTS = *p*-toluenesulfonyloxy group.

CÁLCULO DE DESL. QUÍM. EM BENZENOS POLISSUBSTITUIDOS

Effect of a Substituent on the Chemical Shift of the Ring-Protons
in Benzene (δ in ppm relative to TMS)



$$\delta_{H_i} = 7.26 + z_i$$

Substituent X	z_2	z_3	z_4
-H	0	0	0
-CH ₃	-0.20	-0.12	-0.22
-CH ₂ CH ₃	-0.14	-0.06	-0.17
-CH(CH ₃) ₂	-0.13	-0.08	-0.18
-C(CH ₃) ₃	0.02	-0.08	-0.21
-CH ₂ Cl	0.00	0.00	0.00
-CF ₃	0.32	0.14	0.20
C -CCl ₃	0.64	0.13	0.10
-CH ₂ OH	-0.07	-0.07	-0.07
-CH=CH ₂	0.06	-0.03	-0.10
-CH=CH-phenyl	0.15	-0.01	-0.16
-C≡CH	0.15	-0.02	-0.01
-C≡C-phenyl	0.19	0.02	0.00
-phenyl	0.37	0.20	0.10
H -F	-0.26	0.00	-0.20
A -Cl	0.03	-0.02	-0.09
L -Br	0.18	-0.08	-0.04
-I	0.39	-0.21	0.00
-OH	-0.56	-0.12	-0.45
-OCH ₃	-0.48	-0.09	-0.44
-OCH ₂ CH ₃	-0.46	-0.10	-0.43
O -O-phenyl	-0.29	-0.05	-0.23
-OCOCH ₃	-0.25	0.03	-0.13
-OCO-phenyl	-0.09	0.09	-0.08
-OSO ₂ CH ₃	-0.05	0.07	-0.01

CÁLCULO DE DESL. QUÍM. EM BENZENOS POLISSUBSTITUIDOS

BENZENE, SUBSTITUENT EFFECTS

Substituent X	ρ_2	ρ_3	ρ_4
-NH ₂	-0.75	-0.25	-0.65
-NHCH ₃	-0.80	-0.22	-0.68
-N(CH ₃) ₂	-0.66	-0.18	-0.67
-N ⁺ (CH ₃) ₃ I ⁻	0.69	0.36	0.31
N -NHCOCH ₃	0.12	-0.07	-0.28
-N(CH ₃)COCH ₃	-0.16	0.05	-0.02
-NHNH ₂	-0.60	-0.08	-0.55
-N=N-phenyl	0.67	0.20	0.20
-NO	0.58	0.31	0.37
-NO ₂	0.95	0.26	0.38
-SH	-0.08	-0.16	-0.22
-SCH ₃	-0.08	-0.10	-0.24
S -S-phenyl	0.06	-0.09	-0.15
-SO ₃ CH ₃	0.60	0.26	0.33
-SO ₂ Cl	0.76	0.35	0.45
-CHO	0.56	0.22	0.29
-COCH ₃	0.62	0.14	0.21
-COCH ₂ CH ₃	0.63	0.13	0.20
-COC(CH ₃) ₃	0.44	0.05	0.05
C=O -CO-phenyl	0.47	0.13	0.22
-COOH	0.85	0.18	0.27
-COOCH ₃	0.71	0.11	0.21
-COOCH(CH ₃) ₂	0.70	0.09	0.19
-COO-phenyl	0.90	0.17	0.27
-CONH ₂	0.61	0.10	0.17
-COCl	0.84	0.22	0.36
-COBr	0.80	0.21	0.37
-CH=N-phenyl	0.6	0.2	0.2
-CN	0.36	0.18	0.28
-Si(CH ₃) ₃	0.22	-0.02	-0.02
-PO(OCH ₃) ₂	0.48	0.16	0.24

MUDANÇAS EM DESL. QUÍMICO EM BENZENOS MONOSSUBSTITUÍDOS

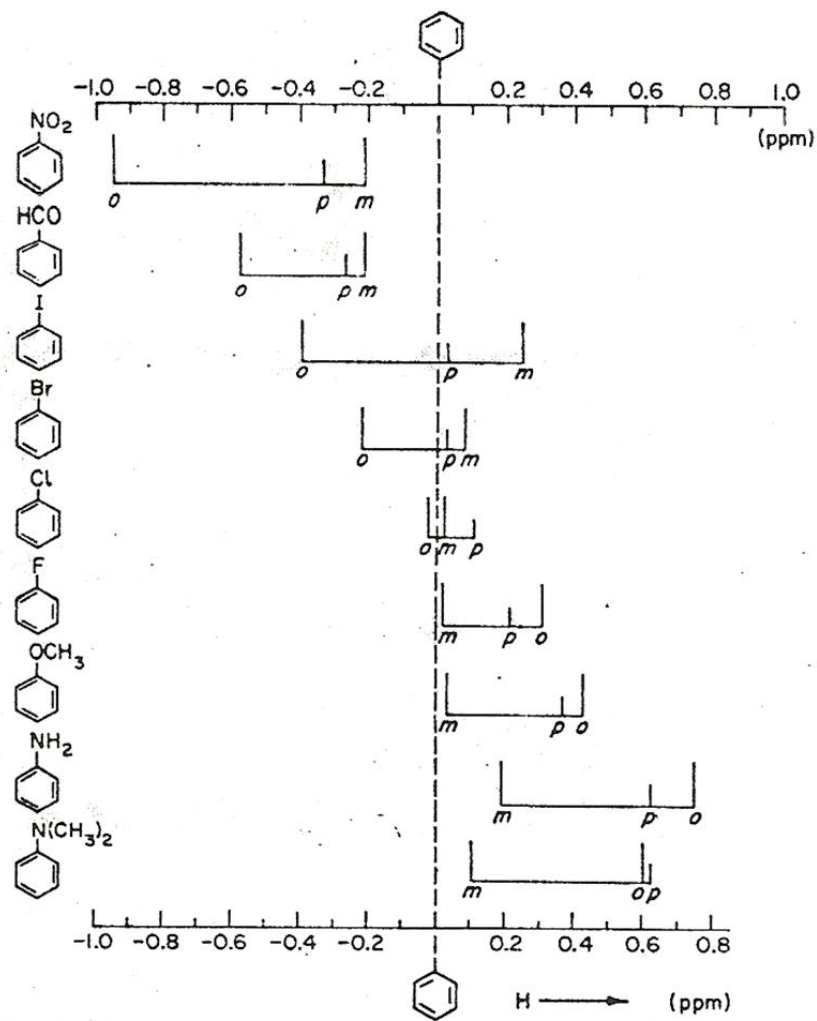


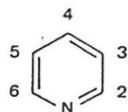
Fig. 4.10 Changes in ^1H chemical shifts in monosubstituted benzenes relative to benzene. Values are given as $(\delta_{\text{benzene}} - \delta_{\text{subs}})$ (Spiesscke and Schneider⁶¹).

CONSTANTES DE BLINDAGEM EM PIRIDINAS SUBSTITUÍDAS

Effect of a Substituent on the Chemical Shift of the Ring-Protons in Monosubstituted Pyridines

(δ in ppm relative to TMS, solvent: dimethyl sulfoxide)

(For couplings and chemical shifts in CDCl_3 as the solvent see p. H275.)



$$\delta_{H_2} = 8.59 + Z_{i2}$$

$$\delta_{H_3} = 7.38 + Z_{i3}$$

$$\delta_{H_4} = 7.75 + Z_{i4}$$

$$\delta_{H_5} = 7.38 + Z_{i5}$$

$$\delta_{H_6} = 8.59 + Z_{i6}$$

2- or 6-Substituent (i = 2 or 6)	$Z_{23} = Z_{65}$	$Z_{24} = Z_{64}$	$Z_{25} = Z_{63}$	$Z_{26} = Z_{62}$
-H	0	0	0	0
-CH ₃	-0.11	-0.01	-0.16	0.08
-CH ₂ CH ₃	-0.09	-0.08	-0.15	0.03
-CH ₂ -phenyl	0.12	-0.08	-0.20	0.02
-CH ₂ OH	0.37	0.30	0.02	0.06
C -CH ₂ NH ₂	0.20	0.07	-0.09	0.05
-CH ₂ SC ₃ H ₇	0.04	-0.08	-0.26	-0.06
-CH ₂ SO ₂ -Phenyl	~0	~-0.3	~0	-0.2
-CH=CH ₂	0.11	-0.14	-0.11	0.04
-phenyl	0.16	-0.28	-0.40	-0.03
-2-pyridyl	1.12	-0.09	-0.26	0.00
H -F	-0.10	0.40	0.12	-0.13
A -Cl	0.32	0.29	0.29	0.20
L -Br	0.41	0.17	0.19	0.02
-OH	-0.7	0.0	-1.0	-0.9
-O-n-C ₄ H ₉	-0.53	-0.03	-0.49	-0.32
-NH ₂	-0.68	-0.31	-0.78	-0.48
-NHCOCH ₃	0.94	0.16	-0.20	-0.10
N -NHCOOCH ₂ CH ₃	0.59	0.07	-0.24	-0.21
-NHNO ₂	0.34	0.31	-0.03	-0.41
-NO ₂	1.09	0.67	0.74	0.26
-CHO	0.93	0.42	0.50	0.44
O -COCH ₃	0.82	0.37	0.39	0.28
-CO-phenyl	0.62	0.55	0.32	0.28
-COOH	0.97	0.43	0.48	0.42
C -COO-n-C ₄ H ₉	0.86	0.39	0.35	0.35
-CONH ₂	1.05	0.47	0.43	0.30
-CSNH ₂	1.41	0.37	0.33	0.25
-CH=NOH	0.40	0.28	0.01	0.16
-CN	0.88	0.38	0.55	0.39

CONSTANTES DE BLINDAGEM EM PIRIDINAS SUBSTITUÍDAS

¹H-NMR

PYRIDINE, SUBSTITUENT EFFECTS

3- or 5-Substituent (i = 3 or 5)	$Z_{32} = Z_{56}$	$Z_{34} = Z_{54}$	$Z_{35} = Z_{53}$	$Z_{36} = Z_{52}$
-H	0	0	0	0
-CH ₃	-0.02	-0.06	-0.09	-0.02
-CH ₂ OH	0.11	0.15	0.04	-0.04
-CH ₂ NH ₂	0.16	0.13	0.04	0.00
-CH ₂ SO ₂ -phenyl	-0.24	-0.15	-0.22	0.01
-CH=CHCOOH	0.45	0.52	0.34	0.17
HAL				
-Cl	0.20	0.24	0.19	0.09
-Br	0.20	0.43	0.34	0.18
-OH	-0.03	-0.37	0.15	-0.24
N				
-NH ₂	-0.06	-0.49	0.02	-0.36
-NHCOCH ₃	0.37	0.50	0.06	-0.16
-SO ₃ H	0.70	1.14	0.81	0.70
O				
-CHO	0.45	0.42	0.12	0.20
-COCH ₃	0.72	0.68	0.30	0.37
-CO-phenyl	0.47	0.54	0.37	0.34
C				
-COOCH ₃	0.62	0.60	0.23	0.34
-CSNH ₂	0.68	0.67	0.24	0.26
-CH=NOH	0.39	0.43	0.19	0.15
-CN	0.63	0.72	0.43	0.50

4-Substituent (i = 4)	$Z_{42} = Z_{46}$	$Z_{43} = Z_{45}$
-H	0	0
-CH ₃	0.01	-0.10
-CH ₂ -phenyl	0.00	-0.15
-CH ₂ OH	0.07	0.14
-CH ₂ NH ₂	0.01	0.03
-CH ₂ S-n-C ₃ H ₇	-0.06	-0.13
-CH ₂ SO ₂ -phenyl	-0.09	-0.18
-CH=CH ₂	0.12	0.13
-Cl	0.00	0.05
-Br	0.09	0.35
-OCH ₃	0.02	-0.29
-NH ₂	-0.15	-0.74
N		
-NHCOCH ₃	-0.05	0.31
S		
-SCH ₂ -phenyl	-0.02	0.04
-S-phenyl	0.05	-0.16
-CHO	0.47	0.58
-COCH ₃	0.40	0.58
-CO-phenyl	0.36	0.40
O		
-COO-n-C ₄ H ₉	0.34	0.54
-CSNH ₂	0.35	0.68
-CH=NOH	0.24	0.37
-CN	0.46	0.62

CONSTANTES DE BLINDAGEM PARA PIRRÓIS



$\delta_{H_1} = 7-12$ (strongly solvent-dependent, generally broad)

$$\delta_{H_2} = 6.62 + z_{12}$$

$$\delta_{H_3} = 6.05 + z_{13}$$

$$\delta_{H_4} = 6.05 + z_{14}$$

$$\delta_{H_5} = 6.62 + z_{15}$$

1-Substituent (i = 1)	$z_{12} = z_{15}$	$z_{13} = z_{14}$
-H	0	0
-CH ₃	-0.25	-0.13
-CH ₂ CH ₃	-0.16	-0.12
-CH ₂ -phenyl	-0.12	-0.04
-phenyl	0.33	0.14
-COCH ₃	0.56	0.12

2- or 5-Substituent (i = 2 or 5)	$z_{23} = z_{54}$	$z_{24} = z_{53}$	$z_{25} = z_{52}$
-H	0	0	0
-CH ₃	-0.33	-0.16	-0.26
-NO ₂	1.06	0.24	0.43
-SCH ₃	0.18	0.05	0.10
-SCN	0.48	0.10	0.28
-CHO	0.93	0.27	0.61
-COCH ₃	0.78	0.10	0.44
-COOCH ₃	0.79	0.13	0.29
-CN	0.83	0.23	0.51

3- or 4-Substituent (i = 3 or 4)	$z_{32} = z_{45}$	$z_{34} = z_{43}$	$z_{35} = z_{42}$
-H	0	0	0
-CH ₃	-0.34	-0.20	-0.20
-NO ₂	1.04	0.70	0.13
-COCH ₃	0.79	0.63	0.15
-COOCH ₃	0.90	0.73	0.16

CONSTANTES DE BLINDAGEM PARA FURANOS



$$\delta_{H_2} = 7.38 + z_{i2}$$

$$\delta_{H_3} = 6.30 + z_{i3}$$

$$\delta_{H_4} = 6.30 + z_{i4}$$

$$\delta_{H_5} = 7.38 + z_{i5}$$

2- or 5-Substituent (i = 2 or 5)	z ₂₃ = z ₅₄	z ₂₄ = z ₅₃	z ₂₅ = z ₅₂
C			
-H	0	0	0
-CH ₃	-0.42	-0.12	-0.17
-CH ₂ OH	-0.11	-0.05	-0.08
-CH ₂ NH ₂	-0.24	-0.06	-0.10
-CH=CHCHO	0.70	0.35	0.42
HAL			
-Br	-0.02	0.03	-0.01
-I	0.12	-0.13	-0.01
O			
-OCH ₃	-1.34	-0.23	-0.68
N			
-NO ₂	1.21	0.55	0.51
S			
-SCH ₃	-0.12	-0.06	-0.09
-SCN	0.40	0.06	0.10
-CHO	0.93	0.31	0.34
-COCH ₃	0.81	0.23	0.19
O			
-COCF ₃	1.34	0.50	0.64
-COOH	0.94	0.33	0.41
C			
-COOCH ₃	0.85	0.22	0.25
-COCl	1.20	0.39	0.48
-CN	0.85	0.32	0.28
3- or 4-Substituent (i = 3 or 4)	z₃₂ = z₄₅	z₃₄ = z₄₃	z₃₅ = z₄₂
-H	0	0	0
-CH ₃	-0.27	-0.17	-0.15
-I	-0.13	0.04	-0.22
-OCH ₃	-0.46	-0.28	-0.37
-SCH ₃	-0.18	-0.05	-0.15
-SCN	0.19	0.19	0.03
-CHO	0.48	0.37	-0.07
-COCH ₃	0.46	0.36	-0.12
-COOH	0.89	0.54	0.36
-COOCH ₃	0.45	0.33	-0.14
-CN	0.45	0.22	-0.02

CONSTANTES DE BLINDAGEM PARA TIOFENOS



$$\begin{aligned}\delta_{H_2} &= 7.20 + Z_{12} \\ \delta_{H_3} &= 6.96 + Z_{13} \\ \delta_{H_4} &= 6.96 + Z_{14} \\ \delta_{H_5} &= 7.20 + Z_{15}\end{aligned}$$

2- or 5-Substituent (i = 2 or 5)	$Z_{23} = Z_{54}$	$Z_{24} = Z_{53}$	$Z_{25} = Z_{52}$
-H	0	0	0
C -CH ₃	-0.36	-0.24	-0.29
-C≡CH	0.15	-0.16	-0.12
-Cl	-0.25	-0.22	-0.22
HAL -Br	-0.05	-0.27	-0.11
-I	0.13	-0.33	0.01
O -OH ¹⁾	-0.72	0.59	-3.10
-OCH ₃	-0.94	-0.43	-0.82
N -NH ₂	-0.95	-0.45	-0.85
-NO ₂	0.82	-0.03	0.30
-SH	0.00	-0.20	-0.07
S -SCH ₃	-0.03	-0.18	-0.05
-SCN	0.30	-0.05	0.28
-SO ₂ CH ₃	1.03	0.20	0.79
-SO ₂ Cl	0.73	0.06	0.45
-CHO	0.65	0.10	0.45
O C -COCH ₃	0.57	0.00	0.28
-COOH	0.80	0.08	0.40
 / \ -COOCH ₃	0.70	-0.05	0.20
-COCl	0.88	0.06	0.44
-CN	0.47	0.00	0.28
3- or 4-Substituent (i = 3 or 4)	$Z_{32} = Z_{45}$	$Z_{34} = Z_{43}$	$Z_{35} = Z_{42}$
-H	0	0	0
C -CH ₃	-0.45	-0.22	-0.14
-Cl	-0.22	-0.11	-0.03
HAL -Br	-0.12	-0.08	-0.10
-I	0.06	0.00	-0.19
O -OCH ₃	-1.10	-0.38	-0.20
N -NH ₂	-1.25	-0.53	-0.25
-NO ₂	0.95	0.60	0.03
-SH	-0.22	-0.20	-0.10
S -SCH ₃	-0.33	-0.10	-0.03
-SCN	0.25	0.05	0.05
-SO ₂ CH ₃	0.96	0.48	0.46
-CHO	0.79	0.45	0.03
O C -COCH ₃	0.68	0.47	-0.02
-COOH	0.99	0.48	0.24
 / \ -COOCH ₃	0.78	0.47	-0.05
-COCl	1.05	0.50	0.03
-CN	0.63	0.20	0.15

DESLOCAMENTOS QUÍMICOS DE ALGUNS AROMÁTICOS E HETEROAROMÁTICOS

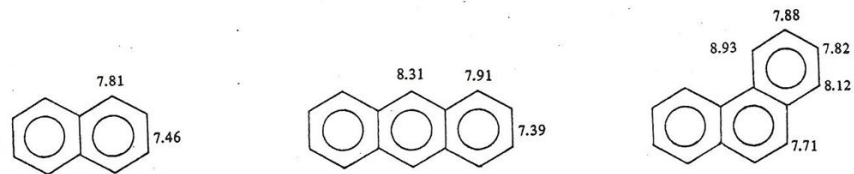


Table V. Chemical Shifts of Protons on Heteroaromatic Rings

