CÁLCULO DO DESLOCAMENTO QUÍMICO

Absorções características dos deslocamentos químicos

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

M—CH₂R
M—C—C
M—C—C
M—C—O
M—P
M—Cl
M—Br
M—I
M—OEt
M—OR
M—O
M—OC(=O)R
M—OC(=O)O
M—OC(=O)F₂
M—OEt*
M—Cl(=O)H
M—Cl(=O)O
M—Cl(=O)OH
M—Cl(=O)OR
M—Cl(=O)NR₂
M—CN
M—NH₂
M—NR₂
M—NHR
M—N’R₂
M—NHC(=O)R
M—NCO₂
CHART 2. CHEMICAL SHIFTS OF PROTONS ON A CARBON
ATOM ONCE REMOVED (β-POSITION) FROM A
FUNCTIONAL GROUP IN ALIPHATIC COMPOUNDS (M-C-Y).
appendix b. effect on chemical shifts of two or three functional groups (Y-CH₂-Z, and Y-CH-Z)

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:

<table>
<thead>
<tr>
<th></th>
<th>0.23</th>
<th>4.18</th>
<th>4.41</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅</td>
<td>1.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>2.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus, 4.41 = δ value for the -CH₂- group.

Table 1. Shielding Constants

<table>
<thead>
<tr>
<th>Y or Z</th>
<th>Shielding Constants</th>
<th>Y or Z</th>
<th>Shielding Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₃</td>
<td>0.47</td>
<td>-C(=O)NR₂</td>
<td>1.59</td>
</tr>
<tr>
<td>-C≡C</td>
<td>1.32</td>
<td>-CN</td>
<td>1.70</td>
</tr>
<tr>
<td>-C≡C</td>
<td>1.44</td>
<td>-NR₂</td>
<td>1.47</td>
</tr>
<tr>
<td>-φ</td>
<td>1.85</td>
<td>-NHC(=O)R</td>
<td>2.27</td>
</tr>
<tr>
<td>-CF₃</td>
<td>1.21</td>
<td>-N₃</td>
<td>1.97</td>
</tr>
<tr>
<td>-CF₃</td>
<td>1.14</td>
<td>-SR</td>
<td>1.64</td>
</tr>
<tr>
<td>-Cl</td>
<td>2.53</td>
<td>-OSO₄R</td>
<td>3.13</td>
</tr>
<tr>
<td>-Br</td>
<td>2.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-I</td>
<td>1.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-OH</td>
<td>2.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-OR</td>
<td>2.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-OH</td>
<td>3.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-OC(=O)R</td>
<td>3.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C(=O)R</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C(=O)φ</td>
<td>1.64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C(=O)OR</td>
<td>1.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 I 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.

<table>
<thead>
<tr>
<th>GROUP</th>
<th>-CH₃</th>
<th>-C≡C</th>
<th>-C≡N</th>
<th>-C≡S</th>
<th>-C≡O</th>
<th>-C≡OH</th>
<th>-C≡SH</th>
<th>-C=O</th>
<th>-C=ONR₂</th>
<th>-C=N</th>
<th>-N≡O</th>
<th>-N≡S</th>
<th>-SR</th>
<th>-N₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH₃</td>
<td>1.90</td>
<td>2.02</td>
<td>2.14</td>
<td>2.55</td>
<td>1.91</td>
<td>1.84</td>
<td>1.95</td>
<td>3.57</td>
<td>3.43</td>
<td>3.76</td>
<td>3.70</td>
<td>3.40</td>
<td>4.25</td>
<td>2.47</td>
</tr>
<tr>
<td>-C≡C</td>
<td>3.39</td>
<td>3.20</td>
<td>2.60</td>
<td>2.87</td>
<td>2.99</td>
<td>3.40</td>
<td>2.76</td>
<td>2.69</td>
<td>4.08</td>
<td>3.88</td>
<td>3.77</td>
<td>4.13</td>
<td>3.91</td>
<td>4.76</td>
</tr>
<tr>
<td>-C≡N</td>
<td>3.97</td>
<td>3.29</td>
<td>3.29</td>
<td>4.22</td>
<td>3.90</td>
<td>4.51</td>
<td>3.78</td>
<td>3.92</td>
<td>4.31</td>
<td>4.44</td>
<td>5.28</td>
<td>4.30</td>
<td>5.65</td>
<td>5.48</td>
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<tr>
<td>-C≡S</td>
<td>3.90</td>
<td>4.56</td>
<td>4.56</td>
<td>4.15</td>
<td>3.90</td>
<td>4.51</td>
<td>3.78</td>
<td>3.92</td>
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<td>4.44</td>
<td>5.28</td>
<td>4.30</td>
<td>5.65</td>
<td>5.48</td>
</tr>
<tr>
<td>-C≡O</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
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<td>4.94</td>
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<td>4.94</td>
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<tr>
<td>-C=N</td>
<td>4.94</td>
<td>4.94</td>
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<td>4.94</td>
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</tr>
<tr>
<td>-C≡O</td>
<td>4.94</td>
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<tr>
<td>-C≡O</td>
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<tr>
<td>-C≡O</td>
<td>4.94</td>
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<td>4.94</td>
</tr>
<tr>
<td>-C≡O</td>
<td>4.94</td>
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<td>4.94</td>
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<td>4.94</td>
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<tr>
<td>-C≡O</td>
<td>4.94</td>
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<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
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<td>4.94</td>
<td>4.94</td>
</tr>
<tr>
<td>-C≡O</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
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<td>4.94</td>
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<td>4.94</td>
<td>4.94</td>
</tr>
<tr>
<td>-C≡O</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
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<td>4.94</td>
<td>4.94</td>
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<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
<td>4.94</td>
</tr>
</tbody>
</table>
CORREÇÃO DA TABELA DE DOIS E TRÊS GRUPOS FUNCIONAIS

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

\[
Y = \text{CH} - _Z Y = \text{CH} - _Z
\]

O deslocamento químico de um grupo metílico ligado a dois grupos funcionais pode ser calculado com o auxílio das constantes de substituição \( (\delta) \) da Tabela B.1. A regra de Shooley\footnote{Shooley, J. K. (1960). Varian Technical Information Bulletin, Vol. 2, No. 3.} determina que as constantes de cátio grupo funcional sejam adicionadas a \( \delta \), e o deslocamento químico do CH\(_2\) é dado por:

\[
\delta (Y = \text{CH} - _Z) = \delta + \sigma_Y + \sigma_Z
\]

O deslocamento químico dos hidrogênios do grupo metílico de C\(_2\)H\(_5\)Br, por exemplo, pode ser calculado a partir dos valores de \( \delta \) tirados da Tabela B.1:

\[
\begin{align*}
\delta &= 0.22 \\
\sigma_Y &= 1.85 \\
\sigma_Z &= 2.53 \\
\delta (Y = \text{CH} - _Z) &= 4.43
\end{align*}
\]

As constantes originais de Shooley foram revisadas e seu número aumentado (Tabela B.1). Os deslocamentos químicos observados e calculados para 82% das amostras testadas estavam dentro de \( \pm1.0 \) ppm, 92% em torno de \( \pm0.5 \) ppm, 96% em torno de \( \pm0.4 \) ppm e 99% em torno de \( \pm0.3 \) ppm. A Tabela 3.1 contém constantes de substituição (Friedrich e Rink, 1984) para os grupos funcionais mais comuns. Observe que os deslocamentos químicos dos grupos metila podem ser calculados usando a constante do grupo H (0.34). Por exemplo, H – CH\(_3\) = Br é o mesmo que CH\(_3\)Br.

**Tabelas B.2a, B.2b e B.2c: Correlações de Deslocamento Químico para Hidrogênicos do Grupo Metíno**

A Tabela B.2a dá as constantes de substituição\footnote{**Corrigido:** O erro padrão estimado é igual a 0.20 ppm. Assim, por exemplo, o deslocamento químico do hidrogênio de CH\(_3\)OH é em OEt.} a serem usadas com:

\[
\delta (CHXZ) = 2.50 + \sigma_X + \sigma_Y + \sigma_Z
\]

que dá resultados satisfatórios se pelo menos dois dos substituintes forem grupos que contêm elétrons. Em outras palavras, se um dos grupos pode ser um grupo alquila (R). Dados desses lineares, o erro padrão estimado é igual a 0.20 ppm. Assim, por exemplo, o deslocamento químico do hidrogênio de CH\(_3\)OH em OEt:

\[
\text{CH} - _Z \quad \text{OEt}
\]

É calculado a partir da Tabela B.2a, da seguinte forma:

\[
\delta = 2.50 + 1.14 + 1.14 + 0.00 = 4.78
\]

O valor encurtado é 4.72.

As Tabelas B.2b e B.2c são usadas conjuntamente para hidrogênicos do grupo metíno substituídos por pelo menos dois grupos.

**Tabela B.1: Constantes de Substituição de Hidrogênios de Grupos Metílicos e Metila**

<table>
<thead>
<tr>
<th>Y ou Z</th>
<th>Constantes de Substituição (( \delta ))</th>
<th>Constantes de Substituição (( \sigma ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>0.68</td>
<td>-</td>
</tr>
<tr>
<td>SiC</td>
<td>0.32</td>
<td>-</td>
</tr>
<tr>
<td>SiC(_3)</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>SiC(_4)</td>
<td>1.04</td>
<td>-</td>
</tr>
<tr>
<td>SiC(_5)</td>
<td>1.33</td>
<td>-</td>
</tr>
<tr>
<td>SiC(_6)</td>
<td>1.14</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>0.68</td>
<td>-</td>
</tr>
<tr>
<td>Br</td>
<td>0.32</td>
<td>-</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>NH(_2)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>NR(_2)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>NHCOR</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>OH(_2)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>O(_2)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>C(_2)</td>
<td>0.32</td>
<td>-</td>
</tr>
<tr>
<td>C(_3)</td>
<td>0.68</td>
<td>-</td>
</tr>
<tr>
<td>C(_4)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>C(_5)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>C(_6)</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>OR</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>SR</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.24</td>
<td>-</td>
</tr>
</tbody>
</table>

**Tabela B.2a: Constantes de Substituição de Hidrogênios de Grupos Metínicos**

<table>
<thead>
<tr>
<th>Grupo</th>
<th>Constantes de Substituição</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH} - _Z )</td>
<td>0.24</td>
</tr>
<tr>
<td>( \text{C} - _Z )</td>
<td>0.32</td>
</tr>
<tr>
<td>( \text{Si} - _Z )</td>
<td>1.00</td>
</tr>
<tr>
<td>( \text{F} - _Z )</td>
<td>0.24</td>
</tr>
<tr>
<td>( \text{Cl} - _Z )</td>
<td>0.68</td>
</tr>
<tr>
<td>( \text{Br} - _Z )</td>
<td>0.32</td>
</tr>
<tr>
<td>( \text{NO}_2 - _Z )</td>
<td>1.00</td>
</tr>
<tr>
<td>( \text{NH}_2 - _Z )</td>
<td>1.00</td>
</tr>
<tr>
<td>( \text{NR}_2 - _Z )</td>
<td>1.00</td>
</tr>
<tr>
<td>( \text{NHCOR} - _Z )</td>
<td>1.00</td>
</tr>
<tr>
<td>( \text{OH}_2 - _Z )</td>
<td>1.00</td>
</tr>
<tr>
<td>( \text{O}_2 - _Z )</td>
<td>1.00</td>
</tr>
</tbody>
</table>
TABLE B.2b  Observed Methine Proton Chemical Shifts of Isopropyl Derivatives.

<table>
<thead>
<tr>
<th>Z</th>
<th>δ (ppm) obs</th>
<th>Z</th>
<th>δ (ppm) obs</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.33</td>
<td>HO</td>
<td>3.94</td>
</tr>
<tr>
<td>H₂C</td>
<td>1.56</td>
<td>RO</td>
<td>3.55</td>
</tr>
<tr>
<td>R</td>
<td>1.50</td>
<td>C₆H₅O</td>
<td>4.51</td>
</tr>
<tr>
<td>XCH₂</td>
<td>1.85</td>
<td>R(H)C(==O)</td>
<td>4.94</td>
</tr>
<tr>
<td>R(H)C(==O)</td>
<td>2.54</td>
<td>C₆H₅C(==O)</td>
<td>5.22</td>
</tr>
<tr>
<td>R(C)=C(==O)</td>
<td>3.58</td>
<td>Fe₂C(==O)</td>
<td>5.20</td>
</tr>
<tr>
<td>R(H)OC(==O)</td>
<td>2.52</td>
<td>ArSO₂O</td>
<td>4.70</td>
</tr>
<tr>
<td>R₂(H)NC(==O)</td>
<td>2.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>2.89</td>
<td>R(H)S</td>
<td>3.16</td>
</tr>
<tr>
<td>R₂(H)C==CR(H)</td>
<td>2.62</td>
<td>RSS</td>
<td>2.63</td>
</tr>
<tr>
<td>R(H)C==C</td>
<td>2.59</td>
<td>F</td>
<td>4.50</td>
</tr>
<tr>
<td>N=O</td>
<td>2.67</td>
<td>Cl</td>
<td>4.14</td>
</tr>
<tr>
<td>R₂(H)N</td>
<td>3.07</td>
<td>Br</td>
<td>4.21</td>
</tr>
<tr>
<td>R(H)C(==O)NH</td>
<td>4.01</td>
<td>I</td>
<td>4.24</td>
</tr>
<tr>
<td>O₂N</td>
<td>4.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[ \delta_{CHXYZ} = \delta_{CH₃CH₂Z} = \Delta xy \]

in which the X and Y substituents are alkyl groups or other groups of low polarity. The Z substituent covers a range of polarities. \( \Delta xy \) 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 \( \Delta xy \) 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.

\[ \delta X-CH-Y = \delta CH₃-CH-CH=CH₂ = \delta CH₃-CH-CH₃ + \Delta xy \]

From Table B.2b, \( \delta = 2.89 \) for CH₃—CH—CH₃.

From Table B.2c, \( \Delta xy = 0.40 \) for CH₃—CH=CH₂.

Therefore, \( \delta CH₃-CH-CH=CH₃ = 2.89 + 0.00 + 0.40 = 3.29 \) (Found: \( \delta = 3.44 \)).
Table II can be used to calculate chemical shifts of \( \text{Y-CH}_3 \), \( \text{Y-CH}_2\text{Z} \), or \( \text{Y-CH}_2\text{Br} \) groups. Thus, the \( \text{CH}_3 \) chemical shifts in \( \text{BrCH}_2\text{CH}_3\text{OCH}_2\text{CH}_3\text{Br} \) can be calculated.

\[
\begin{array}{cc}
1-\text{CH}_3 & 2-\text{CH}_3 \\
\text{CH}_2 \text{standard (footnote b)} & 1.20 \\
\alpha-\text{OR} & 2.35 \\
\beta-\text{Br} & 0.60 \\
4.15 & 3.53
\end{array}
\]

Determined: 1-\( \text{CH}_3 \) at \( \approx 3.80 \); 2-\( \text{CH}_3 \) at \( \approx 3.40 \).

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( \text{C}^\beta-C^\alpha )</th>
<th>Type of Hydrogen</th>
<th>Alpha Shift</th>
<th>Beta Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>( -\text{C}=\text{C}=\cdot )</td>
<td>( \text{CH}_3 )</td>
<td>1.60</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>( -\text{C}=\text{C} )</td>
<td>CH</td>
<td>1.45</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>( -\text{Cl} )</td>
<td>CH</td>
<td>1.23</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>( -\text{Br} )</td>
<td>CH</td>
<td>1.80</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>( -\text{I} )</td>
<td>CH</td>
<td>2.18</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>( -\text{OH} )</td>
<td>CH</td>
<td>2.68</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>( -\text{OR} )</td>
<td>CH</td>
<td>2.43</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>( -\text{Ar} )</td>
<td>CH</td>
<td>2.00</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>( -\text{OC}=\text{O}, -\text{OC-OR}, -\text{OR} )</td>
<td>CH</td>
<td>2.88</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>( -\text{CR}, \text{where } R \text{ is alkyl} )</td>
<td>CH</td>
<td>2.98</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>( -\text{CR}, \text{where } R \text{ is alkyl} )</td>
<td>CH</td>
<td>3.43 (inter only)</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) From the Ph.D. dissertation of T.J. Curphey, Harvard University, by permission.

\(^b\) Standard positions are \( \text{CH}_3 \), 0.87; \( \text{CH}_2 \), 1.20; \( \text{CH} \), 1.55.
**DESLOCAMENTOS QUÍMICOS E CONSTANTES DE ACOPLAMENTO EM ALCINOS**

<table>
<thead>
<tr>
<th>Chemical Shifts (in ppm relative to TMS) and Coupling Constants (in Hz) in Acetylene Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H-Chemical Shifts (δ in ppm relative to TMS) and Coupling Constants (J in Hz) in Acetylene Derivatives</td>
</tr>
<tr>
<td>H-C≡C-H</td>
</tr>
<tr>
<td>H-C≡C-alkyl</td>
</tr>
<tr>
<td>H-C≡C-C≡C</td>
</tr>
<tr>
<td>H-C≡C-C≡C</td>
</tr>
<tr>
<td>H-C≡C-C≡C</td>
</tr>
<tr>
<td>H-C≡C-O-alkyl</td>
</tr>
<tr>
<td>H-C≡C-CO</td>
</tr>
<tr>
<td>CH$_3$-C≡C-H</td>
</tr>
<tr>
<td>CH$_3$-C≡C-CH$_3$</td>
</tr>
<tr>
<td>H-C≡C-C≡C-H</td>
</tr>
</tbody>
</table>
CONSIDERAÇÕES GERAIS SOBRE ACOPLAMENTO SPIN-SPIN

(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 de multiplicidade: \( 2mI + 1 \)

(d) Sinal de J: \( \pm \) (sentidos opostos) \( \mp \) (mesmo sentido)

(e) Representação do J: \( J = \sum_{x,y} \) \( m_x \) \( m_y \) \( n_x = \# \) de lig. entre spins \( n_y = \) núcleos acoplados

(f) Espetos de 1ª ordem: \( \frac{\Delta J}{2} \geq 10 \text{ Hz} \)

* A resolução das linhas espectrais dependem do B₀
### 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).

<table>
<thead>
<tr>
<th>( n )</th>
<th>Multiplicidade</th>
<th>Intensidade Relativa</th>
<th>Spins</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Singleto (s)</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Dupleto (d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Tripleto (t)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Quarteto (q)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Quinteto</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Sexteto</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Septeto</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Octeto</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Noneto</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ESPECTROMETRIA DE RMN DE HIDROGÉNIO
### Appendix F Proton Spin-Coupling Constants

<table>
<thead>
<tr>
<th>Type</th>
<th>( J_{\alpha} ) (Hz)</th>
<th>( J_{\alpha} ) Typical</th>
<th>Type</th>
<th>( J_{\alpha} ) (Hz)</th>
<th>( J_{\alpha} ) Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_2-CH_2 ) (free rotation)</td>
<td>6–8</td>
<td>7</td>
<td>( CH_2-CH_2 )</td>
<td>0–3</td>
<td>1–2</td>
</tr>
<tr>
<td>( CH_2=CH_2 )</td>
<td>0–1</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_2 )</td>
<td>6–12</td>
<td>10</td>
<td>( H_2 )</td>
<td>0–3</td>
<td>2</td>
</tr>
<tr>
<td>( CH_2=CH_2 )</td>
<td>6–3</td>
<td>1.5</td>
<td>( CH_2=CH_2 )</td>
<td>9–13</td>
<td>10</td>
</tr>
<tr>
<td>ox-ox</td>
<td>6–14</td>
<td>8–10</td>
<td>( C-CH_2=CH_2 )</td>
<td>3 member</td>
<td>0.5–2.0</td>
</tr>
<tr>
<td>ox-eq</td>
<td>0–5</td>
<td>2–3</td>
<td>( CH_2=CH_2 )</td>
<td>4 member</td>
<td>2.5–4.0</td>
</tr>
<tr>
<td>eq-eq</td>
<td>0–5</td>
<td>2–3</td>
<td>( CH_2=CH_2 )</td>
<td>5 member</td>
<td>5.1–7.0</td>
</tr>
<tr>
<td>( cis )</td>
<td>5–10</td>
<td></td>
<td>( CH_2=CH=CH=CH_2 )</td>
<td>6 member</td>
<td>8.8–11.0</td>
</tr>
<tr>
<td>( trans )</td>
<td>5–10</td>
<td></td>
<td>( CH_2=CH=CH_2 )</td>
<td>7 member</td>
<td>9–13</td>
</tr>
<tr>
<td>( CH_2=CH=CH_2 )</td>
<td>4–12</td>
<td>2–10</td>
<td>( CH_2=CH=CH_2 )</td>
<td>8 member</td>
<td>10–13</td>
</tr>
<tr>
<td>( cis )</td>
<td>7–13</td>
<td>4–0</td>
<td>( CH_2=CH=CH_2 )</td>
<td>2–3</td>
<td>2.3</td>
</tr>
<tr>
<td>( trans )</td>
<td>7–13</td>
<td>4–0</td>
<td>( CH_2=CH=CH_2 )</td>
<td>2–3</td>
<td>2.3</td>
</tr>
<tr>
<td>( CH_3-OH ) (no exchange)</td>
<td>4–10</td>
<td>5</td>
<td>( CH_3-OH )</td>
<td>6–10</td>
<td>9</td>
</tr>
<tr>
<td>( CH_2=CH_2 )</td>
<td>1–3</td>
<td>2–3</td>
<td>( CH_3-OH )</td>
<td>6–10</td>
<td>9</td>
</tr>
<tr>
<td>( CH_2=CH_2 )</td>
<td>1–3</td>
<td>2–3</td>
<td>( CH_3-OH )</td>
<td>6–10</td>
<td>9</td>
</tr>
<tr>
<td>( C=CH_2-CH_2 )</td>
<td>5–8</td>
<td>6</td>
<td>( CH_3-OH )</td>
<td>6–10</td>
<td>9</td>
</tr>
<tr>
<td>( C=CH_2-CH_2 )</td>
<td>12–18</td>
<td>17</td>
<td>( CH_3-OH )</td>
<td>6–10</td>
<td>9</td>
</tr>
<tr>
<td>( CH_2=CH_2 )</td>
<td>0–3</td>
<td>0–2</td>
<td>( CH_3-OH )</td>
<td>6–10</td>
<td>9</td>
</tr>
</tbody>
</table>

\( J \) (ortho) 6–10 9
\( J \) (meta) 1–3 3
\( J \) (para) 6–1 6

\( J(2-3) \) 5–6 5
\( J(3-4) \) 7–9 8
\( J(1-2) \) 1–2 1.5
\( J(1-3) \) 1–2 1.5
\( J(2-5) \) 0–1 0
\( J(2-6) \) 0–1 0
\( J(3-4) \) 1.3–2.0 1.8
\( J(3-4) \) 3.1–3.8 3.6
\( J(2-4) \) 0–1 0
\( J(2-5) \) 1–2 1.5
### CONSTANTES DE ACOPLAMENTO

<table>
<thead>
<tr>
<th>Type</th>
<th>$J_{ab}$ (Hz)</th>
<th>$J_{ab}$ Typical</th>
<th>Type</th>
<th>$J_{ab}$ (Hz)</th>
<th>$J_{ab}$ Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J(2\rightarrow3)$</td>
<td>4.9–6.2</td>
<td>5.4</td>
<td>Proton–Carbon-13</td>
<td>(See Tables 5.17, 5.18)</td>
<td></td>
</tr>
<tr>
<td>$J(3\rightarrow4)$</td>
<td>3.4–5.0</td>
<td>4.0</td>
<td>Proton–Fluorine</td>
<td>44–81</td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow4)$</td>
<td>1.2–1.7</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow5)$</td>
<td>3.2–3.7</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(1\rightarrow3)$</td>
<td>2–3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(3\rightarrow4)$</td>
<td>3–4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow4)$</td>
<td>1–2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow5)$</td>
<td>1.5–2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(4\rightarrow5)$</td>
<td>4–6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow5)$</td>
<td>1–2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow4)$</td>
<td>0–1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(4\rightarrow6)$</td>
<td>2–3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(4\rightarrow5)$</td>
<td>3–4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow4)$</td>
<td>~0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J(2\rightarrow5)$</td>
<td>1–2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Proton–Phosphorus**

<table>
<thead>
<tr>
<th>Structure</th>
<th>$J_{ab}$ (Hz)</th>
<th>$J_{ab}$ Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PH}$</td>
<td>650–707</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{P}$</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{P}=0$</td>
<td>13.4</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2)_2\text{P}$</td>
<td>0.5 (HCCP) 13.7 (HCP)</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3\text{CH}_2)_2\text{P}=0$</td>
<td>11.9 (HCCP) 16.3 (HCP)</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2\text{P}(\text{OR})_2$</td>
<td>10–13</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2\text{C}_2\text{P}(\text{OR})_2$</td>
<td>15–20</td>
<td></td>
</tr>
<tr>
<td>$\text{CH}_2\text{OP}(\text{OR})_2$</td>
<td>10.5–12</td>
<td></td>
</tr>
<tr>
<td>$\text{P}[\text{N}(\text{CH}_3)]_3$</td>
<td>10.5–12</td>
<td></td>
</tr>
<tr>
<td>$\text{O}[\text{P}[\text{N}(\text{CH}_3)]_3]$</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>$\text{O}[\text{P}[\text{N}(\text{CH}_3)]_3]$</td>
<td>9.5</td>
<td></td>
</tr>
</tbody>
</table>
CÁLCULO DE DESLOC. QUÍMICO PARA ALCENOS

CHEMICAL SHIFTS IN UNSATURATED AND AROMATIC SYSTEMS

(See Table D.1)

For example, the chemical shifts of the alkene protons in

\[
\begin{align*}
\text{C}_2\text{H}_4 & \quad \text{OC}_2\text{H}_5 \\
\text{H}_a & \quad \text{H}_b
\end{align*}
\]

are calculated:

\[
\begin{align*}
\delta_{\text{H}a} &= 5.25 + Z_{\text{gem}} + Z_{\text{cis}} + Z_{\text{trans}} \\
\delta_{\text{H}b} &= 1.18 + 1.06 + 1.00 + 0.88
\end{align*}
\]

\[
\begin{align*}
\text{H}_a & \quad \text{C}_2\text{H}_4_{\text{gem}} & 1.35 & 0.07 & 3.52 \\
& \quad \text{OR}_{\text{gem}} & -1.28 & 0.07 & 0.07 \\
\text{H}_b & \quad \text{OR}_{\text{trans}} & 1.18 & 3.25 & 1.00 \\
& \quad \text{C}_2\text{H}_4_{\text{trans}} & -0.10 & 0.06 & 0.08 \\
& \quad \text{CO}_2\text{H} & 1.58 & 1.15 & 0.35
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Substituent R</th>
<th>Z</th>
<th>Substituent R</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gem</td>
<td>cis</td>
<td>trans</td>
</tr>
<tr>
<td>−H</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>−Alkyl</td>
<td>0.44</td>
<td>−0.26</td>
<td>−0.29</td>
</tr>
<tr>
<td>−Alkyl ring²</td>
<td>0.71</td>
<td>−0.33</td>
<td>−0.30</td>
</tr>
<tr>
<td>−CH₂O−</td>
<td>0.67</td>
<td>−0.02</td>
<td>−0.07</td>
</tr>
<tr>
<td>−CH₃</td>
<td>0.53</td>
<td>−0.15</td>
<td>−0.15</td>
</tr>
<tr>
<td>−CH₂Cl−</td>
<td>0.72</td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>−CH₃N</td>
<td>0.66</td>
<td>−0.05</td>
<td>−0.23</td>
</tr>
<tr>
<td>−CON</td>
<td>0.50</td>
<td>0.35</td>
<td>0.10</td>
</tr>
<tr>
<td>−CONN</td>
<td>0.23</td>
<td>0.78</td>
<td>0.58</td>
</tr>
<tr>
<td>−C−C conj⁴</td>
<td>0.98</td>
<td>−0.04</td>
<td>−0.21</td>
</tr>
<tr>
<td>−C−O</td>
<td>1.26</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>−C−O conj⁵</td>
<td>1.19</td>
<td>1.13</td>
<td>0.81</td>
</tr>
<tr>
<td>−COOH</td>
<td>1.26</td>
<td>1.01</td>
<td>0.95</td>
</tr>
<tr>
<td>−COOH conj³</td>
<td>0.69</td>
<td>0.97</td>
<td>0.39</td>
</tr>
<tr>
<td>−COOR</td>
<td>0.84</td>
<td>1.15</td>
<td>0.56</td>
</tr>
<tr>
<td>−COOR conj⁴</td>
<td>0.58</td>
<td>1.02</td>
<td>0.33</td>
</tr>
<tr>
<td>−COOR conj⁵</td>
<td>1.58</td>
<td>1.15</td>
<td>0.95</td>
</tr>
</tbody>
</table>

⁴ Alkyl ring indicates that the double bond is part of the ring.

⁵ The Z factor for the conjugated substituents is used when either the substituent or the double bond is further conjugated with other groups.

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.
FIGURE 3.19 Simulated 60, 100, and 300 MHz spectra of acrylonitrile; 300 MHz experimental spectrum (in CDCl₃) for comparison.
ESPECTRO TÍPICO DE UM COMPOSTO VINÍLICO DISSUBSTITUÍDO

ABX₃ Analysis

δₓ  6.28 ppm
δₓ B 5.59 ppm
δₓ  1.87 ppm
JₓB  11.6 Hz
JₓA  1.6 Hz
Jₓx  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

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\(^a\) The benzena ring proton is at \(\delta\) 7.27, from which the shift increments are calculated as shown at the end of Section 3.4.

\(^a\) OTS = \(p\)-toluenesulfonyl group.
Effect of a Substituent on the Chemical Shift of the Ring-Protons in Benzene ($\delta$ in ppm relative to TMS)

$$\delta_H = 7.26 + z_1$$

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MUDANÇAS EM DESL. QUÍMICO EM BENZENOS MONOSSUBSTITUÍDOS

Fig. 4.10 Changes in $^1$H chemical shifts in monosubstituted benzenes relative to benzene. Values are given as ($\delta_{\text{benzene}} - \delta_{\text{substituted}}$) (Spiesecke and Schneider$^{41}$).
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 CDCl₃ as the solvent see p. H275.)

\[
\begin{align*}
\delta_{H_2} &= 8.59 + z_{12} \\
\delta_{H_3} &= 7.38 + z_{13} \\
\delta_{H_4} &= 7.75 + z_{14} \\
\delta_{H_5} &= 7.38 + z_{15} \\
\delta_{H_6} &= 8.59 + z_{16}
\end{align*}
\]

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<th>2- or 6-Substituent (l = 2 or 6)</th>
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<th>( z_{24} = z_{64} )</th>
<th>( z_{25} = z_{63} )</th>
<th>( z_{26} = z_{62} )</th>
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<td>-0.20</td>
<td>0.02</td>
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<tr>
<td>(-CH₂OH)</td>
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<tr>
<td>(-CH₂NH₂)</td>
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<td>0.07</td>
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<td>0.05</td>
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<tr>
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<td>-0.26</td>
<td>-0.06</td>
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<td>0.29</td>
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<td>(-Br)</td>
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### CONSTANTES DE BLINDAGEM EM PIRIDINAS SUBSTITUÍDAS

**1H-NMR**

**PYRIDINE, SUBSTITUENT EFFECTS**

#### 3- or 5-Substituent (1=3 or 5)

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<tr>
<th>Substituent</th>
<th>( z_{32} = z_{56} )</th>
<th>( z_{34} = z_{54} )</th>
<th>( z_{35} = z_{53} )</th>
<th>( z_{36} = z_{52} )</th>
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<td>0.04</td>
<td>0.00</td>
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<td>0.72</td>
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#### 4-Substituent (1=4)

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<tr>
<td>-CH₃</td>
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<td>-0.13</td>
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<td>-0.18</td>
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<td>0.13</td>
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<tr>
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<tr>
<td>-Br</td>
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**CONSTANTES DE BLINDAGEM PARA PIRRÓIS**

- $\delta_{N1} = 7-12$ (strongly solvent-dependent, generally broad)
- $\delta_{N2} = 6.62 + \varepsilon_{12}$
- $\delta_{N3} = 6.05 + \varepsilon_{13}$
- $\delta_{N4} = 6.05 + \varepsilon_{14}$
- $\delta_{N5} = 6.62 + \varepsilon_{15}$

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<tr>
<td>-CH₂CH₃</td>
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<td>-CH₃-phenyl</td>
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<td>0</td>
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<td>-0.26</td>
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<td>=SCH₂</td>
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## Constantes de Blindagem para Furanos

### Formulas

\[
\delta_{H_2} = 7.38 + Z_{12} \\
\delta_{H_3} = 6.30 + Z_{13} \\
\delta_{H_4} = 6.30 + Z_{14} \\
\delta_{H_5} = 7.38 + Z_{15}
\]

### Tabela de Constantes para Substituintes

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<tr>
<th>2- or 5-Substituent ((i = 2) or (5))</th>
<th>(Z_{23} = Z_{54})</th>
<th>(Z_{24} = Z_{53})</th>
<th>(Z_{25} = Z_{52})</th>
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<td>-0.01</td>
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<tr>
<td>-CHO</td>
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<td>0.34</td>
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<th>(Z_{34} = Z_{43})</th>
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### Constantes de Blindagem para Tiofenos

#### 2- ou 5-Substituente

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<tr>
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<tr>
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#### 3- ou 4-Substituente

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DESLOCAMENTOS QUÍMICOS DE ALGUNS AROMÁTICOS E HETEROAROMÁTICOS

Table V. Chemical Shifts of Protons on Heteroaromatic Rings

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- 6.30 and 6.50 refer to chemical shifts in ppm (parts per million).
- The values are given for different aromatic rings with specific functional groups and atom configurations.