1-Nitropropane

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these protons sense a larger effective magnetic field, so come into resonance at a higher frequency

these protons sense a smaller effective magnetic field, so come into resonance at a lower frequency

deshielded nuclei

shielded nuclei

"downfield"  "upfield"

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The molecule \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \) contains chemically equivalent protons.
\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \text{ three signals} \]
\[ \text{CH}_3\text{CHCH}_3 \text{ two signals} \]
\[ \text{CH}_3\text{CH}_2\text{OCH}_3 \text{ three signals} \]
\[ \text{CH}_3\text{OCH}_3 \text{ one signal} \]
\[ \text{CH}_3\text{COCH}_3 \text{ two signals} \]
CH₃OCHCl₂ two signals

H₃C C═C H two signals
H₃C H

C═C H three signals
H H b

C═C H a
H H b

H H a
H H a

H H a
H H a

H a
H a

H CNO₂
H H a

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its $^1$H NMR spectrum has five signals

chlorocyclobutane

$H_a$ and $H_b$ are not equivalent

$H_c$ and $H_d$ are not equivalent
tetramethylmethylsilane

TMS

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<table>
<thead>
<tr>
<th>Protons in electron-poor environments</th>
<th>Protons in electron-dense environments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deshielded protons</td>
<td>Shielded protons</td>
</tr>
<tr>
<td>Downfield</td>
<td>Upfield</td>
</tr>
<tr>
<td>High frequency</td>
<td>Low frequency</td>
</tr>
<tr>
<td>Large $\delta$ values</td>
<td>Small $\delta$ values</td>
</tr>
</tbody>
</table>

$\delta$ ppm  \hspace{2cm} \text{frequency}
\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2
\]

- 1.04 ppm
- 2.07 ppm
- 4.37 ppm
—CH—
methine

—CH₂—
methylene

—CH₃—
methyl
<table>
<thead>
<tr>
<th>Type of proton</th>
<th>Approximate chemical shift (ppm)</th>
<th>Type of proton</th>
<th>Approximate chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{CH}_3)</td>
<td>0.85</td>
<td>(\text{I} - \text{C} - \text{H})</td>
<td>2.5–4</td>
</tr>
<tr>
<td>(-\text{CH}_2-)</td>
<td>1.20</td>
<td>(\text{Br} - \text{C} - \text{H})</td>
<td>2.5–4</td>
</tr>
<tr>
<td>(-\text{CH}-)</td>
<td>1.55</td>
<td>(\text{Cl} - \text{C} - \text{H})</td>
<td>3–4</td>
</tr>
<tr>
<td>(-\text{C} = \text{C} - \text{CH}_3)</td>
<td>1.7</td>
<td>(\text{F} - \text{C} - \text{H})</td>
<td>4–4.5</td>
</tr>
<tr>
<td>(-\text{C} - \text{CH}_3)</td>
<td>2.1</td>
<td>(\text{RNH}_2)</td>
<td>Variable, 1.5–4</td>
</tr>
<tr>
<td>(-\text{C} = \text{C} - \text{H})</td>
<td>2.4</td>
<td>(\text{ROH})</td>
<td>Variable, 2–5</td>
</tr>
<tr>
<td>(\text{R} - \text{O} - \text{CH}_3)</td>
<td>3.3</td>
<td>(\text{ArOH})</td>
<td>Variable, 4–7</td>
</tr>
<tr>
<td>(\text{R} - \text{C} = \text{CH}_2)</td>
<td>4.7</td>
<td>(\text{H} - \text{H})</td>
<td>6.5–8</td>
</tr>
<tr>
<td>(\text{R} - \text{C} = \text{C} - \text{H})</td>
<td>5.3</td>
<td>(\text{C} - \text{H})</td>
<td>9.0–10</td>
</tr>
<tr>
<td>(\text{R} - \text{C} = \text{C} - \text{H})</td>
<td>5.3</td>
<td>(\text{C} - \text{OH})</td>
<td>Variable, 10–12</td>
</tr>
<tr>
<td>(\text{R} - \text{C} - \text{NH}_2)</td>
<td></td>
<td>(\text{C} - \text{NH}_2)</td>
<td>Variable, 5–8</td>
</tr>
</tbody>
</table>

*The values are approximate because they are affected by neighboring substituents.*
methine proton

1.55 ppm

methylene proton

1.20 ppm

methyl proton

0.85 ppm
induced magnetic field is in the same direction as the applied magnetic field in the region where the protons are located
induced magnetic field is in the same direction as the applied magnetic field in the region where the proton is located.
induced magnetic field is in the direction opposite to that of the applied magnetic field in the region where the proton is located.
1,1-dichloroethane
ratio of protons = 1:3

1,2-dichloro-2-methylpropane
ratio of protons 2:6 = 1:3
\( \text{CH}_3\text{CHCl}_2 \)
CH$_3$Br  
**bromomethane**

ClCH$_2$CH$_2$Cl  
**1,2-dichloroethane**

each compound has an NMR spectrum that shows one singlet because equivalent protons do not split each other’s signals
direction of the applied field

if the magnetic field of the methine proton is in the same direction as the applied magnetic field, it will add to the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly higher frequency

if the magnetic field of the methine proton is lined up against the applied magnetic field, it will subtract from the applied magnetic field, so the adjacent methyl protons will show a signal at a slightly lower frequency

CH₃CHCl₂

chemical shift of the signal for the methyl protons if there were no protons on the adjacent carbon

frequency
The chemical shift of the methine proton if there were no protons on the adjacent carbon is split into a quartet.
all with

all against

2 with and 2 against
and 1 against
and 1 with

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$H_a$ and $H_b$ split each other's signal because they are separated by three $\sigma$ bonds.

$H_a$ and $H_b$ do not split each other's signal because they are separated by four $\sigma$ bonds.

$H_a$ and $H_b$ may split each other's signal because they are separated by four bonds one of which is a double bond.
a quartet
relative intensities: 1 : 3 : 3 : 1

a doublet of doublets
relative intensities: 1 : 1 : 1 : 1
\[ \text{CH}_3\text{CHCl}_2 \]

\[ J_{ba} \]

\[ J_{ba} \]

\[ J_{ab} \]

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### Table 13.3  Approximate Values of Coupling Constants

<table>
<thead>
<tr>
<th>Approximate value of $J_{ab}$ (Hz)</th>
<th>Approximate value of $J_{ab}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Chemical Structure] (12)</td>
<td>![Chemical Structure] (15 (trans))</td>
</tr>
<tr>
<td>![Chemical Structure] (7)</td>
<td>![Chemical Structure] (10 (cis))</td>
</tr>
<tr>
<td>![Chemical Structure] (0)</td>
<td>![Chemical Structure] (1 (long-range coupling))</td>
</tr>
<tr>
<td>![Chemical Structure] (2)</td>
<td>![Chemical Structure] (1 (geminal coupling))</td>
</tr>
</tbody>
</table>

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trans-3-chloropropenoic acid

$J_{ba} = 14$ Hz

$J_{ab} = 14$ Hz

cis-3-chloropropenoic acid

$J_{ba} = 9$ Hz

$J_{ab} = 9$ Hz

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1,1,2-trichloro-3-methylbutane

a splitting diagram

chemical shift of the signal for the $H_c$ proton if there were no splitting

splitting by the $H_b$ proton

splitting by the $H_d$ proton

a doublet of doublets

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\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \]

1-bromopropane

\[ ^a_b_c \]

- For \( J_{ba} \gg J_{bc} \), 12 peaks.
- For \( J_{ba} = 2J_{bc} \), 9 peaks.
- For \( J_{ba} = J_{bc} \), 6 peaks.
enantiotoptic hydrogen

\[ \text{CH}_3\text{C}-\text{OH} \]

enantiotoptic hydrogen

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H<sub>a</sub> and H<sub>b</sub> are diastereotopic hydrogens

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H_aBr + H_bBr → slower → faster →

\[\text{cis-2-butene} → \text{trans-2-butene}\]
CH₃CHCH₂CH₃

Br

nonequivalent diastereotopic hydrogens
anti  gauche  eclipsed
Mechanism for acid-catalyzed proton exchange

seen in 'H NMR

not seen in 'H NMR

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\[ \text{CH}_3\text{CH}_2\text{X} \]

\[ J_{ab} = 5.0 \text{ Hz} \]

\[ \Delta \nu = 100 \text{ Hz} \quad \Delta \nu/J = 20 \]

\[ \Delta \nu = 25 \text{ Hz} \quad \Delta \nu/J = 5 \]

\[ \Delta \nu = 15 \text{ Hz} \quad \Delta \nu/J = 3 \]

\[ \Delta \nu = 10 \text{ Hz} \quad \Delta \nu/J = 2 \]

\[ \Delta \nu = 5 \text{ Hz} \quad \Delta \nu/J = 1 \]
<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>Approximate chemical shift (ppm)</th>
<th>Type of carbon</th>
<th>Approximate chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{CH}_3\text{)}_4\text{Si})</td>
<td>0</td>
<td>(\text{C}–\text{I})</td>
<td>0–40</td>
</tr>
<tr>
<td>(\text{R}–\text{CH}_3)</td>
<td>8–35</td>
<td>(\text{C}–\text{Br})</td>
<td>25–65</td>
</tr>
<tr>
<td>(\text{R}–\text{CH}_2–\text{R})</td>
<td>15–50</td>
<td>(\text{C}–\text{Cl})</td>
<td>35–80</td>
</tr>
<tr>
<td>(\text{R}–\text{C}–\text{R})</td>
<td>20–60</td>
<td>(\text{C}–\text{N})</td>
<td>40–60</td>
</tr>
<tr>
<td>(\text{R}–\text{C}–\text{R})</td>
<td>30–40</td>
<td>(\text{C}–\text{O})</td>
<td>50–80</td>
</tr>
<tr>
<td>(\equiv\text{C})</td>
<td>65–85</td>
<td>(\text{HO}–\text{C}–\text{O})</td>
<td>175–185</td>
</tr>
<tr>
<td>(\equiv\text{C})</td>
<td>100–150</td>
<td>(\text{H}–\text{C}–\text{O})</td>
<td>190–200</td>
</tr>
<tr>
<td>(\equiv\text{C})</td>
<td>110–170</td>
<td>(\text{R}–\text{C}–\text{O})</td>
<td>205–220</td>
</tr>
</tbody>
</table>
ethyl benzoate  phenyl propanoate
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NO}_2$
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<table>
<thead>
<tr>
<th>Number of equivalent protons causing splitting</th>
<th>Multiplicity of the signal</th>
<th>Relative peak intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>singlet</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>doublet</td>
<td>1 : 1</td>
</tr>
<tr>
<td>2</td>
<td>triplet</td>
<td>1 : 2 : 1</td>
</tr>
<tr>
<td>3</td>
<td>quartet</td>
<td>1 : 3 : 3 : 3 : 1</td>
</tr>
<tr>
<td>4</td>
<td>quintet</td>
<td>1 : 4 : 6 : 4 : 1</td>
</tr>
<tr>
<td>5</td>
<td>sextet</td>
<td>1 : 5 : 10 : 10 : 5 : 1</td>
</tr>
</tbody>
</table>