Problem R-07H (C₇H₁₄O₂).
200 MHz ¹H NMR Spectrum in CDCl₃.
Source: Gui-Bai Liang/Gellman (Reich digitized hard copy)
Problem R-07H \((C_7H_{14}O_2)\). Interpret a proton NMR spectrum (next page).

(a) Identify \(H_X\) (give \(\delta\) and J values)

(b) Below is reproduced the multiplet at \(\delta\ 1.8\). Which protons are these (circle: A, B, M, N, X). Label the spectrum and extract the coupling constants (you may use first-order analysis) and report the couplings (e.g., \(J_{PO} = 33\) Hz). Draw a coupling tree to show you understand the pattern.

(c) Show the probable conformation looking down the bond marked with an arrow (fill in the Newman projection below).

(d) Which of the couplings you extracted in part (a) using first-order analysis do you expect to be accurate? Which will be only approximate? Explain, and predict the direction of the expected error for these couplings (be specific).
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\[\delta 3.09, \text{dd, } J = 10.8, 3.7\]

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2. Only the \(J_{\text{MN}}\) coupling will be accurate.

Since the AB protons are strongly coupled \((\Delta_{\text{AB}} < J_{\text{AB}})\), then all couplings to them will be changed (virtual coupling effects will be seen). Thus the true values of \(J_{\text{MA}}\) and \(J_{\text{MB}}\) will be further apart than the measured numbers (true values might be 7 and 3 instead of 6 and 4). Similarly, the values for \(J_{\text{MX}}\) and \(J_{\text{NX}}\) will be affected since M and N are fairly close, but the errors here will be smaller, since \(\Delta_{\text{MN}} > J_{\text{MN}}\).

See simulation and a more detailed analysis on next page.
Simulation with WINDNMR (http://www.chem.wisc.edu/areas/reich/plt/windnmr.htm)

Parameters

\[ \nu_M = 339.15 \quad \nu_N = 369.58 \]
\[ J_{MN} = -16.00 \]
\[ J_{MX} = 3.00 \quad J_{NX} = 11.40 \]
\[ J_{MA} = 4.20 \quad J_{NA} = 9.70 \]
\[ J_{MB} = 6.30 \quad J_{NB} = 4.90 \]
\[ J_{AB} = -12.20 \]

\[ \Delta \nu_{AB} = 8 \text{ Hz (} J_{AB} = -12.1 \text{)} \]
\[ \Delta \nu_{MN} = 20.2 \text{ Hz (} J_{MN} = -16 \text{ Hz)} \]

Simulation (actual \( J \))

First order analysis \( J \)

\[ J_{MA} = 4.20 \quad J_{MA} = 5.8 \text{ Hz} \]
\[ J_{MB} = 6.30 \quad J_{MB} = 4.8 \text{ Hz} \]
\[ J_{NA} = 9.70 \quad J_{NA} = 8.8 \text{ Hz} \]
\[ J_{NB} = 4.90 \quad J_{NA} = 5.6 \text{ Hz} \]
\[ J_{MX} = 3.00 \quad J_{MX} = 3.6 \text{ Hz} \]
\[ J_{NX} = 11.40 \quad J_{NX} = 10.8 \text{ Hz} \]

For coupling to \( M, N \) \( J \) errors from a first order analysis are 1.6, 1.5, 0.9 and 0.7 Hz for coupling to A and B, but only 0.6 and 0.6 Hz for coupling to X. The errors are larger for coupling to A and B because \( \nu_{AB} \) (8 Hz) is smaller than \( J_{AB} \). As is usual for virtual coupling effects, the errors are in the direction towards the average of the true coupling.
dd, J = 10.8, 3.6