If you were using the spectra to assign the (*E*)- and (*Z*)- stereochemistry, the exercise of using representative *J*-values and thinking about the theoretical appearance of the peaks is useful because it can give you an idea of what the biggest differences in the spectra might be as you think about which one is which.

As illustrated in the branching diagrams using the experimental values, a noteworthy distinction in the spectra of the two isomers is that the widths of the multiple line patterns differ according to whether the cis or trans *J*-value is involved. For H_A in the (*E*)-isomer, the total width of the multiline pattern is the **13.2** doublet coupling plus three times the 1.8 quartet coupling (i.e., there are three 1.8 Hz spaces between the four lines). This gives an 18.6 Hz width to the signal. If the operating frequency of the NMR was 200 MHz, then each ppm is 200 Hz and 18.6/200 = 0.093 ppm. The 0.093 ppm width is symmetric around the chemical shift value, so the set of lines would span the 0.093 ppm distance from δ 6.11–6.01 ppm. By the same calculation, the width of the H_A signal for the (*Z*)-isomer is 0.062 ppm.

This is a distance that will be detectably different, even if the details of the two signals are not. In the actual spectra (not reproduced here), seeing the actual pattern of the individual lines depends on the resolution of the instrument and the operating frequency, but even at fairly low resolution, the overall widths of the signals are consistent with the analysis from these diagrams. In addition, the coincidentally close 3-bond coupling constants in the (*Z*)-isomer means that the appearance of H_B as a nearly ideal pentet is also quite distinctive.

C. Chemical Shift and Integration

Because NMR spectra are recorded at different operating frequencies, the relative distance from an internal standard, TMS, is used to report the position of an absorption. This δ ppm value is the chemical shift. When the signal is a singlet, it occurs at the chemical shift value. Multiline signals that arise from spin-spin coupling can create anywhere from simple to complex patterns, but they are always centered symmetrically around the chemical shift as there will always be equal parts of addition and subtraction to the external field due to the spin of neighboring atoms.

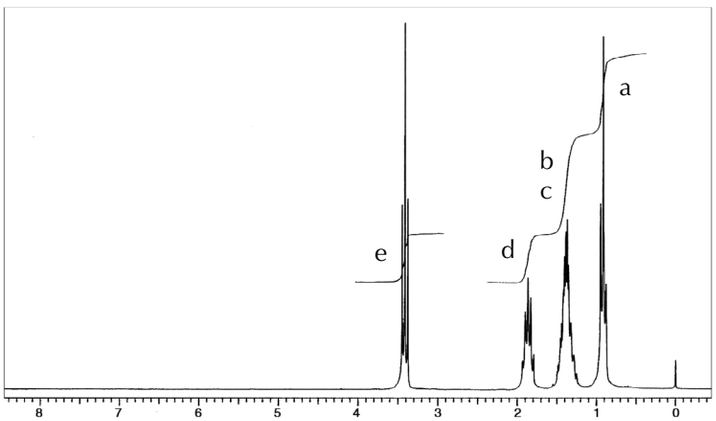
The position of a spin-coupled absorption is never reported as the list of lines, but rather as the single chemical shift value, multiplicity, and coupling constants. The combination of the multiplicity and the coupling constant(s) are used to characterize the absorption. When a signal is too complex or too unresolved to identify its multiplicity, it is reported as "multiplet" (m) or a "broad multiplet" (bm). If the signal is relatively narrow and likely due to only one group of hydrogen atoms, then the central point is used for reporting the chemical shift, otherwise the ppm range is used.

The ^{1}H-NMR spectrum of 1-bromopentane is shown in Figure AP0933 and illustrates this point.

Figure AP0933

^{1}H-NMR spectrum of 1-bromopentane.

1-bromopentane



e d c b a
$Br—CH_2CH_2CH_2CH_2CH_3$

a δ 0.9 ppm, 3H, triplet, *J*=7
b and c δ 1.2-1.5 ppm, 4H, multiplet
d δ 1.85 ppm, 1H, b pentet
e δ 3.4 ppm, 2H, triplet, *J*=7