

For 2-bond coupling, the  $^2J_{\text{HH}}$  value is observed to differ based on the hybridization of the intervening carbon atom ( $\text{sp}^3$  HCH are 12–15 Hz;  $\text{sp}^2$  HCH are 0–2 Hz).

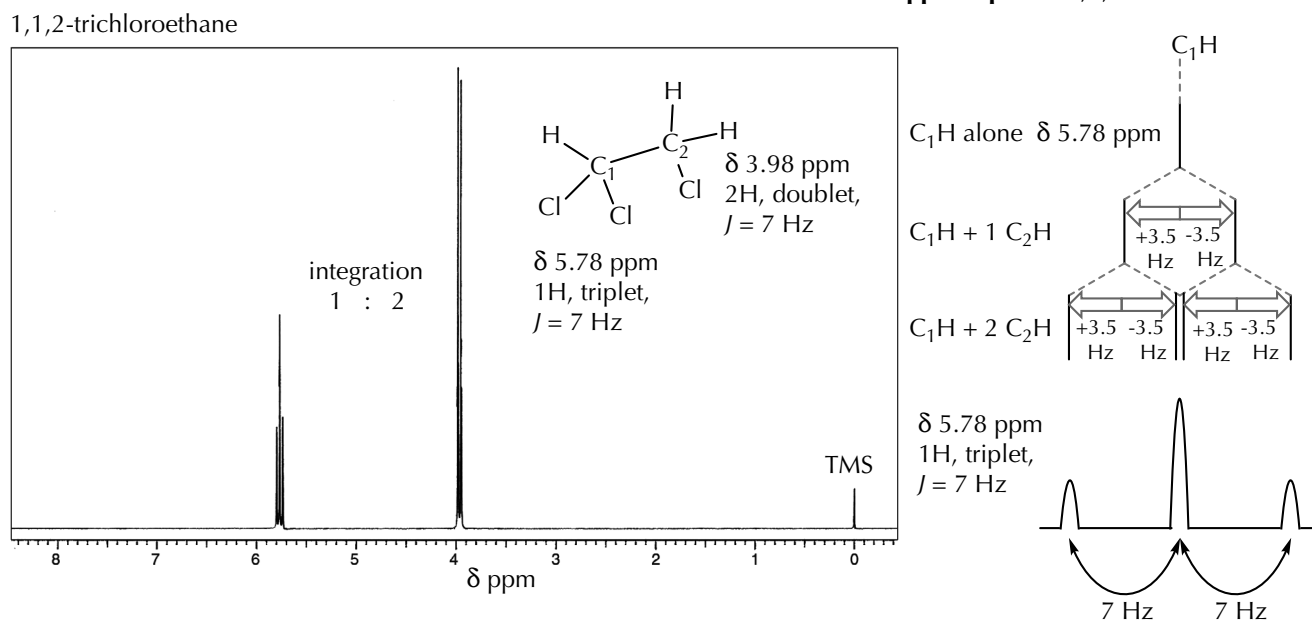
In freely rotating systems, the typical  $^3J_{\text{HH}}$  value is 7 Hz, representing the average contribution from all conformations. In fixed geometry systems, such as with cis and trans hydrogens, the different values are consistent with the Karplus generalization ( $^3J_{\text{HH}}$  for cis hydrogens, with a  $0^\circ$  dihedral angle, is 6–12 Hz, while that for trans hydrogens is 12–18 Hz).

Coupling constants for 4-bond systems and above are generally unobservable, except for allylic systems ( $^4J_{\text{HH}} = 0\text{--}3$  Hz), propargylic systems ( $^3J_{\text{HH}} = 2\text{--}3$  Hz), and on aromatic rings (ortho  $^3J_{\text{HH}} = 6\text{--}10$  Hz; meta  $^4J_{\text{HH}} = 1\text{--}3$  Hz; **para**  $^5J_{\text{HH}} = 0\text{--}1$  Hz).

*Equivalent versus nonequivalent neighbors.* In 1,1,2-trichloroethane, whose  $^1\text{H}$ -NMR spectrum was shown in Figure AP0925, we consider the two hydrogen atoms in the methylene group of carbon-2 to be equivalent. The carbon-carbon bond is freely rotating, and each of those two hydrogens have the same average neighboring interaction in their spin-spin coupling. As a result, the signal for the carbon-1 hydrogen appears as a 1:2:1 triplet. The general construction for how that pattern arises was shown in Figure 0919, along with Pascal's triangle.

In 1,1,2-trichloroethane, the experimentally determined  $^3J_{\text{HH}} = 7$  Hz. Figure AP0928 summarizes the origin of the appearance of the  $^1\text{H}$ -NMR signal for the single hydrogen carbon-1 and shows how the triplet can be imagined as the sequential addition of each of the two equivalent neighboring hydrogens and their field (splitting) effect.

Figure AP0928

Construction of the  $\delta$  5.78 ppm triplet in 1,1,2-trichloroethane.

In the branching diagram, we start with the carbon-1 hydrogen signal as though there were no neighboring atoms, which would be a singlet at a chemical shift of  $\delta$  5.78 ppm. Then we add the effect of the first neighboring hydrogen, which divides the signal into two populations that are separated by 7 Hz, the  $^3J_{\text{HH}}$  value. The effect is to move half of the original population by +3.5 Hz and the other half by -3.5 Hz. With one neighbor, in other words, the appearance of the signal would be a doublet, centered at  $\delta$  5.78 ppm (which is still the chemical shift value for the absorption), and with a  $^3J_{\text{HH}} = 7$  Hz. Adding into the second neighboring hydrogen completes the picture. Each of the lines of the imagined doublet is split again, sending half in the +3.5 Hz direction and half in the -3.5 Hz direction. The triplet is now present.