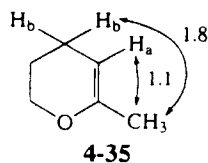
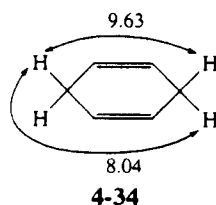
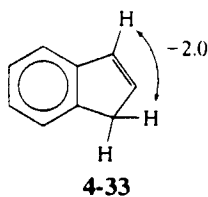
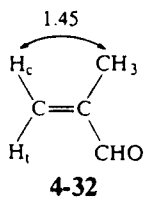
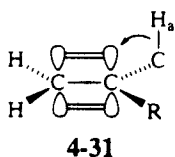


of the other two substituents. In cycloalkenes the value varies from 1.3 Hz in cyclopropene to 8.8 Hz in cyclohexene. In acyclic alkenes, J_{trans} has a range of 10–24 Hz and J_{cis} of 2–19 Hz. Because the ranges overlap, the distinction between cis and trans isomers is fully reliable only when both isomers are in hand. When bonds are intermediate between single and double bonds, 3J is proportional to the overall bond order, as in $^3J_{12} = 8.6$ Hz and $^3J_{23} = 6.0$ Hz in naphthalene.

The ortho coupling in benzene derivatives varies over the relatively small range of 6.7–8.5 Hz, depending on the resonance and inductive effects of the substituents. The presence of heteroatoms in the ring expands the range at the lower end down to 2 Hz, because of the effects of electronegativity (pyridines) and of smaller rings (furans, pyrroles). When one carbon is sp^3 and one is sp^2 ($H-C-C(=X)-H$) the range is 5–8 Hz for freely rotating acyclic hydrocarbons ($X = CR_2$) and 1–5 Hz for aldehydes ($X = O$). The value varies in hydrocarbon rings from -0.8 Hz in cyclobutene to $+3.1$ Hz in cyclohexene and $+5.7$ Hz in cycloheptene. For the central bond in dienes ($H-C(=X)-C(=Y)-H$), the range is 10–12 Hz for transoid systems ($X, Y = CR_2$). When constrained to rings, the pathway is cisoid and the coupling is 1.9 Hz in cyclopentadiene and 5.1 Hz in 1,3-cyclohexadiene. In α, β -unsaturated aldehydes ($X = O, Y = CR_2$), the coupling is about 8 Hz if transoid and 3 Hz if cisoid.

The $H-C-C-C$, $H-C-C-F$, and $C-C-C-C$ couplings also follow Karplus-like relationships. The $^3J(C-C-C-C)$ couplings have a range of values (3–15 Hz) that is larger than the two bond case (the range for $^2J(C-C-C)$ is 1–10 Hz). The $F-C-C-F$ and $H-C-C-P$ couplings appear not to follow the Karplus pattern.

4-6 LONG-RANGE COUPLINGS



Coupling between protons that occurs over more than three bonds is said to be long range. Sometimes coupling between ^{13}C and protons over more than one bond also is called long range, but the term is inappropriate for $^2J(CCH)$ and $^3J(CCCH)$. Long-range coupling constants between protons normally are less than 1 Hz and frequently are unobservably small. In two structural circumstances, however, such couplings commonly become significant.

Interactions of $C-H$ bonds with π electrons of double and triple bonds and aromatic rings along the coupling pathway often increase the magnitude of the coupling constant. One such case is the four bond allylic coupling, $HC-C=CH$, with a range of about $+1$ to -3 Hz and typical values close to -1 Hz. Larger values are observed when the saturated $C-H_a$ bond (4-31) is parallel to the π orbitals. This $\sigma-\pi$ overlap enables coupling to be transmitted more effectively. When the $C-H_a$ bond is orthogonal to the π orbitals, there is no $\sigma-\pi$ contribution and couplings are small (< 1 Hz). In acyclic systems, the dihedral angle is averaged over both favorable and unfavorable arrangements, so an average 4J is found, as in 2-methylacryloin (4-32, $^4J = 1.45$ Hz). Ring constraints can freeze bonds into the favorable arrangement, as in indene (4-33, $^4J = -2.0$ Hz).

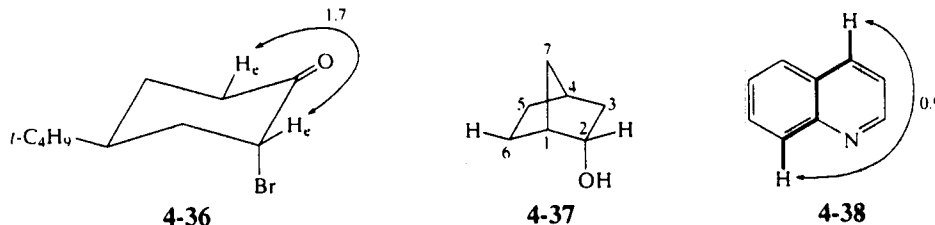
The five bond doubly allylic coupling (also called homoallylic), $HC-C=C-CH$, depends on the orientation of two $C-H$ bonds with respect to the π orbitals. For acyclic systems such as the 2-butenes, 5J typically is 2 Hz, with a range of 0–3 Hz. When both protons are well aligned, the coupling can be quite large, as in the planar 1,4-cyclohexadiene (4-34), for which the cis coupling is 9.63 Hz and the trans coupling is 8.04 Hz. It is not unusual for the doubly allylic coupling to be larger than the allylic, as in 4-35 ($^4J(CH_3-H_a) = 1.1$ Hz, $^5J = 1.8$ Hz).

Coupling constants are particularly large in alkynic and allenic systems, in which $\sigma-\pi$ overlap can be very effective. In allene itself ($CH_2=C=CH_2$), 4J is -7 Hz. In 1,1-dimethylallene, 5J decreases to 3 Hz. In both propyne (methylacetylene, $^4J = 2.9$ Hz) and 2-butyne (dimethylacetylene, $^5J = 2.7$ Hz), the long-range coupling is enhanced because the triple bond imposes no steric limitations on $\sigma-\pi$ overlap. Appreciable long-range couplings have been observed over up to seven bonds in polyalkynes.

Conjugated double bonds provide a more complicated situation. In butadiene, there are two four-bond (-0.86 , -0.83 Hz) and three five-bond ($+0.60$, $+1.30$, $+0.69$)

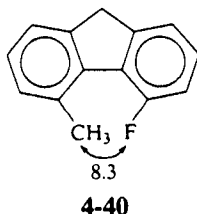
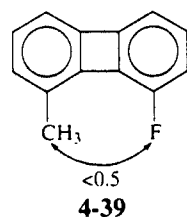
couplings. In aromatic rings, the meta coupling is a 4J (range 1–3 Hz) and the para coupling is a 5J (range 0–1 Hz). In benzene itself, $^3J_{ortho}$ is 7.54 Hz, $^4J_{meta}$ is 1.37 Hz, and $^5J_{para}$ is 0.69 Hz. None of these couplings in butadiene and benzene involves σ - π overlap. Protons on saturated carbon atoms attached to an aromatic ring (CH_3 - C_6H_5) couple with all three types of protons on the ring. These benzylic couplings depend on the σ - π interaction between the substituent C—H bonds and the aromatic π electrons, much like the allylic coupling ($^4J_{ortho} = 0.6$ – 0.9 Hz, $^5J_{meta} = 0.3$ – 0.4 Hz, $^6J_{para} = 0.5$ – 0.6 Hz). A doubly benzylic coupling can take place between protons on different saturated carbons directly attached to the benzene ring (CH_3 - C_6H_4 - CH_3), as in xylenes ($^5J_{ortho} = 0.3$ – 0.5 Hz).

In the second major category of long-range coupling, enhanced values often are observed between protons that are related by a planar W or zigzag pathway. This geometry is seen, for example, in the 1,3-diequatorial arrangement between protons in six-membered rings (4-36, $^4J = 1.7$ Hz). The norbornane framework (4-37) contains several



W arrangements, including that illustrated between the 2 and 6 exo protons, but also between the bridgehead protons (1 and 4) and between 3-endo and 7-anti protons.

In the planar, zigzag arrangement, there is favorable overlap between parallel C—H and C—C bonds, analogous to the optimal vicinal coupling at $\phi = 180^\circ$. The zigzag pathway is entirely within the σ framework but is important for many π systems, including aromatic meta couplings (hence the enhanced $^4J = 1.37$ Hz in benzene). Five-bond zigzag pathways similarly can give rise to enhanced long-range couplings, such as the $^5J = +1.3$ Hz in 1,3-butadiene ($\text{H}-\text{C}=\text{C}-\text{C}=\text{C}-\text{H}$) and the $^5J = 0.9$ Hz coupling between the indicated protons in quinoline (4-38).



Although coupling information is always passed via electron-mediated pathways, in some cases part of the through bond pathway may be skipped, as in allylic and benzylic couplings with σ - π overlap. Two nuclei that are within van der Waals contact in space over any number of bonds can interchange spin information if at least one of the nuclei possesses lone pair electrons. These so-called through space couplings are found most commonly, but not exclusively, in H—F and F—F pairs. The six bond CH_3 -F coupling is negligible in 4-39 (H—F distance 2.84 Å) but is 8.3 Hz in 4-40 (1.44 Å) (the sum of the H and F van der Waals radii is 2.55 Å). In the latter case coupling information is probably passed from the proton through the lone pair electrons to the fluorine nucleus. Such a mechanism very likely is important in the geminal F—C—F coupling, which is unusually large. Values of $^2J(\text{FCF})$ are larger for sp^3 CF_2 than for sp^2 CF_2 , as the smaller tetrahedral angle brings the fluorine atoms closer together.

4-7 SPECTRAL ANALYSIS

We have not said much about how coupling constants are extracted from spectra. Measurement is straightforward when the spectrum is first order, as chemical shifts correspond to the midpoint of a resonance multiplet. The midpoint falls between the components of a doublet from coupling to one other spin, it is coincident with the middle peak of a triplet from coupling to two other spins, and so on. The coupling constant corresponds to the distance between adjacent peaks in the resonance multiplet. These simple characteristics may fail in second-order spectra. Because most nuclei other than the proton have very large chemical shift ranges and because these nuclei often are in low natural abundance and hence do not show coupling to each other, second-order analysis is primarily a consideration for proton spectra alone. For protons, spectra measured above 500 MHz are usually first order from the $\Delta\nu/J$ criterion. Magnetic nonequiva-