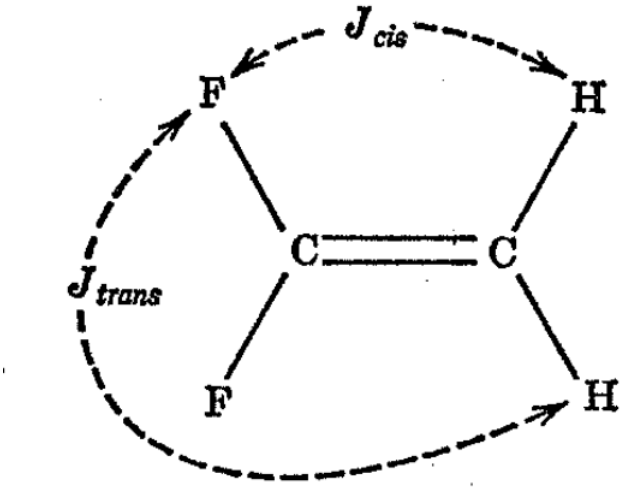
3.8: Spin-Spin Couplings in Rigid Systems

Difficulties in interpretation of spin-spin couplings are very often encountered in more or less rigid complex molecules such as cyclic compounds. There are several reasons for expecting difficulties. First, as shown for styrene oxide, the protons of adjacent methylenes in a rigid system will generally have at least two spin-spin coupling constants which correspond to interactions between the various combinations of cis and trans protons. Second, J for protons on adjacent carbons shows a strong angular dependence and, as a result, the couplings in more or less rigid systems vary between zero and the values normally encountered for open-chain substances. Furthermore, it should be remembered that whenever J is large compared with the chemical shift, no splitting or chemical shift may be apparent in the spectrum. An example is cyclopentanone, which shows only a single proton resonance line.

A further and serious complication is introduced in rigid systems when chemically equivalent nuclei which are close enough to each other to be strongly coupled are also strongly coupled to other nuclei.[7] An excellent illustration is afforded by 1,l-difluoroethylene. Here, the first-order treatment predicts four resonance lines of equal intensity because each proton should be coupled to the two fluorines with different coupling constants, one fluorine being cis to a given proton and the other being trans. However, the observed spectrum shows ten lines (Fig. 3-10), and in the detailed mathematical treatment of spin-spin coupling for this molecule, both the fluorine-fluorine and proton-proton coupling make important contributions to the splitting. Generally, one will expect complications from couplings between formally equivalent nuclei wherever such nuclei are so located as to have different intramolecular coupling constants to other magnetic nuclei.



7 H. M. McConnell, A. D. McLean, and C. A. Reilly, J. Chem. Phys., 23, 1152 (1955).