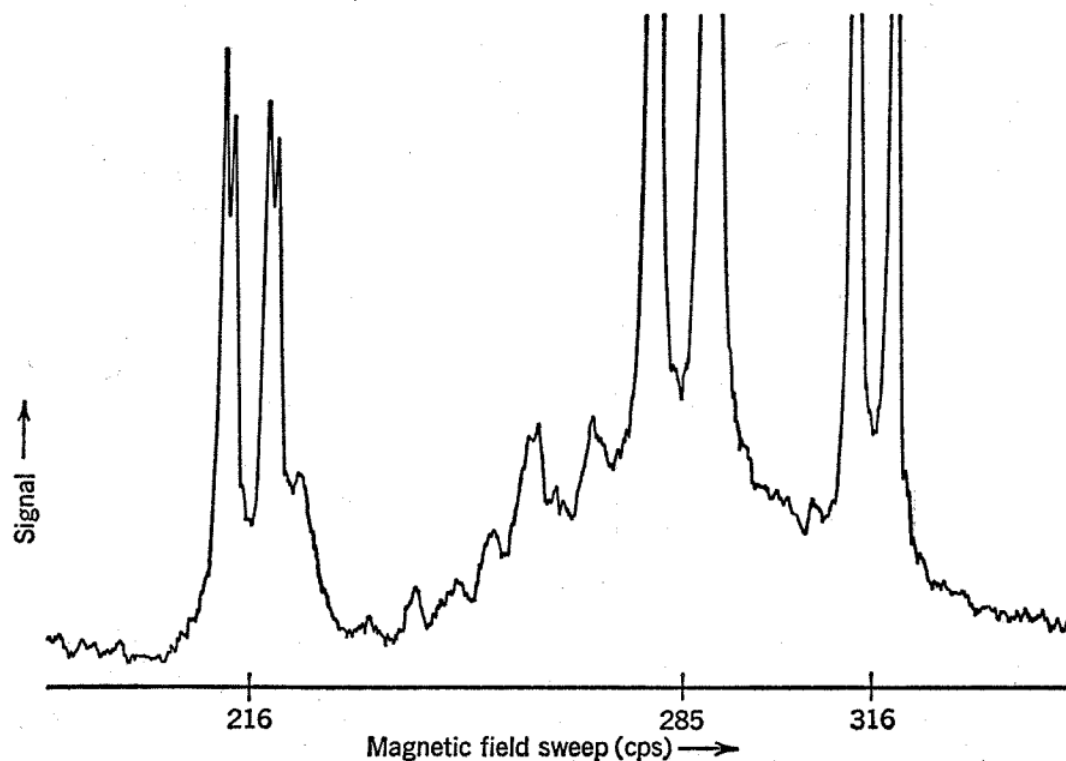


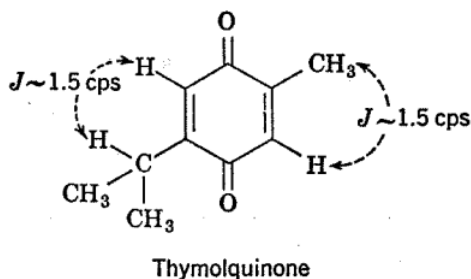
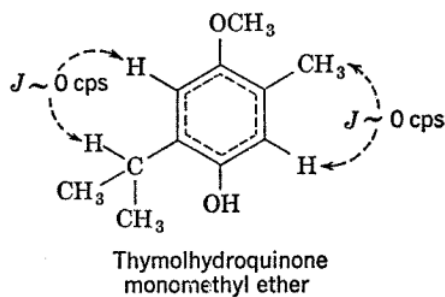
3.6: Magnitudes of Coupling Constants

In saturated noncyclic compounds, spin-spin coupling constants for protons located on adjacent carbons (three bonds apart) are more or less constant from molecule to molecule at about 7 cps. Generally, J becomes immeasurably small with four bonds intervening, except when one or two of these is a double bond. Thus, as mentioned earlier, rather large couplings (~ 10 cps) are observed across the double bonds of an allenic system, and we note now that J is much smaller (1 to 2 cps) across one single and one double C-C bond, as in isobutylene.

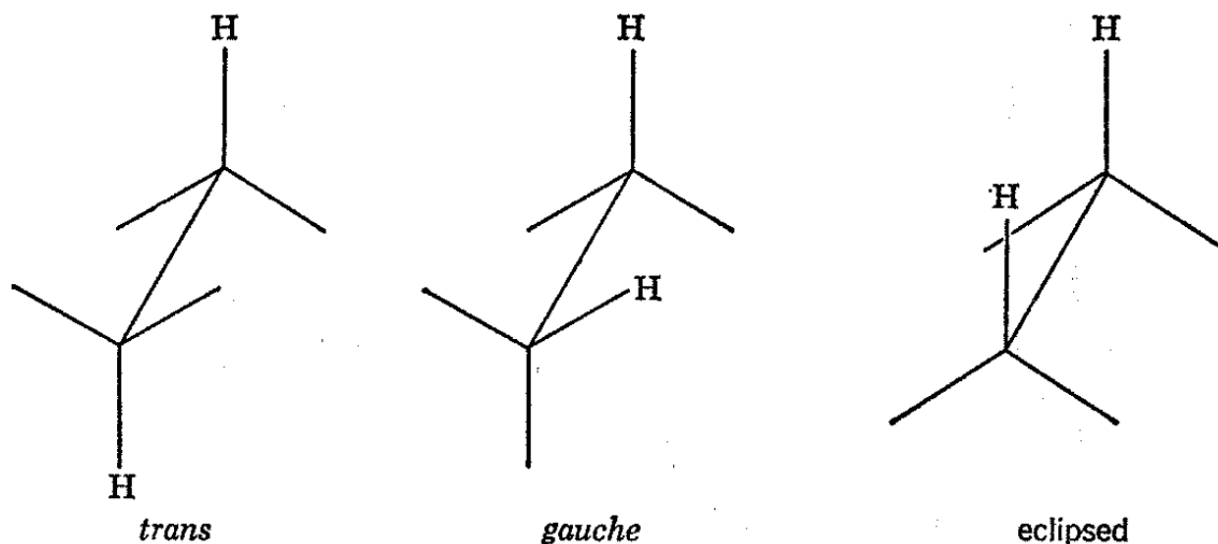


(Courtesy of E. E. van Tamelen.)

An interesting variation of J with bond type has been noted by Shooley⁴ for couplings through the double bonds of a quinone and a derivative of the corresponding hydroquinone with a fully aromatic ring. Thus, the benzenoid thymol system shows no resolvable coupling between the ring protons and those on the adjacent alkyl groups whereas, with thymoquinone, one of the ring-proton resonances is split into a 1:3:3:1 quartet through spin-spin coupling involving the neighboring CH_3 group, while the other ring-proton resonance is split into a doublet by the α proton of the isopropyl group.



Proton spin-spin couplings are powerfully influenced by molecular geometry. Trans conformations of protons in saturated compounds appear to lead to substantially larger couplings than corresponding gauche or eclipsed arrangements. Couplings between trans protons attached to double bonds are similarly larger than between cis protons.



In some compounds such as cyclobutene, spin-spin splitting is unexpectedly small or completely absent. Consequently, any structure interpretation which suggests that groups of nonequivalent protons are not contiguous because of failure to observe spin-spin couplings may be seriously in error.

4 J. N. Shoolery, Varian Associates Tech. Bull., 2, 8 (1957).

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