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Sternhell S. Correlation of interproton spin-spin coupling constants with structure.
Quart. Rev. 23:236-70, 1969.
[Department of Organic Chemistry, University of Sydney, New South Wales, Australia]

This review summarised the most important correlations between interproton coupling constants and structure available at the time. It cited 148 references, many of them multiple, and contained 109 structures with hundreds of numerical values for coupling constants as well as graphical and tabular results defining the variation of ^{1}H,^{1}H coupling constants with stereoelectronic factors. [The *SCI*® indicates that this paper has been cited in over 610 publications, making it the most-cited paper for this journal.]

Sever Sternhell
Department of Organic Chemistry
University of Sydney
New South Wales 2006
Australia

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The most obvious reason for the power of NMR spectroscopy as a structural tool in organic chemistry was defined early by J.D. Roberts by the phrase that "hydrogen has become a functional group." Nowadays, we would be inclined to state more generally that NMR permits us to detect any structural element containing hydrogen, carbon, or, indeed, many other elements. However, the power of NMR spectroscopy is vastly augmented by the fact that it not only permits us to identify structural elements but also provides information about their juxtaposition or connectivity. Powerful NMR methods for establishing juxtaposition include the relatively modern techniques of NOESY and 2D INADEQUATE, but the most widely used remain the humble interproton coupling constants, which, properly interpreted, give a wealth of information about relative positions of protons in a molecule.

In 1969 many of the basic correlations between the magnitude of interproton coupling constants and structure were already available, but the editors of *Quarterly Reviews* felt that a critical overall review of the subject would be useful and approached me to produce one. The timing of this request was fortunate because I had recently completed a general monograph with L.M. Jackman on the applications of NMR spectroscopy in organic chemistry[1] and had kept up a very complete file on interproton coupling constants, which were also a part of my own research interests. I was thus able to produce this fairly extensive review quickly, and it apparently has been widely used as a source of correlations for interpreting NMR spectra in terms of structure.

While I have kept up some interest in this field, e.g., in connection with allylic,[2] geminal,[3] and benzylic[4,5] coupling constants, I note that very little systematic work has appeared recently on the correlation of coupling constants with structure. It is possible that the problem of determination of structures of organic molecules by spectroscopic techniques (largely NMR) has now been solved, if not overdetermined, by the appearance of powerful 2D methods, but it is also possible that the correlations between interproton coupling constants and structure are so good that little incentive exists for improvement. In any case, progress in X-ray crystallography has ensured that the structure of practically any nonpolymeric organic compound, however fractious, can be determined. Nevertheless, proton NMR spectra of organic compounds and mixtures will continue to be obtained and interpreted in astronomical numbers, and this, in turn, requires some knowledge of the significance of these *little* numbers—the coupling constants.

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1. **Jackman L M & Sternhell S.** *Applications of NMR spectroscopy in organic chemistry.* Oxford: Pergamon Press, 1969. 546 p. (Cited 3,705 times.)
2. **Barfield M, Spear R J & Sternhell S.** Allylic interproton spin-spin coupling. *Chem. Rev.* 76:593-624, 1976. (Cited 60 times.)
3. **Spear R J & Sternhell S.** Influence of ring size on geminal interproton coupling constants in exocyclic methylene groups. *Aust. J. Chem.* 38:889-97, 1985.
4. **Barfield M, Fallick C J, Hata K, Sternhell S & Westerman P W.** Conformational, bond-order, and substituent dependencies of orthobenzylic coupling constants. *J. Amer. Chem. Soc.* 105:2178-86, 1983.
5. **Collins M J, Hatton P M, Sternhell S & Tansey C W.** Substituent and ring size dependence of the ^4J(Me—C ≡ C—H) coupling constant. *Magn. Resonance Chem.* 25:824-8, 1987.