This Week's Citation Classic

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McConnell H M & Chestnut D B. Theory of isotropic **hyperfine interactions in** π-electron radicals.*J. Chem. Phys.* **28**:107-17**,** 1958.
[Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, CA]

Many organic free radicals and organic molecules in photoexcited triplet states absorb microwaves in the presence of an externally applied magnetic field, the effect being known as electron paramagnetic resonance. The paramagnetic resonance spectra of these molecules generally show a rich hyperfine structure due to the magnetic interaction between the unpaired electrons of the molecules and nuclei having magnetic moments, especially protons. The subject paper shows how this proton hyperfine structure can be related to the electronic structure of these molecules. [The SCI® **indicates that this paper has been cited over 555 times since 1961.]**

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"Although I had been very much interested in theories of the electronic structures of organic mole-cules prior to 1956, I was continually frustrated by the difficulties of quantitatively relating these theories to experiment. I was dubious about the validity of much of the literature that claimed agreement between one or another theory and experiment. With the initial discoveries of nuclear hyperfine structure in the paramagnetic resonance spectra of organic radicals by S.I.Weissman, G.K. Frankel, and C. Hutchinson, Jr. and their colleagues, I immediately realized that the large body of experimental data on various radicals that would follow could be of great theoretical interest if there existed some simple, reliable way to relate nuclear hyperfine structure in these molecules, especially 'ð-electron molecules,' to their electronic structures.

"The subject paper with Donald Chestnut, then a graduate student at Cal Tech, represented the culmination of a number of theoretical studies by me to demonstrate that there did indeed exist a simple relationship between electronic structure (specifically ð-electron density on carbon atoms) and attached protons. This relation, referred to subsequently as 'McConnell's relation' in the literature, has been verified for a number of molecules by detailed theoretical calculations.

"A second significant feature of the theory was the prediction that the proton hyperfine coupling constants of aromatic hydrogen atoms attached to aromatic carbon atoms should have an anomalous sign, negative when the carbon atom spin density is positive. This prediction was first verified experimentally in my laboratory at Cal Tech with T. Cole, C. Heller, and R. W. Fessenden, and has since been verified by numerous experiments in other laboratories."[1]

1. **McConnell H M, Heller C, Cole T & Fessenden R W.** Radiation damage in organic crystals. *J. Amer. Chem. Soc.* **82**:766-75, 1960.