One-bond C^{13}-H coupling constants are presented for 13 hydrocarbons, including cases where the hybridization of the carbon orbitals is approximately sp^3, sp^2, and sp. The coupling constants appear to be proportional to the percent s-character, and this is rationalized using simple theoretical considerations. [The *SCI®* indicates that this paper has been cited over 405 times since 1961.]

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"Among the comparatively few chemists doing NMR spectroscopy in the mid-1950s there was much excitement about the possibility that the newly available values of chemical shifts and indirect spin-spin coupling constants might be simply related to parameters widely used to characterize chemical bonds, such as ionicity, bond order, and hybridization, and thus provide a new and powerful means of validating predictions of bonding theories. In 1957, Paul Lauterbur published the first collection of values of J_{CH}, the directly bonded C^{13}-H coupling constant.[1] It was evident that J_{CH} varied widely from molecule to molecule, but the compounds included were of such diverse types that one could not decide which structural feature or features controlled the magnitude of the coupling. The idea of using J_{CH} more systematically to probe the nature of the C-H bond was included in a 1957 proposal to the NSF, resulting in a grant that made possible the purchase in 1958 of Purdue University's first high-resolution NMR spectrometer.

"Don Pritchard and I decided to inaugurate this instrument by undertaking a survey of J_{CH} values for several groups of compounds chosen so that the effects of various bonding parameters on the coupling could be examined separately. We began with an assortment of unsubstituted hydrocarbons, expecting that here J_{CH} would be determined primarily by the hybridization of the carbon atomic orbitals and perhaps to a lesser extent by small changes in the bond polarities. It quickly became apparent that J_{CH} was well correlated with accepted values of the percent s-character of the carbon orbitals, and it was not difficult to devise a simple semiempirical theory which accounted for such a relation.

"Our findings attracted the attention of bonding theorists and, as NMR became increasingly popular, of many organic chemists, especially those interested in strained cyclic or polycyclic compounds, where the hybridization cannot immediately be inferred from the interbond angles. Together with measurements on substituted methanes,[2] our results suggested that even in noncyclic molecules the relation between bond angles and hybridization coefficients might be less straightforward than had often been supposed; in effect, the data sometimes seemed to call for 'bent' bonds. This stimulated much further theoretical and experimental work aimed at showing how much J_{CH} is influenced by variables not explicitly included in our simple theory, such as the effective nuclear charge on the carbon atom. For C-H bonds adjacent to atoms of elements other than carbon or hydrogen, the question has never been settled to everyone's complete satisfaction, but the consensus seems to be that at least for the hydrocarbons J_{CH} does provide a gauge of carbon orbital s-character."[3]

1. Lauterbur P C. C^{13} nuclear magnetic resonance spectra. *J. Chem. Phys.* **26**:217-18, 1957.
2. Muller N & Pritchard D E. C^{13} splittings in proton magnetic resonance spectra. II. Bonding in substituted methanes. *J Chem. Phys.* **31**:1471-76, 1959.
3. Stothers J B. *Carbon-13 NMR spectroscopy.* New York: Academic Press, 1972. 574 p.