

Grant D M & Paul E G. Carbon-13 magnetic resonance. II. Chemical shift data for the alkanes. *J. Amer. Chem. Soc.* 86:2984-90, 1964.
[Department of Chemistry, University of Utah, Salt Lake City, UT]

Carbon-13 chemical shift data were given for linear and branched alkanes. Systematic trends in these shifts were found to correlate nicely with structural parameters, which have high predictability. A sizable γ -substituent parameter was observed for the first time on which conformational analysis may be based. [The SCI® indicates that this paper has been cited in over 545 publications since 1964.]

David M. Grant
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

December 5, 1983

"In 1963, carbon-13 magnetic resonance (CMR) spectra were obtainable only for isotopically enriched compounds or for small molecules which could be observed by a low resolution adiabatic rapid passage technique. Using proton decoupling to collapse the proton induced multiplets. Also, to produce a sizable nuclear Overhauser enhancement (NOE) factor,¹ a new way to obtain CMR spectra was reported for the first time in a companion paper.² Unfortunately, the experimental procedures were at best laborious for a few compounds and impossible for most samples.

"Edward Paul, my first postdoctoral associate, had joined the laboratory from a background in organic synthesis and readily appreciated the ultimate importance of CMR in organic chemis-

try. It was his dogged persistence in the development of a CMR technique² which ultimately led to highly reproducible spectroscopic results. This paper on the alkanes represented the first application of the new CMR technique. The present ubiquitous use of CMR likely accounts for the recognition of this work.

"From the very beginning, systematic trends in CMR shifts were noted to correlate with molecular structure, and the resulting parametric shifts have since been used in numerous instances³⁻⁵ to provide detailed structural characterizations. The first chemical shift anomaly encountered in our study of the linear alkanes was in n-heptane where the C-4 shift was 2.93 ppm upfield from C-3. For the smaller alkanes, the shifts had monotonically shifted downfield as one moved down the chain from the methyl carbon. The C-4 shift in n-heptane had been expected either to be downfield from C-3 or at least to become degenerate with the C-3 shift. The excitement in the laboratory produced much speculation which ran from total disbelief (after all, the procedures were painful and even Paul could make a mistake) to elaborate schemes now long forgotten. The effect persisted however in a repeat experiment on n-heptane and in other higher homologues and in branched alkanes. The so-called γ -substituent effect was first encountered in this work and results from aliphatic chain coiling. This effect has formed the basis for the use of CMR in conformational analysis.³⁻⁵ A review series provides adequate evidence of the vitality and importance of CMR studies in chemistry."⁶

1. Kuhlmann K F & Grant D M. The nuclear Overhauser enhancement of the carbon-13 magnetic resonance spectrum of formic acid. *J. Amer. Chem. Soc.* 90:7355-7, 1968. (Cited 100 times.)
2. Paul E G & Grant D M. Carbon-13 magnetic resonance. I. Improved carbon-13 magnetic resonance spectra obtained by proton decoupling and rapid sample spinning. *J. Amer. Chem. Soc.* 86:2977-83, 1964. (Cited 60 times.)
3. Dalling D K & Grant D M. Carbon-13 magnetic resonance. IX. The methyl cyclohexanes. *J. Amer. Chem. Soc.* 89:6612-22, 1967.
4. Dalling D K. Citation Classic. Commentary on *J. Amer. Chem. Soc.* 89:6612-22, 1967. *Current Contents/Physical, Chemical & Earth Sciences* 23(38):22, 19 September 1983.
5. Stothers J B. *Carbon-13 NMR spectroscopy*. New York: Academic Press, 1972. 559 p.
6. Levy G C, ed. *Topics in carbon-13 NMR spectroscopy*. New York: Wiley, 1976-1979. Vols. 1-3.