

Laszlo P & von Raguë Schleyer P. Analysis of the nuclear magnetic resonance spectra of norbornene derivatives. *J. Amer. Chem. Soc.* 86:1171-9, 1964.
[Frick Chemical Laboratory, Princeton University, NJ]

By the use of ^{13}C -satellites and of selective solvent shifts, all the proton resonances and all the chemical shifts and coupling constants were measured for several norbornene derivatives. [The SCI® indicates that this paper has been cited in over 400 publications since 1964.]

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"In 1962, when I was 24 years old, I started work at Princeton University with Paul von Raguë Schleyer, an assistant professor in his early 30s. I was his first postdoc. He asked me to prepare 2-fluoronorbornane as a precursor for the 2-norbornyl cation. I made it, physically as well as figuratively. But we both decided that synthetic organic chemistry was not my forte.

"Since my previous work in France had been to analyze spin-spin coupling in the ^1H nuclear magnetic resonance (NMR) of terpenes, Paul suggested that I take a look at the NMR of bicyclo (2.2.1) heptane derivatives of which he had a large collection. I started recording spectra on a brand-new Varian A-60 machine. We had improved it so that repeated traces could be accumulated in a multichannel analyzer. I could thus obtain, besides the resonances for the molecule proper, the weaker ^{13}C -satellites due to the ca. one percent natural abundance. These gave me the otherwise elusive coupling between isochronous nuclei. I realized then that I could measure most of the 20-30 nonzero couplings present in these molecules. The article we published in 1964 (it was completed on the France when

we sailed home) compiled all such data. I had picked a system of about the right size for a near-complete analysis by hand of the coupling scheme. The procedure was readily transferable to organic molecules of comparable size. Publication was extremely timely. Physical organic chemistry was at its peak in the US. Organic chemists were making and studying numerous norbornane derivatives because of the then beginning classical-nonclassical ion controversy about the structure of the 2-norbornyl cation. More generally, the question of through-space versus through-bond interactions could be addressed with molecules such as I had studied. Hence, the popularity of this paper stems from these three factors: the A-60 spectrometer was an instrument tailored to the organic chemists; we rode on the wave of a glut of norbornane derivatives; and we showed the extent of structural information to be extracted by inspection of a proton NMR spectrum. I suspect also that the artwork, done by my wife, was another asset!

"The difficulties were mostly mechanical and electronic. Fortunately, Paul was not only a superb supervisor who taught me the importance of scrutinizing the evidence and understanding it fully; he was also a wizard with a screwdriver or a soldering iron, and we never had to wait for an improbable repairman.

"Twenty years later, the field is still alive. A recent book, *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*, by Alan P. Marchand, surveys it.¹ Ironically, in recent months I have started to work again with bicyclics: we are seeking new catalysts for the Diels-Alder reaction."

1. Marchand A P. *Stereochemical applications of NMR studies in rigid bicyclic systems*. Deerfield Beach, FL: Verlag Chemie International, 1982. 231 p.