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Why Don't Equivalent Protons Split Each Other?

Hai-Feng Ji*

Department of Chemistry, Drexel University, PA 19104, USA

"Magnetically equivalent protons don't split each other", or "they don't split each other because they are equivalent", you have seen these sentences or the like in every organic textbook when the Nuclear Magnetic Resonance (NMR) technique is introduced. However, no textbook, as far as I am aware of, explains why the equivalent protons don't split each other.

Upon further research, the only explanation comes from the quantum mechanical theory, which has not been introduced to the first or second year undergraduate students. This might explain why the explanation was not observed in any textbooks.

Just as William of Ockham stated: "All things being equal, the simplest solution tends to be the best one", there should be a simple explanation, as do many other concepts in organic and general chemistry. The answer lies in the decoupling techniques in NMR, such as proton spin decoupling in 13C NMR and specific proton decoupling, homonuclear and heteronuclear decoupling in ^{1}H NMR [1-3].

In proton spin decoupling 13C spectra, the protons attached on carbons are uninterruptedly irradiated with a broadband of radio waves, so the protons are rapidly flipping from the two spin states, ending with one average spin state from all the possible spin states. Thus, each carbon only shows a singlet peak due to the presence of only one averaged spin state proton attached on the carbon. Similarly, in specific proton decoupling, homonuclear decoupling, or heteronuclear decoupling, a certain part of protons are irradiated to decouple their connectivity with the signal proton, i.e., the coupling no longer exist or the coupling constant becomes zero when both coupling protons are irradiated.

This explanation can be applied for magnetically equivalent protons–when a proton is irradiated at a radio wavelength to give a signal, its equivalent proton(s) is(are) also irradiated at the same time from the same radio wave, thus the irradiated equivalent protons do not have the capability to split the signal proton.

In conclusion, I suggest the following sentence or the like to be included in organic chemistry textbooks. "For magnetically equivalent protons, the protons are irradiated at the same radio wavelength, so the protons are rapidly flipping from the two spin states, resulting in only one average spin state from all the possible spin states, i.e., the magnetic fields generated from the coupling protons averages to zero. Thus, the protons only show a singlet peak due to the lack of the coupling splitting between the irradiated protons." I also suggest removing the following sentence from some textbooks: "Equivalent protons are still coupled to each other, but the spectra do not show it". This is not an accurate statement. When both irradiated, equivalent protons no longer couple with each other, although they are coupled to each other at ground state, or when only one is irradiated. Irradiating only one proton out of two or more equivalent protons requires ultra-low radiation intensity, which is not common practice in taking NMR spectra because of the significant noises.

References

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***Corresponding author :** Hai-Feng Ji, Department of Chemistry, Drexel University, PA 19104, USA, Tel: 01-215-895-2562; E-mail: mailto:hj56@drexel.edu

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