

# This Week's Citation Classic

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Sanders J K M & Williams D H. A shift reagent for use in nuclear magnetic resonance spectroscopy. A first-order spectrum of n-hexanol. *J. Chem. Soc. Chem. Commun.* 7:422-3, 1970.  
[University Chemical Laboratory, Cambridge, England]

The use of a lanthanide complex [Eu(DPM)<sub>3</sub>] in obtaining first-order, or more readily analysable, proton n.m.r. spectra for lone-pair bearing organic compounds with complex spectra is described. Implications for structural studies are discussed. [The *SCI*<sup>®</sup> indicates that this paper has been cited over 280 times since 1970.]

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"I moved to Cambridge in October 1969, aged 21, to begin research. My supervisor, Dudley Williams, was excited about a paper which had just been published by Conrad Hinckley.<sup>1</sup> Hinckley had shown that the pyridine adduct of the lanthanide complex Eu(DPM)<sub>3</sub>, by complexing with cholesterol, was capable of drastically changing the n.m.r. spectrum of the steroid so as to reveal a tremendous amount of structural information. He called the complex a shift reagent. Hinckley was clearly an inorganic chemist, and apparently not in a position to fully exploit his discovery. Williams, however, as an accomplished steroid chemist and organic spectroscopist, knew the kind of problem which needed this solution and put me to work on the topic.

"Williams felt that the pyridine in Hinckley's complex was getting in the way by competing for the lanthanide. By early January 1970, I had made some pyridine-free Eu(DPM)<sub>3</sub> and I did a cholesterol run similar to Hinckley's. Everything had shifted

so far that the spectrum was unrecognisable: leaving out pyridine increased shifts fourfold!

"As a novice I was uncomfortable with such complex molecules as steroids so I decided to explore the shift reagent's potential by using simple compounds with intractable spectra. N-hexanol was the first; essentially only two protons are normally resolved, but late on the night of January 20, as I added small amounts of Eu(DPM)<sub>3</sub>, one new signal after another separated until every detail of every proton was resolved. The satisfaction and excitement were extraordinarily intense—but everyone I knew was at home, asleep. Within five weeks we had looked at a range of compound types and submitted this first paper.

"We sent another paper to the same journal soon after, but it was rejected. A referee felt that 'the first...had crystallised all the novelty.' That rejected paper, slightly filled out, was published elsewhere<sup>2</sup> and became the most-cited 1971 paper in 1971 and 1972.<sup>3</sup> Why was our work highly cited? Our first paper (and Hinckley's) set off an explosion of shift reagent work. Anybody could magically persuade impossibly difficult spectra to reveal a wealth of new information for a trivial cost in chemicals. The intellectual credit belongs to Hinckley. Our role was to improve the shift power very substantially and, by fortunate choice of n-hexanol, demonstrate the power of the technique with a spectacular spectrum every organic chemist could appreciate. I suspect that the long-term importance of this whole area is much less than citation counts would indicate: it was popular because it was easy.

"As a result of this work I was awarded the Meldola Medal of the Royal Institute of Chemistry. The work also helped Williams toward the position of most-cited organic chemist outside the US, 1965-1978."<sup>4</sup>

1. Hinckley C C. Paramagnetic shifts in solutions of cholesterol and the dipyrindine adduct of trisdipivalomethanatoeuropium (III). A shift reagent. *J. Amer. Chem. Soc.* 91:5160-2, 1969.
2. Sanders J K M & Williams D H. Tris(dipivalomethanato)europium. A paramagnetic shift reagent for use in nuclear magnetic resonance spectroscopy. *J. Amer. Chem. Soc.* 93:641-5, 1971.
3. Garfield E. The 25 most cited 1971 papers reveal a great deal about research in 1971. *Current Contents* (44):5-8, 31 October 1973.
4. -----, The 1,000 contemporary scientists most-cited 1965-1978. Part I. The basic list and introduction. *Current Contents* (41):5-14, 12 October 1981.

\*Reprinted in: Garfield E. *Essays of an information scientist*. Philadelphia: ISI Press, 1981. 4 Vols.