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This Week's Citation Classic

Schaefer T & Schneider W G. Proton magnetic resonance shifts and the electron density distribution in aromatic systems. *Can. J. Chem.* **41**:966-82, 1963.
[Div. Pure hemistry, National Research Council, Ottawa, Canada]

Proton chemical shifts are related to calculated electron density distributions for a variety of neutral and charged aromatic species. Perturbations from substituents, ring currents, ion pairing, and solvents may obscure a linear relationship between shift and electron density. [The *SCI*® indicates that this paper has been cited over 275 times since 1963.]

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"Twenty years ago an interest developed in the correlation of nmr chemical shifts with molecular electron density distributions. The interest was stimulated by developments in molecular orbital theory, in nmr instrumentation, and in organic synthesis. The paper was not the first to discuss the correlations, but it appeared at the right time, was simply written, contained an evocative spectrum, discussed a variety of molecular species, and pointed out the pitfalls on the road from shifts to electron densities. Probably it was read by organic chemists interested in 'aromaticity,' in an-nulenes, in carbanions, and in carbocations. This interest has not flagged[1] and helps to account for its frequent citation. The concepts in the paper are now familiar to undergraduates, so I will continue with some memories.

"Any clarity in the paper came from W.G. Schneider. He gave me precedence because of kindness. I was the junior author. My association with Schneider went back to 1955, when I spent four months as a summer student in his laboratory at the National Research Council in Ottawa. Schneider and H.J. Bernstein were playing with a new Varian nmr spectrometer. It had no field stabilizer, not to mention a lock system. I watched in fascination as Bill and Harold chased a spectrum across the oscilloscope or tried to catch it on a fast recorder (a basket for the spewed paper was an essential accessory). They were measuring proton shifts of condensed aromatics and this work is described in their book[2] with John Pople.

"Bill was able to arrange my doctoral work with Sir Rex Richards at Oxford. Rex was building a high resolution spectrometer and watched patiently as I built version after version of an nmr probe. Sardonic comments by the inimitable Ray Freeman, who was finishing his thesis, kept me at it.

"By 1962 I was an assistant professor in my home province and was married to a girl from Oxford. Our first child, Catherine, was eight months old and had severe problems.[3] Nicola, my wife, deserved a holiday at home. As usual, Bill came to the rescue and offered me a summer job. We drove to Montreal, Nicola and Catherine boarded a ship for Liverpool, and I got to Ottawa just as Bill was leaving for London to receive his FRS. He suggested I try the measurements described in the paper.

"This I did, with essential help from Yves Lupien in vacuum line techniques and under the knowledgeable eyes of John Martin and Allan Reddoch. They grinned amicably as I churned out HMOs on a mechanical calculator.

"I spent three wonderful summers in Schneider's laboratory; productive midnight shifts on the spectrometer, emerging into the cool dawn to head for bacon and eggs. Bill went on to become president of the National Research Council. He inspired many a young chemist in Canada.

"Oh yes, the paper must have helped to get me a promotion and other delicious things."

1. **Young R N.** NMR spectroscopy of carbanions and carbocations. *Progr. Nucl. Magn. Res. Spectrosc.* **12**:261-86, 1979.
2. **Pople J A, Schneider W G & Bernstein H J.** *High resolution nuclear magnetic resonance.* New York: McGraw Hill, 1959. 501 p.
3. **Schaefer N.** *Does she know she's there?* Toronto: Fitzhenry & Whitesides, 1978. 240 p.