

This Week's Citation Classic®

Churchill M R. Some comments on carbon-hydrogen and nitrogen-hydrogen distances assumed in, and determined from, recent X-ray diffraction studies on inorganic complexes. *Inorg. Chem.* 12:1213-4, 1973.
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This paper was written to convince skeptics that the hydrogen atoms in transition-metal complexes could be both located and refined from X-ray diffraction data. It compiled results showing that the derived C—H bond length was not equivalent to the spectroscopic (internuclear) distance of 1.08Å, but was reduced to 0.95Å. This latter value represents the distance between the centroids of electron density about carbon and hydrogen and is systematically shorter than the true internuclear distance. [The SC[®] indicates that this paper has been cited in over 425 publications.]

How to Find Hydrogen Atoms

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In August 1971 I left Harvard University to take a tenured professorship at the University of Illinois at Chicago. My new position provided me with a Picker diffractometer (far superior to my equipment at Harvard) along with rapid access to, and essentially unlimited time on, an IBM 370/155 computer. With the extraordinarily capable assistance of Dr. Barry G. De Boer, my new research group began a series of X-ray diffraction studies on organometallic complexes. In each case we were able to observe the electron density associated with the hydrogen atoms. (Note that X-rays are diffracted by electrons; an X-ray diffraction study yields an electron-density map in which the peak heights are roughly proportional to the atomic numbers [Z] of the atoms. Since hydrogen has Z = 1, it yields the smallest peaks, which may be "lost" in random background unless the diffraction data are collected carefully.) With the delightful incentive of free computer time, we started to "play" and to

see how well these hydrogen atoms would behave under standard refinement processes. We were pleasantly surprised to discover that the hydrogen atoms consistently refined to yield C—H distances averaging 0.95Å and that this process worked even where heavy atoms (iron [Z = 26] to rhodium [Z = 45]) were present in the structure. Later we were able to extend our studies to the refinement of hydrogen atoms bridging two tungsten atoms (Z = 74)¹ and attached directly to a tris-osmium (Z = 76) framework.² We also were able to refine the anisotropic thermal parameters of all the hydrogen atoms in the species $[\text{N}(\text{CH}_3)_4]^+ [(\text{CH}_3)_2\text{B}_{10}\text{C}_2\text{H}_{11}]^-$.³

The cited paper probably would never have been written had I not also been the associate editor of *Inorganic Chemistry* responsible for crystallographic papers. I had noticed that many authors incorporated calculated positions for hydrogen atoms into their structural reports, but that many used the *invalid* spectroscopic internuclear distance of 1.08Å.

The cited paper was written with the following items in mind: (1) The "X-ray determined" C—H distance is less than the true internuclear separation. (This was already well documented⁴ but apparently unrecognized by many crystallographers at the time.) (2) Authors had used inappropriate C—H distances in calculating H-atom positions or had simply omitted H atoms from their structural models. (3) I provided a compilation of C—H distances determined in recent inorganic structures (including the first seven studies carried out by my new research group). (4) I wanted to convince structural chemists that hydrogen atoms could be located and their positions refined even where heavy atoms were present.

It might amuse readers to know that the concept of writing this paper occurred one afternoon, the principal theses and content were finalized in a traffic jam on the Eisenhower Expressway, and the paper was typed at home and submitted that same evening.

1. Churchill M R & Chang S W-Y. X-ray crystallographic determination of the molecular structure of bis(tetraethylammonium)di- μ -hydrido-octacarbonylditungstate(2-), $[\text{Et}_4\text{N}^+]_2[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$. A unique example of the successful location and refinement of hydride ligands in positions bridging third-row transition-metal atoms. *Inorg. Chem.* 13:2413-9, 1974. (Cited 60 times.)
2. Churchill M R & De Boer B G. Structural studies on polynuclear osmium carbonyl hydrides. 3. Crystal structure and molecular geometry of $\text{H}_2\text{Os}_2(\text{CO})_{10}(\text{PPh}_3)_2$, including the direct location of both terminal and μ_2 -bridging hydride ligands. *Inorg. Chem.* 16:2397-403, 1977. (Cited 75 times.)
3. ———. Crystal structure and molecular geometry of $[\text{Me}_5\text{N}^+][\text{Me}_6\text{B}_{10}\text{C}_2\text{H}_{11}]^-$, including refinement of positional and anisotropic thermal parameters for all hydrogen atoms. *Inorg. Chem.* 12:2674-82, 1973. (Cited 25 times.)
4. Stewart R F, Davidson E R & Simpson W T. Coherent x-ray scattering for the hydrogen atom in the hydrogen molecule. *J. Chem. Phys.* 42:3175-87, 1965. (Cited 7,815 times.) [See also: Davidson E. Citation Classic. (Barrett J T, ed.) *Contemporary classics in the life sciences. Volume 2: the molecules of life.* Philadelphia: ISI Press, 1986. p. 216.]