William Nunn Lipscomb Jr (1919-2011)

Chemist who discovered a new kind of bonding.

illiam Nunn Lipscomb Jr could have made a career in music or science. He was an accomplished clarinetist who played Mozart with ease and grace, and attended the University of Kentucky in Lexington on a music scholarship. It is chemistry's good fortune that he ultimately chose science. His work on the boron hydrides led to a major rethink of how atoms bind together to form stable molecules.

Lipscomb, who died on 14 April, was born in Cleveland, Ohio, to a physician father and housewife mother. The family moved to Lexington when he was a year old. Both his grandfather and great-grandfather had been physicians, and Lipscomb was expected to continue the family tradition. But after graduating with a degree in chemistry from the University of Kentucky in 1941, he entered the graduate programme in physics at the California Institute of Technology in Pasadena.

Lipscomb soon returned to chemistry and under the influence of his mentor, Nobel laureate Linus Pauling, he developed an intense interest in chemical bonding. After completing his PhD in structural chemistry (during which he also conducted classified Second World War related research that involved, as he recounted, "walking around with beakers of nitroglycerine"), he joined the faculty at the University of Minnesota in Minneapolis in 1946. In 1959, he was appointed professor of chemistry at Harvard University in Cambridge, Massachusetts.

Lipscomb's research from 1960 onwards included important structural studies of enzymes. But it was his investigations of the boron hydrides, or boranes, from the late 1940s until the 1970s that led to his being the sole recipient of the 1976 Nobel Prize in Chemistry.

The impact of this work is best appreciated in light of the ideas on chemical bonding that prevailed at the time. Organic synthesis, a highly successful branch of chemistry concerned with manipulating hydrocarbons and their derivatives, is based on the perception that carbon atoms bind to other atoms through covalent bonds consisting of a pair of electrons. It was assumed that boron, a neighbour of carbon in the periodic table, would behave similarly, but its hydrides posed a major problem.

Boron's unconventional chemistry had fascinated and confounded researchers for years. At first, following its isolation in 1808, the element seemed unremarkable, forming the expected trivalent compounds such as BCl₃ and B(CH₃)₃. Its simplest hydride, it was thought, must be BH₃. William Ramsay, who had won a Nobel prize in 1904 for his discovery of the noble gases, was convinced of this. Not so the German chemist Alfred Stock, who took up the study of boranes in 1909. Using an ingenious vacuum glass apparatus of his own invention, Stock prepared and isolated a whole family of boron hydrides, none



of which was BH₃. In fact, he painstakingly proved that the simplest borane was B_2H_6 (diborane). For many years the molecular structures of these hydrides, which included B_4H_{10} , B_5H_9 , B_6H_{10} and $B_{10}H_{14}$, among others, remained unknown. In 1948, the basket shape of B₁₀H₁₄, which is a solid at room temperature, was established by the US chemist John Kasper and his colleagues.

A general understanding of borane structures emerged only when Lipscomb and his co-workers investigated the hydrides using both theory and X-ray crystallography. The challenge was formidable, as the boranes smaller than B₁₀H₁₄ are gases or volatile liquids at room temperature. This meant that the crystals had to be grown in sealed capillaries at very cold temperatures using liquid nitrogen (-196 °C) and maintained in that state while X-ray diffraction data were collected. For B_2H_6 , the crystallography needed even colder temperatures, requiring liquid helium (-269 °C), an approach that

had never before been attempted.

Lipscomb and his colleagues discovered that these molecules had unprecedented cage-like shapes quite unlike hydrocarbons, and they developed a detailed theory to explain why. The central idea was the 'two-electron, three-centre bond', in which three atoms are bound together by a single pair of electrons. Although three-centre B-H-B bonds had been postulated earlier by others, Lipscomb's extension of the idea to the B-B-B bond was a major conceptual advance.

This intuitive leap was the key to understanding the borane structures. More broadly, it implied that such multicentre bonding might allow the stable existence of many other types of molecular clusters. Indeed it does, in the form of thousands of known carboranes (clusters containing carbon and boron) and other compounds that incorporate most of the elements in the periodic table, including the 'nonclassical hydrocarbons' such as the pyramidalshaped $C_6(CH_3)_6^{2+}$ ion.

Bill encouraged unconventional thinking even at the risk of occasional error, as he put ü it in a classic paper in 1954. Those of us who worked with the Colonel (he was delighted to be named a Kentucky Colonel by the state's governor in 1973) came to appreciate his philosophy of the 'intuitive leap' as a method of advancing science.

Throughout his scientific career, music remained a serious avocation. He served as principal clarinetist with the Pasadena and Minneapolis Civic Orchestras, helped to found the New Friends of Chamber Music in Minneapolis and played regularly for years with members of the Boston Symphony Orchestra.

A member of the Baker Street Irregulars (devotees of Sherlock Holmes), Bill was also given to quoting from Arthur Conan Doyle and Lewis Carroll in his papers to make a point. These facets of his personality, as well as the revolution he fomented in the understanding of the covalent bond, form his lasting legacy.

Russell N. Grimes is a professor emeritus of chemistry at the University of Virginia. He was a graduate student in the Lipscomb group at the University of Minnesota in 1958-59 and at Harvard University in 1960-62.

e-mail: rng@virginia.edu