BIOGRAPHICAL MEMOIRS

Kenneth B. Wiberg

September 22, 1927–May 10, 2026
Elected to the NAS, 1967

A Biographical Memoir by Robert H. Crabtree

A man of few words but with abundant energy and resource, Ken Wiberg became a leading light of physical organic chemistry during the 1950s and 1960s, the glory days of that field. In a period stretching from 1949 to 2021, a span that includes a very active period of official retirement, he published over 500 papers on both experimental and computational problems. His flagship work on ring strain led to the synthesis of a series of increasingly exotic compounds, culminating in the synthesis of the apparently impossibly strained [1,1,1]propellane (compound 1). His 1968 proposal of what soon came to be called the Wiberg Bond Index, a way of computationally assessing bond orders, continues to be influential today and is now built into all the standard computational packages.

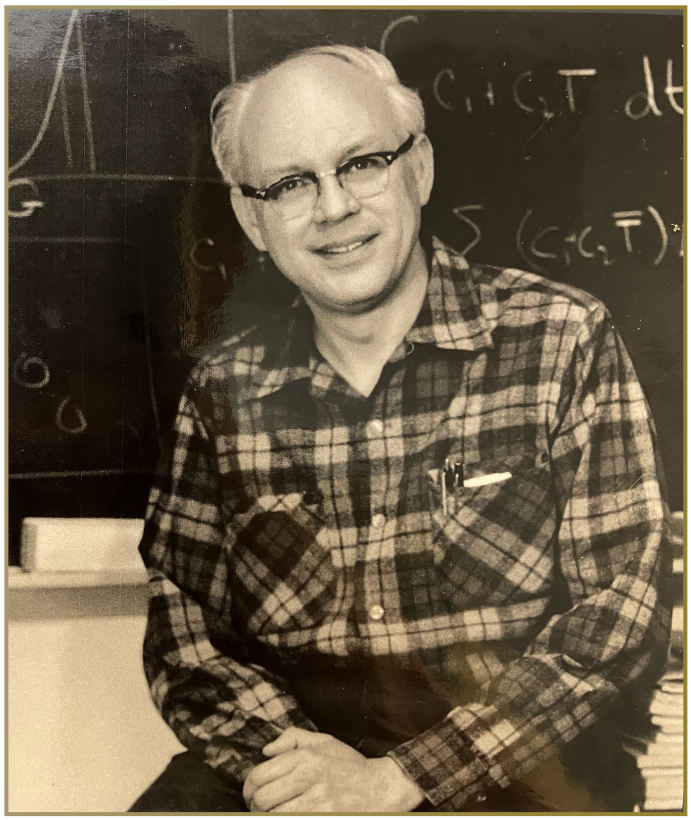

Figure 1 Kenneth B. Wiberg. *From his privately printed autobiography* My Life *(2021).*

Early Life, Education, and Academic Career

Ken was born on September 22, 1927, in Brooklyn, New York, to Norwegian immigrant parents, Halfdan and Solveig Wiberg, who met at a dance run by the local lodge of the "Sons of Norway." The family lived in a Norwegian enclave in Brooklyn, where Ken spoke only Norwegian until he went to school. He made the school baseball team, but his abilities could not have been regarded in a particularly good light, seeing that he was placed in the distant outfield where few balls were expected to reach.

His parents lived a rather precarious existence in various food-related jobs, and at one time ran a "mom and pop" delicatessen, where his father was noted for the excellence of his pies. One year, his best friend at elementary school, Chris Geible, received a big chemistry set for Christmas that contained a large variety of chemicals, flasks, test tubes, a balance, and even an alcohol lamp. Working with this set afforded both of them many hours of entertainment as well as instruction. Ken's grade record was strong enough to ensure entry to the best high schools, among which he chose Brooklyn Technical High School for its three-year chemistry program. He found the workshop skills that he acquired there very useful in his later research.

After graduating, Ken entered MIT in June 1945. Courses were on an accelerated schedule that involved three full semesters a year and no summer vacation. The good wages and abundant jobs then available in the field made chemistry the most

popular major. Because of Ken's excellent preparation, he was able to skip most of the standard courses by taking the final exams to demonstrate his competence. His strenuous program of study allowed him to graduate early in 1947, but this had a disadvantage in that his graduate work would be delayed if he stuck with his initial preference, Harvard, because it did not accept students mid-year. At Columbia, in contrast, he gained an early entry and enjoyed the additional pecuniary advantage of living at home with his parents. His intended advisor, the heterocyclic chemist Robert Elderfield, was unavailable owing to ill health, but Bill Doering, who had arrived at Columbia in 1942, looked attractive. It was also a fortunate switch in that Doering's specialty of physical organic chemistry was not only a rising field but also one particularly well adapted to Ken's skills.

He was expected to take the standard graduate courses, but having already transferred credit for almost all of these from MIT, the only remaining course that was left was food chemistry. In research, he proved more efficient than his colleagues through detailed planning, including preparing the next day's apparatus and reagents before leaving the lab at night. Things went so well that in early 1950 Doering recommended Ken for an open faculty position at University of Washington (UW) in Seattle, which Ken eagerly accepted in lieu of a postdoc, being keen to work on his own projects. He was pleased to find that the annual salary was $3,300.

Discussions with his girlfriend, Marge, resulted in her willingness to get engaged, even though they were too poor to afford a ring. Ken then rushed to finish his thesis, typed in seven copies with the help of much carbon paper, and to get on a plane to Seattle. This flight was scheduled for seventeen hours because of contrary winds and the low cruising airspeed (around 200 mph) for the war surplus DC-3 that carried passengers in those days; with two refueling stops, the trip in fact took 24 hours. Accompanying Ken to the plane, his father noted numerous metal patches on the wings, presumably the result of having sustained enemy gunfire. Perhaps as a consequence of this first taste of air travel, when Ken returned to Brooklyn to get married, he and Marge drove back west in a Ford coupe. Marge had earned an education degree from Brooklyn College and soon obtained a teaching position in Seattle. In 1954, their daughter, Pat, was born, followed by Robert in 1955 and Bill in 1959. Pat later became an oceanography professor at the University of Virginia, Robert went into real estate, and Bill into venture capital.

As their family expanded, the Wibergs moved to a larger house that required a total rewiring. Ken showed his practical skills by doing it himself, with the subsequent thumbs up and official seal of approval from the town electrical inspector. An enthusiastic hobbyist in his garage workshop, Ken continued to make numerous home improvements in subsequent years.

At UW, Ken had a small office and lab, and although there were no setup funds, he could check out from the stockroom anything there that he wanted. For anything else, he had to get the signature of the department head, Paul Cross. Ken made his presence felt early on when he successfully opposed the department's initial selection of a Baird infrared spectrometer, with its obsolete design and lead-acid batteries, in favor of a modern Perkin-Elmer instrument. His objections were fortunate, because shortly afterward Baird went out of business. In those days, the incoming graduate students were steered by the chair toward certain research groups, and Ken was favored in this way with two very good students, Bert Rowland and Tom Hutton.

UW proved very suitable for Ken because he could talk easily with the analytical and physical chemists, not just with the organic chemists, and these interactions produced a number of successful collaborative projects. At this time, too, Ken's interest in computation began with the discovery that an IBM computer had just become available there, in connection with which he took the quantum chemistry course that Bill Simpson gave at UW.

By 1957, with Ken's star rising, a call came from Frank Westheimer at Harvard inviting him for a yearlong visiting professorship to teach his physical organic course. Teaching the course provided the seed for the physical organic textbook that Ken later wrote, which was distinctive in having a greater physical orientation than prior texts. He also took the opportunity to attend E. Bright Wilson's statistical mechanics course and to do a few experiments on persulfate oxidation of isopropyl alcohol, while of course keeping contact with his graduate students at UW.

Ken returned to UW and in 1960 received a job offer from the eloquent and ever-persuasive Yale organic chemist Harry Wasserman. To help him decide, Ken then discussed UW's future plans with the then-president Charles Odergaard, who made it clear that chemistry was not high on his list of priorities. On the other hand, Yale had just received funding for a new building.

Ken decided to make the move to Yale, where he would contribute to raising the profile of the department to national leadership in the field. When Bill Doering left for Harvard in 1967, Ken and Harry used the opportunity to recruit Jerry Berson from the University of Wisconsin and Ian Scott from the University of Sussex. Complemented by Martin Saunders and Mike McBride, the department attracted outstanding physical organic students, postdocs, and visitors for years to come.

With a sabbatical year in hand from UW, Ken delayed his move in order to spend a year in Europe. The family boarded the newly built luxury liner *S.S. Rotterdam* and sailed from New York to its home port of Rotterdam and then traveled

by rail to their final destination of Karlsruhe, Germany. There, at the Technische Hochschule, he had an office but no access to the library, because it had been bombed out during the war. This was a big problem in an era when scientific literature only existed on the printed page. After some effort, he gained library privileges at Heidelberg, over forty miles away, resulting in much driving back and forth. Thanks to the contacts he made, he was invited to give a series of speaking engagements around Germany that had the additional advantage of attracting a number of excellent German postdocs to his research group.

When he settled at Yale, he both continued and expanded his research themes and also served as department chair from 1968–71. He was able to oil the political wheels of the department so effectively as to foster a smooth-running and harmonious climate. His scientific work, to be summarized in the next section, resulted in numerous awards, including the American Chemical Society's (ACS) Cope Award, Award in Physical-Organic Chemistry, and Linus Pauling medal. In addition, he was elected to the National Academy of Sciences in 1967 and the American Academy of Arts and Sciences in 1968. He described his approach to research as not simply experimenting in one area, as some people do, but instead working on a variety of different things, which he considered more fun.

Ken was unusual in looking forward to his retirement in 1997, at age seventy, so that he could get back into the lab and do experiments again. He continued for fifteen years in that mode, retaining his office and lab space until 2012, when he felt he was no longer steady enough to continue experimental work safely. Nevertheless, he published an impressive 131 papers during this post-retirement period, either as sole author or in collaboration. He also continued to enjoy trips with his extended family to such places as Alaska, Italy, the Netherlands, Russia, and Norway. In 2013, feeling the effects of increasing age, Ken and Marge moved to a Massachusetts senior residence, where they enjoyed the activities and made new friends. Sadly, in May 2019 Marge died in her sleep, and Ken followed her in May 2026.

Scientific Work

Ken is probably best known for his work on highly strained organic multiring compounds. His initial achievement in the field was the synthesis of the first bicyclobutane derivative in 1959, followed by increasingly exotic species such as bicyclo[2.1.1]hexane (1961), bicyclo[1.1.0]butane (1963), bicyclo[1.1.1]pentane (1963), but his crowning achievement was the 1982 synthesis of compound 1, termed [1,1,1]propellane, an apparently impossibly strained hydrocarbon with all four bonds directed well over to one side of a carbon-centered plane. Because higher, presumably less-strained propellanes, such as the [2,2,1] and [2,2,2] versions, rapidly polymerize by a radical pathway involving scission of the weak central C-C bond, the [1,1,1] version might have been expected to have only a fleeting existence. Undaunted, Ken first made a computational prediction that compound 1 would prove to be kinetically stable because there appeared to be no good decomposition pathways available. He then devised and executed a concise synthesis that validated all his expectations in that compound 1 proved much more stable than any of the larger-ring propellanes that he had made earlier. This example also shows how some of his best scientific work relied on a close combination of experiment and computation with much cross-fertilization between the two. Indeed, he was a very early organic chemist entrant into the field of computation as applied to physical organic problems.

This work continues to have relevance today. The bicyclopentane substructure 2, obtained by opening the weak central bond of compound 1, finds current use in medicinal chemistry, where it acts as an isosteric, lipophilic replacement for para-substituted benzene rings, facilitating optimization of drug properties. Also of great contemporary interest in alternative energy and nanoscience applications, are rigid, nonconducting rod-like staffanes (substructure 3) that involve multiple repeats of substructure 2. Here we see an example of pure curiosity-driven research, unfundable today, having important practical benefits decades later.

One of Ken's bicyclic attempts was initially problematic but was saved by an unconventional borrowing from organometallic chemistry. Bicyclo-[2,2,0]-hexene proved to be too labile to isolate conveniently but was trapped by Pt(II) to give the stable alkene complex 4. One target proved recalcitrant to the end, however: Ken's attempts to make fenestrane (structure 5), in order to probe the possibility of producing a nearly square-planar central carbon, never got further than structure 6.

Ken began a series of calorimetric studies to obtain thermodynamic data on compounds of special interest. This was originally intended to probe the extent of aromatic stabilization in the two π-electron cyclopropenium ion. A more elaborate calorimeter later proved applicable to solution reactions

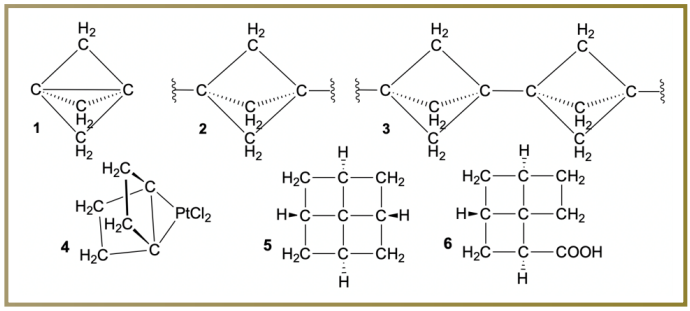

Figure 2 Some of Ken's most notable structures.

such as hydrogenation and hydration so as to determine the heat of formation of a reactant alkene, given the known heat of formation of the product alkane or alcohol.

Ken was also very interested in vibrational spectroscopy and, with colleague Steve Colson, carried out an infrared study on ammonia with the aid of a supersonic expansion apparatus that they had constructed. This apparatus cooled the sample and revealed new spectral details. Similar studies on benzene, pyridine, and methyl chloride followed.

A continuing interest from Ken's UW days was computation, but the numerous roadblocks present in the early days meant that this theme only really got going in the mid-1970s, when he ordered an Altair personal computer for $350. It came in parts, which Ken put together, with soldering iron in hand. The advantage of Altair over prior machines was that it had integrated circuits rather than transistors, so it was smaller and had more memory. Soon after, Ken obtained the standard Gaussian76 computational chemistry program, which he recalled having received in the form of multiple boxes of punch cards. He obtained some useful results at Yale's computer center, but he realized that he needed a larger machine for more serious work and was able to get time on the Brookhaven National Laboratory equipment using a modem for remote operation; from this time on, most of his papers had a computational component. He had a close collaboration with the Gaussian company over several decades that included ten joint postdocs and resulted in forty joint publications, including some highly influential ones.

One of the numerous problems he tackled computationally was the determination of the heats of formation of relevant structures, permitting access to the strain energies of his ring compounds. Another point of interest was the charges on significant atoms in a molecule, for which Ken tested various suggested approaches to find that, of the existing methods, Hirshfeld charges seemed to be most satisfactory. He also suggested his own scheme, CHELPG charges. Computation of solvent effects proved to be a challenging but productive area that resulted in a well-regarded series of papers. Perhaps his best-known computational work, however, is the 1968 proposal of what is now called the Wiberg Bond Index, an estimate of bond order based on the number of electrons shared between the two atoms involved in the bond.

An early experimental interest was the application of H/D kinetic isotope effects for mechanistic analysis, which resulted in a series of papers on specific applications, such as organic oxidations with persulfate, permanganate, and chromate, but more importantly, in a very useful *Chemical Review* in 1955. This report did much to broaden the use of H/D KIEs in general, as well as raising Ken's personal profile in the field. Because it covered all the main organic reaction types, it soon became a key resource for a wide range of readers. Other isotope studies proved productive as well. For example, O-18 tracer work showed that in the cis-hydroxylation of alkenes the isotope from the permanganate oxidant ended up on the diol product, implying that a cyclic Mn(V) ester is the key intermediate.

After retirement, Ken engaged in a number of collaborative studies, acting as either the computational or experimental partner. For example, the origin of the anomeric effect, in which an electronegative substituent prefers an axial position when adjacent to a ring oxygen (such as in a pyran), was the subject of inconclusive discussions over many years. Probed by Ken and Bill Bailey of the University of Connecticut in a joint experimental and computational investigation, the effect was shown to result in large part from a pair of coulombic attractions in the favored conformer augmented by unfavorable ones in the other.

The experimental testing of computational predictions of optical activity in chiral molecules is complicated by the solvent typically used in the measurement, because this often adopts a time-averaged chiral arrangement around the molecule of interest and thus greatly contributes to the observed optical rotation. From 2000, Ken collaborated with colleague Pat Vaccaro to measure the chiroptical effects of isolated chiral molecules in the vapor phase at low pressure, using a meter-long cell with capping mirrors that produced the required very long path length via multiple reflections. The computational work proved equally challenging because a very large number of excited electronic states, well in excess of a thousand in some cases, had to be included for success.

One of his last projects, carried out as late as 2018, involved gaining an understanding of why the syn conformer of butadiene is nonplanar by as much as 35 degrees. Repulsion between the endo hydrogens was ruled out in favor of a weak π overlap of Möbius topology between the terminal carbon p orbitals, thus stabilizing this 4 π-electron system.

Ken was also a productive book author whose publications include *Physical Organic Chemistry* (1964), *Computing for Organic Chemists* (1965), and the edited collection *Oxidation in Organic Chemistry* (1965), among other works.

Acknowledgments

Many of Ken's colleagues, friends, and admirers have kindly provided valuable information for this memoir, notably Odile Eisenstein, Barney Ellison, Mike Frisch, Nilay Hazari, and Pat Vaccaro. Mike McBride also provided access to a copy of Ken's privately printed autobiography *My Life* (2021).

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