Orville Chapman

1932-2004

BIOGRAPHICAL *Memoirs*

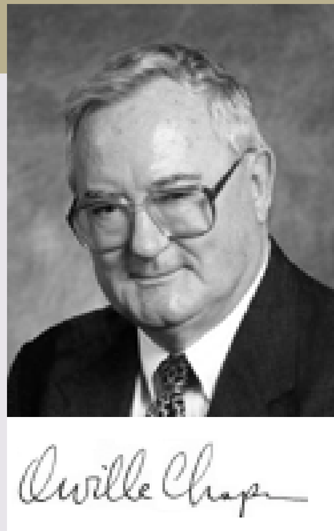
A Biographical Memoir by
Arlene Russell
and Kendall N. Houk

NATIONAL ACADEMY OF SCIENCES

ORVILLE LAMAR **CHAPMAN**

June 26, 1932—January 22, 2004

Elected to the NAS, 1974



By Arlene Russell and Kendall N. Houk

Orville Chapman was widely recognized as a creative scholar and leader in multiple fields of scientific endeavor. He was a trailblazer and innovator in photochemistry, matrix isolation spectroscopy, reaction intermediates, chemical communication, the mechanism of olfactory perception, and polymeric materials. He devoted his energies not only to invention and discovery but also to conceiving and bringing into practice new modes of education; for example, he gained a worldwide reputation for bringing the best of information technology to academia. Chapman's intellect, imagination, and personality attracted tremendously talented students and postdoctoral fellows to his research group, which was a fountain of ideas and inspiration. His achievements were recognized early on by election to the National Academy of Sciences at the age of 42, and by numerous awards and other honors.

Especially well known as a pioneer of organic photochemistry, Chapman left a major mark as well on materials design—notably carbon allotropes, wherein his insights preceded the discoveries of fullerenes, buckytubes, and graphene. As a long-term consultant for Mobil Chemical, he participated in the development of many of the company's industrial processes.

Chapman was born in New London, Connecticut, but spent his early childhood in Panama, as his father, a U.S. Navy seaman, was stationed in the Panama Canal Zone. Returning to the United States with his parents as a youngster, he attended elementary school in Washington, D.C., while his father served as chief engineer on President Franklin D. Roosevelt's yacht. During that time, the young Orville visited many museums with his mother, gaining a lifelong interest in art, symmetry, and structure. At the end of World War II, his father, the a lieutenant commander, was stationed in San Diego, where Orville attended the first two years of high school; the family then moved to Norfolk, Virginia, where he graduated from Granby High School in 1950. Turning down a nomination to the U.S. Naval Academy, Orville chose to attend Virginia Polytechnic Institute, graduating four years later with a double major in English and chemistry. He thus had his start in chemistry while also gaining a lifelong love for prose and poetry.

Chapman continued his study of chemistry in the graduate program of Cornell University and in 1957 received his Ph.D. under the mentorship of Jerrold Meinwald, who cultivated his student's enduring fascination with organic synthesis. Chapman's work with Meinwald at Cornell specifically involved the synthesis of tropolones and rearrangement reactions of related molecules.

In the 1970s, Chapman's lab pioneered in the development of new technologies to observe intermediates and reactive species formed in photochemical reactions. His interest in reaction mechanisms and theoretically interesting molecules led him to adopt techniques that allowed direct experimental detection of reactive species.

After completing his doctorate, Chapman accepted a faculty position at Iowa State University. During the next seven years he quickly moved through the professorial ranks while doing innovative studies in the emerging field of organic photochemistry. His selection of this research area was characteristically bold, in view of his lack of prior experience in physical organic chemistry. Chapman's early work focused on enone photochemistry and the mechanism of photocycloaddition reactions, and he credited his Iowa State colleagues Chuck DePuy and Glen Russell with teaching him the prerequisite knowledge.

Chapman's student Daniel Pasto studied the chemistry of tropolones, picking up on compounds with which Chapman had become expert in his Ph.D. work. Pasto also carried out the first studies of the photochemistry of was a fountain of ideas and inspiration. His achievements were recognized early on by election to the National Academy of Sciences at the age of 42, and by numerous awards and other honors. Organic molecules in the Chapman laboratory at Iowa State and went on to a distinguished career at Notre Dame. The early studies by Chapman and Pasto led to a flood of exciting papers, wherein the early-1960s discovery of photochemical reactions of many seven membered enones, dienes, and related natural products were elucidated. The study of the photo-

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chemistry of numerous types of unsaturated nitro compounds and dienones, and the identification of reactive intermediates such as ketenes and other heterocumulenes, followed in the late 1960s. As editor of the first three volumes of *Organic Photochemistry* during this time, Chapman helped nurture the field; and in 1972 he coauthored with Charles DePuy a seminal monograph, *Molecular Reactions and Photochemistry*, which subsequently was translated into seven languages and is still in print.

In the 1970s, Chapman's lab pioneered in the development of new technologies to observe intermediates and reactive species formed in photochemical reactions. His interest in reaction mechanisms and theoretically interesting molecules led him to adopt techniques that allowed direct experimental detection of reactive species. Early efforts involved IR spectroscopy of intermediates generated upon photolysis of neat precursors at 77°K. A critical advance came in the early 1970s when Jake Pacansky introduced Chapman to rare-gas matrix isolation spectroscopy. They adapted this technique to study reactive intermediates in organic chemistry, including the classic cases of cyclobutadiene and *o*-benzyne. Chapman also reported the synthesis and spectroscopic identification of cyclopentadienone, cyclobutadiene derivatives, benzyne derivatives, silaalkenes, nitrenes, the isomeric azaallenes, and unusual strained unsaturated species such as cyclohepta-1,2,4,6- tetraene.

Also in the early 1970s, Chapman discovered remarkably efficient ways to synthesize quite-complex natural products through simple processes—achievements that continue to be widely admired in the field of synthesis. His synthesis of carpanone—in collaboration with Jon Clardy, his young faculty associate at that time—is an often-cited paradigm of this type of reaction. Chapman was elected to the National Academy of Sciences in 1974.

During this time in Ames, Iowa, Chapman and his wife Faye Morrow had two sons, Kenneth and Kevin. He also enjoyed his avocation as an avid lake sailor and served his community as a deacon of the Baptist church in Ames.

Chapman moved from Iowa State to the University of California, Los Angeles, in 1974, on the heels of his exciting successes in applying matrix isolation spectroscopy to the characterization of cyclobutadiene and benzyne. The years at UCLA were an extremely productive period for his investigation of a wide variety of organic reactive In the 1970s, Chapman's lab pioneered in the development of new technologies to observe intermediates and reactive species formed in photochemical reactions. His interest in reaction mechanisms and theoretically interesting molecules led him to adopt techniques that allowed direct experimental detection of reactive species. Intermediates, including carbenes, nitrenes, propadienones, silenes, carbonyl oxides, and strained alkynes.

In collaboration with colleague Frank Anet and graduate students Robert Sheridan and Michael Squillacote, Chapman observed—through a combination of low-temperature matrix isolation and NMR detection— normally unstable conformers of molecules such as the twist-boat conformer of cyclohexane and the *s-cis* conformers of butadiene. The researchers conceived a novel approach whereby a high-temperature gaseous compound, enriched in the minor isomer by thermal equilibration, was quenched at a low temperature (at which conformational interconversion no longer occurred); the relatively high concentration of the less stable isomer could then be observed directly. Their results were published in 1975 in the *Journal of the American Chemical Society.*

In 1975 as well, Chapman joined the Board of Editors of *Organic Syntheses*, where he actively encouraged and solicited papers illustrating the synthetic applications of photochemistry. He later edited Volume 60 (1981) in this series, which was in large part devoted to photochemical processes.

Also in the 1970s, Chapman began an ambitious and ultimately successful program in the synthesis and study of insect sex pheromones; and he continued the tradition of matrix isolation work begun with Jake Pacansky. Along the way Chapman helped train leaders of this field: Robert McMahon, now at the University of Wisconsin; Robert Sheridan of the University of Nevada-Reno, and Wolfram Sander at the Ruhr Universität in Bochum, Germany.

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In the 1980s Chapman's interests turned to what would be known as fullerenes and to other allotropes of carbon, to polymer chemistry, and to teaching and teaching technology. His ideas concerning the novel molecule C60 germinated in 1980, and in

1981 he initiated efforts directed at the chemical synthesis of C60. This work was but one part of a new effort in the synthesis and characterization of various types of strained nonplanar aromatic compounds. In retrospect, these efforts are now recognized as pioneering contributions to materials chemistry and are being pursued by many research groups. François Diederich, a postdoc at that time, went on to study fullerenes as a faculty member at UCLA, after the thermodynamic synthesis of fullerenes was discovered; he continued a distinguished career at the ETH-Zürich.

During this time Chapman, whose interests were always catholic, also collaborated with young UCLA Love of the English language and concern for clear writing were never far below the surface. For example, in 1976 Chapman participated in campus-wide discussions to improve writing in the undergraduate curriculum and shortly afterward created an adjunct writing course for the junior-level organic chemistry laboratory. Physicist Steven Kivelson (now at Stanford University). Their 1983 paper in *Physical Review*, "Polyacene and a New Class of Quasi-One-Dimensional Conductors," remains one of Chapman's most highly cited.

In 1981, he married Susan Elizabeth Parker, then a teaching associate of French at UCLA. They traveled extensively all over the world and enjoyed opera, classical guitar music, mystery fiction, and cooking.

In 1984, Chapman began to devote his energies and intellect to innovations in education. Intrigued by the emerging meld of computers and video, Chapman began a collaboration with colleague Arlene Russell that would continue for two decades. The production of a laser videodisc, *FT-NMR Problem*s, which contained thousands of hyperlinked NMR spectra accessible to students through IBM PC touchscreens, pioneered the introduction of modern heteronuclear NMR in the lower division organic curriculum. It led to the idea of using 13C NMR spectroscopy for introducing the topic of organic chemistry.

As associate dean for educational innovation at UCLA, a position he held for 10 years, Chapman led the UCLA Science Challenge, a case-study-based approach to revamping lower- division science education using technology. In 1995, this work brought national recognition to UCLA with the ComputerWorld Smithsonian Institute Award for the best use of computers in education and academia.

Chapman and Russell formed a company in 1984 in order to offer short courses in technical writing in industry; the course served as the basis of their development the following year of a graduate-level technical writing course for the chemistry and biochemistry department. A decade later they introduced Calibrated Peer Review® (CPR), an integrated set of network tools that manages the submission and evaluation of students' written work regardless of the class size. CPR has become a major educational tool for many different disciplines at colleges and universities throughout the world.

Chapman's commitment to education reform was never very far from his passion for chemistry. A 1996 paper, coauthored with two graduate students and Russell in the *Journal of Chemical Education*, exemplified his ability to bring new chemistry to the classroom in new ways. It is not surprising that 11 of his last 13 papers were on various pioneering directions in teaching chemistry.

Chapman received many national and international awards, including the Pure Chemistry Award and the Arthur C. Cope Medal from the American Chemical Society; the Havinga Medal from the Stichtung Havinga, Leiden, the Netherlands; and the Texas Instruments Foundation Founders' Prize.

On September 27, 2004, the undergraduate computer center of UCLA's Young Hall was dedicated in his honor. The Orville L. Chapman Learning Center now stands as a testament to the life and achievements of this creative scientist and visionary educator.

This memoir is based on recollections of our longtime association with Orville Chapman as well as on discussions with, and remembrances written by, Robert McMahon of the University of Wisconsin.

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