



Howard E. Zimmerman

1926–2012

BIOGRAPHICAL

Memoirs

*A Biographical Memoir by
Richard S. Givens*

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NATIONAL ACADEMY OF SCIENCES

HOWARD ELLIOT ZIMMERMAN

July 5, 1926–February 12, 2012

Elected to the NAS, 1980

Howard Elliot Zimmerman was one of the founders of the field of mechanistic organic photochemistry, applying the knowledge of organic synthesis and physical organic chemistry to the mechanistic and theoretical treatments of excited state reactions. His approach provided organic chemists with a way to explain photochemical transformations that paralleled the method used for ground state reactions. This added a whole new realm to the organic chemist's mechanistic lexicon. His work demonstrated that excited states of organic compounds undergo novel yet predictable reactions. As a result, chemists could explore new hypothetical photochemical transformations that would find later utility in organic synthesis and in the photochemical generation of reactive intermediates, which were often postulated in ground state reaction mechanisms.



A handwritten signature in dark ink that reads "Howard S. Zimmerman". The signature is written in a cursive style.

By Richard S. Givens

Howard condensed these concepts into a four-step sequence that became known as the Zimmerman Paradigm. This sequence compartmentalized the molecular changes occurring in the excited state to ground state molecular transformations and coupled them with the emerging understanding of the nature of excited state reactivity using molecular orbital theory. Through this contribution, organic photochemistry became more approachable and accessible not only to organic chemists but also to physical and bio-organic chemists and chemical physicists. Many were inspired to initiate studies of organic photochemical reactions applicable to their own fields of interest. Howard and his coworkers remained at the center of the burgeoning field of organic photochemistry, carrying out fundamental investigations across a broad range of photochemistry and photophysics, throughout the second half of the 20th century.

Early life

Howard Zimmerman was born in New York City on July 5, 1926, and grew up in Stamford, Connecticut. He was the first of two children of May and Charles Zimmerman. His younger sister, Leslie, was born six years later. At age ten, Howard's father gave him a chemistry set, which sparked a lifelong interest in chemistry. Howard set up a laboratory in the family basement, and together with three of his classmates he explored elementary chemical reactions. Many trips into New York City from Stamford were necessary to purchase new reagents to replenish their chemical stock. Howard was encouraged to pursue his study of science by a dynamic junior high school science teacher, and as a Boy Scout he earned the merit badge for chemistry, which he treasured.

"Woodward would wander around the group at about 10:00 AM to chat and also would come around about that time late evenings." This made such a deep impression on Howard that throughout his own career as a research supervisor and mentor, he would make similar laboratory tours, three times a day, and would interrogate each of his students working at their benches about their progress.

After graduating from high school, Howard's three childhood chemistry partners were drafted into military service at the height of World War II. Howard quickly joined them by volunteering for service in the Army on Sept. 3, 1944. The four young men remained friends throughout the war and after. Zimmerman served as a tank gunner on the European front and he later suggested that the constant noise from ballistics during his deployment caused his partial hearing loss. Shortly after the conclusion of the military action, as part of the occupation forces, he was assigned to posts in Bergen, Salzburg, and Vienna with the 756th Tank Battalion, which included brief deployments in the Russian sector. During this period his company captain gave him an opportunity to further his education by attending courses in chemistry, math

and German at the Rainbow University in Zell am See, Austria. Near the end of his two years of service, he was promoted to Corporal and, upon returning to the United States, he completed his military duty as a Technical Sergeant and was honorably discharged in August 1946.

Immediately following his discharge, Zimmerman entered Yale as an undergraduate. During his undergraduate years, Professor Werner Bergmann encouraged him to major in organic chemistry. Howard pursued this degree, joining the research group



Howard Zimmerman on one of his thrice daily visits through his laboratory to confer with his students. Here, student Jeff Robbins is working at a gas chromatograph in the Mathews Chemistry Building at the University of Wisconsin-Madison.

of Professor Harry Wasserman, a new organic chemistry faculty member. Zimmerman completed his Bachelor of Science degree in Chemistry in 1950, the same year that he married Jane Kirschenheiter.

Howard chose to remain at Yale for his graduate work, earning his PhD with James English, Jr. in 1953. He conducted postdoctoral studies with Bob Woodward at Harvard in 1953, supported by a fellowship from the Lilly National Research Council Postdoctoral Fellowship Program. Howard worked on the synthesis of the natural product terramycin with Woodward, and participated in long, vigorous discussions at Woodward's weekly group seminars, particularly with fellow graduate

students Ronald Breslow and Martin Saunders. Several other students and faculty were engaged in these freewheeling discussions, which often lasted long into the evening, progressing from the seminar room to the local Howard Johnson restaurant by the Charles River, finally culminating in the early morning with cup of coffee at a shop on Massachusetts Avenue.

Howard found Woodward to be accessible as a mentor, contrary to the rumors from former Woodward students and postdocs. They often met in Woodward's office to discuss research. Howard remembered that in the laboratory "Woodward would wander around the group at about 10:00 AM to chat and also would come around about that time late evenings." This made such a deep impression on Howard that throughout his own career as a research supervisor and mentor, he would make similar laboratory tours, three times a day, and would interrogate each of his students working at their benches about their progress. Often, that progress was a measure of what had been accomplished in the short time since the previous visit. Howard was keenly aware of who was present in the laboratory each time he passed through, especially on weekends and holidays. He retained a particularly high regard for Bob Woodward throughout his life.

Northwestern University

Howard began his independent research career at Northwestern University in 1954. His early efforts were devoted primarily to the study of ground state organic reaction mechanisms. He investigated the mechanism and stereochemistry of ketonization of enols.

Based on work with a Northwestern undergraduate student, Marjorie Traxler, he proposed a transition state model that has come to be known as the Zimmerman-Traxler transition state for describing the product stereochemistry for the Ivanov and the Reformatsky reactions. The predictability of the stereochemistry for kinetically controlled ketonization of enols and the diastereoselectivity in the aldol-type reactions were widely acclaimed by organic chemists who applied his rationale for the determination of the stereochemistry of these and many related reactions. The work first appeared in the *Journal of the American Chemical Society* in two articles in 1956 and 1957, his most frequently cited publications.

While at Northwestern, Zimmerman initiated investigations on the mechanisms of several known carbanion reactions, including the Reformatsky Reaction, the Grovenstein (now Grovenstein-Zimmerman) Rearrangement, and the Birch Reduction. It was here also that he initiated his synthetic quest for a topologically unusual unsaturated tricyclic hydrocarbon with three double bonds positioned in a manner where the π -orbitals are arranged like a barrel. This molecule, bicyclo[2.2.2]octa-2,5,7-triene, possessing C_3 symmetry, was named “barrelene” by Zimmerman, who completed its synthesis in 1964 after his move to Wisconsin.

Also at Northwestern, Zimmerman developed skills and knowledge in several other fields that drew his interest, including physical photochemistry, elementary quantum mechanics, and molecular orbital theory. His colleague Arthur Frost was particularly helpful in furthering his interest in quantum mechanics as applied to organic systems, which Howard initially applied to the unusual orbital interactions in the tricyclic π -overlap of barrelene.

University of Wisconsin

In 1960 Howard, Jane, and their sons Robert and Steve moved to the University of Wisconsin-Madison, where Howard launched a new research program devoted almost entirely to the study of photochemical reactions of organic compounds. He started as an Associate Professor, and advanced to Professor the following year.

At that time, he and George Hammond (1921-2005) were emerging as the two leading figures in the field. Both Hammond and Zimmerman focused their efforts on rationalizing excited state transformations, especially reactions and rearrangements of ketones and aromatic compounds. Whereas Hammond's work concentrated on the photoreactions of relatively simple aliphatic and aromatic ketones and stilbene isomerizations, Zimmerman's efforts centered principally on the unusually complex rearrangements of unsaturated cyclic ketones and on bicyclic alkenes. Zimmerman's first major breakthrough was the development of a mechanistic understanding for the unusually complicated photochemistry of α -santonin reported earlier by Derek H. R. Barton.

A rational treatment of the rearrangements of this natural product had eluded most contemporary organic chemists including Barton, who had solved the structure of the photoproduct, lumisantonin. Howard and his students at the University of Wisconsin-Madison developed a mechanistic approach to rationalize the baffling photochemical rearrangement by applying Kasha's rules (Michael Kasha, 1920-2013) that initially defined the electron configuration of the reactive excited state and then applied "electron pushing" concepts, then popularly employed for ground state organic reactions, to reach the reaction product.¹ He pioneered and then applied this conceptual approach to a variety of other excited state chemical transformations, studies which he published under the general title of *Mechanistic Organic Photochemistry*.

His application of the electron pushing concept coupled with his definition of the reactive nature of excited state electron configurations were keys to defining the subsequent bond reorganizations. The approach provided organic chemists with a readily understood and rational pathway to explain photochemical transformations that paralleled the method used to explain ground state reactions. This added a whole new realm to the organic chemist's mechanistic lexicon. Howard's work demonstrated that excited states of organic compounds undergo novel yet predictable reactions and, as a result, serves a useful method for exploring new hypothetical photochemical transformations that would find later utility in organic synthesis and for the photochemical generation of reactive intermediates, which were often postulated in ground state reaction mechanisms.

Howard parlayed these concepts into a simple four-step sequence, the Zimmerman Paradigm, by relating the excited state electron distribution and reactivity to mechanistic principles developed for well-understood ground state transformations.² The four steps that constituted his paradigm were (1) photoexcitation to an electronic excited state, (



Howard Zimmerman in his office in the Mathews Chemistry Building. Behind him is his world map with colored pins placed where each of his more than two hundred former students and postdocs were located. The Zimmerman Map is now in the Archives of the Chemistry Department at the University of Wisconsin-Madison.

2) adiabatic reorganization in the excited state, (3) relaxation (electron demotion) to the ground state surface and (4) further adiabatic bond reorganization to form stable products.

Howard also developed theoretical treatments of excited state organic reactions that enabled him to provide new approaches to understanding and explaining these transformations. Perhaps the most significant contribution was the development of a new, much simpler approach toward understanding the guiding principles governing concerted ground and excited state processes termed pericyclic reactions.³

Howard was among the first to employ orbital correlation diagrams in assessing the “allowed” and “forbidden” pathways for reaction processes controlled by orbital symmetry. Unlike the Woodward-Hoffmann approach, which relied on the use of orbital symmetry correlation diagrams, Howard’s vision concentrated on the “aromatic and anti-aromatic character” of the cyclic arrays in the transition states in pericyclic processes during the bond-breaking and

bond-making events. This approach, which is more compatible with reasoning utilized by most organic chemists, can be used to evaluate whether a reaction proceeds through a higher energy (anti-aromatic) or lower energy (aromatic) transition state by simply determining whether the transition state orbital array itself possesses a Hückel or Möbius topology and then assessing the number of electrons ($4n$ or $4n+2$) in the array.

At home, Howard spent much of his time on maintenance and repair projects about the house, enlisting the help of his children. Relaxation was either reading science fiction and spy novels or watching TV with a journal in hand.

In addition to his transition state orbital topology approach to symmetry control of reactions, Howard was among the first to recognize that the interaction of an excited state surface with the ground state, a topological condition that is now described as a conical intersection, influences excited state relaxation processes. Howard also applied molecular orbital theory to rationalize the electronic control of bond-breaking process in excited state solvolysis reactions of ortho, meta, and para substituted

aromatic phosphates and related esters. These studies led to the “meta effect” for explaining the regiochemical control for photoreactivity of aromatic compounds.

Personal life

Howard spent little time away from his laboratory in the Mathews Chemistry Building on Johnson Street at the University of Wisconsin. Practically all of his travels were for seminars for his research, short courses at professional meetings, or as an invited speaker at symposia meetings, universities and research centers in the US and Europe. He consulted for chemical firms such as Lederle Laboratories and American Cyanamid. His favorite international travels were to meetings held in Germany, which he frequently combined with visits to nearby universities. These trips included several of the cities and regions where he had been stationed during his service in WWII. During his career and especially on his European tours, Zimmerman developed many enduring personal friendships.

Howard and Jane had three sons: Robert, Steven, and James. At home, Howard spent much of his time on maintenance and repair projects about the house, enlisting the help of his children. Relaxation was either reading science fiction and spy novels or watching TV with a journal in hand. Once a week, he and his wife would venture to a nearby restaurant for a martini and a meal. Many summers he and his students would be joined by a few of his chemistry colleagues on a canoe trip down the nearby Wisconsin or Kickapoo Rivers.

During his early years when the weather was good, he would challenge a friend to a tennis match. On rare occasions at his home, he would bring out one of his two violins and perform for friends and family. When German Professor Hans Muxfeldt became a member of the Wisconsin faculty in 1961, Howard and Jane became close friends with

Hans and his wife Gisele, and together they would drive for outings at Devil's Lake. For the most part, however, Howard spent much of his free time reading, working on research proposals, or readying manuscripts for publication.

Jane died in 1975, following a long battle with cancer. Howard married Martha Kaufman in 1976 and helped raise her son, Peter. They divorced in 1985. Howard married Peggy Baker-Vick in 1991.

Research history

Zimmerman wrote that:

Woodward and Yates elucidated the correct structure for santonin and Derek Barton obtained the correct structure for a photoproduct, lumisantonin. In looking at this transformation, we note a remarkable molecular reorganization. For example, the carbonyl group at C-3 now appears at C-2. The C-10 methyl group is inverted. The C-4 methyl group seemed moved to C-1. At the time, there were no mechanisms to account for this and for the myriad of known photochemical transformations. The problem was that the real reactant in a photochemical reaction is the electronic excited state of the reactant, and organic chemists were not knowledgeable in quantum mechanics. Conversely, the physical chemists were aware of the structures of some excited states, especially in the case of ketones, but were not trained in organic chemistry. It was my good fortune to have had a background in both areas.

Thus I was able to deal with quantum mechanics and excited state structures. The physical chemists knew what the n,π^ excited state of formaldehyde looked like. I realized that was relevant in the excitation of santonin. Also, Dave Schuster was a postdoc with me then and he synthesized and photolyzed 4,4-diphenylcyclohexadienone. I ran a simple Hückel computation of the 4,4-disubstituted cyclohexadienone system and found that the n,π^* excited state had a dramatically increased β,β -bond order. The photoproduct in that simpler cyclohexadienone paralleled that of lumisantonin. When one applied a mechanism starting with the n,π^* excited state and β,β -bonding, the rearrangement led smoothly to lumisantonin with the correct structure and stereochemistry.¹*

Following up on earlier studies by Havinga on photosolvolysis reactions, Zimmerman employed molecular orbital calculations of ground and excited state electrons to rationalize the unusual regioselectivity for photosolvolysis of substituted phenols, and eventually to aryl trityl ethers and benzyl acetates. In contrast to the predictability of para activation (over meta) by electron-rich substituents in ground state electrophilic aromatic substitution reactions, substituents in the meta position in the excited state were found to activate the substitution processes. Zimmerman thereby was able to explain Havinga's results that:

the para isomer uniquely hydrolyzed in the dark as anticipated. But the meta isomer, which was unreactive in the dark, surprisingly hydrolyzed when irradiated. The para isomer showed no enhanced reactivity on irradiation. Havinga noted that this had no rationale in terms of resonance theory. Realizing that the excited state was involved, I did a simple Hückel computation on the meta and para nitrophenyl isomers and found that the meta isomer uniquely showed electron transmission from the phenolic oxygen. My postdoc, Somasekhara,⁴ found a similar behavior when we studied the meta and para nitrophenyl trityl ethers.

This orthogonal relationship in the reactivity of ground vs. excited state was matched by the MOT analysis which led Zimmerman to propose that a “meta effect” controls the photoreactivity of excited state aromatic solvolysis reactions. Articles substantiating these claims and extending the meta effect to several new photochemical reactions began appearing in the literature after 1963.

The 1990s brought a focus on solid state photochemistry. In this area, Howard capitalized on his deep understanding of theoretical and computational chemistry to model the effect of the solid host in a more sophisticated way than others had done. The combination of sophisticated modeling and experimental studies represented the state-of-the-art in the field at that time.

In addition to mentoring graduate, undergraduate and postdoctoral students as well as visiting scientists, Howard taught graduate and undergraduate lecture courses in organic chemistry beginning in 1954 at Northwestern University, continuing at the University of Wisconsin-Madison until his formal retirement in 2010. In all, Howard mentored more than 280 research students, postdoctoral associates and visiting faculty.



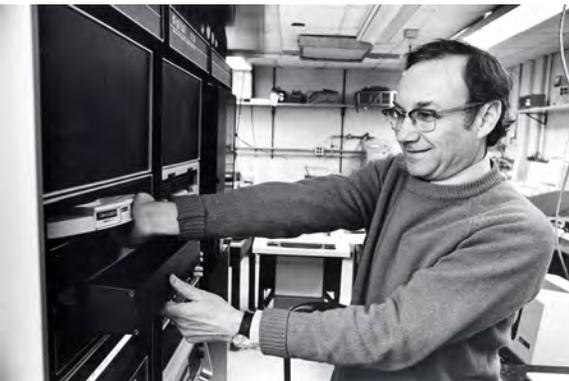
The March 15, 1979 Dedication of the Samuel M. McElvain Laboratories of Organic Chemistry; pictured are (in the front row): Irving Shain (Department Chair), Howard E. Zimmerman and Robert B. Woodward, four months before Woodward's death.

Howard was known for his dogged pursuit of new results that provided a deeper understanding of photochemical mechanisms, especially as they applied to his perception of the fundamental nature of reactions of excited states. His graduate students and postdoctoral researchers remember him as a teacher and a brilliant scholar who was adept at reducing complex problems to a few rational steps, thereby opening the pathway to a solution to a mechanistic problem. To young, beginning graduate students including this author, Howard's ability to demonstrate his logical approach to photochemistry using these new excited state mechanism concepts and orbital theory was very impressive. His Hückel-Möbius

transition state concept for treating concerted reactions, and the Zimmerman-Traxler transition state for explaining the factors that govern the stereochemistry of aldol-type reactions are but two examples of his approach to organic chemistry that drew young scientists to participate in his research program.

Howard and several of his colleagues would gather on Friday for tea and coffee in the earlier years but this gave way to the group migrating to Paisan's for lunch where they would discuss departmental issues and politics and new results from their chemistry research or the literature. Frequently Howard would turn discussion toward his own chemical interests. Through these informal meetings, Howard developed collegial relationships with several of the faculty, especially Frank Weinhold, Hans Reich, Bob McMahon, Harlan Goering, Morris Kupchan, Steve Nelsen, and Barry Trost.

Zimmerman was highly supportive of his students and made certain that they received careful consideration in their search for professional positions, especially at academic research institutions.



Zimmerman working at his computer hardware which he maintained and ran for his own calculations and theory development at the University of Wisconsin-Madison.

Honors and awards

Howard's research was supported by major grants from NIH, NSF and AROD providing continuous, generous funding for more than five decades. He was a member of the American Chemical Society, the IUPAC and the InterAmerican Photochemical Society. He served on the editorial boards of the *Journal of the American Chemical Society*, the *Journal of Organic Chemistry*, *Molecular Photochemistry*, and *Reviews of Chemical Reactive Intermediates*. He was a member of the National Research Council Advisory Committee on Pioneering Chemistry at Natick, the

Organic Division Executive Committee of the ACS, the Research Corporation Grants Committee, on the Board of Trustees of the International Photochemistry Foundation.

In addition to attending many professional society meetings, including IUPAC Symposia, Gordon Research Conferences in Photochemistry and the InterAmerican Photochemistry Society, Howard both organized and participated in a variety of professional meetings, primarily dedicated to photochemistry. He often traveled to European universities, most often in Germany, on lecture tours at the behest of Professors Hans Musso of Marburg University and then Karlsruhe, and Gerhard Schröder, also at Karlsruhe, Gerhard Quinkert of Braunschweig, Dietrich Doepf and others. He organized a 1972 photochemistry symposium at Baden-Baden, and photochemistry symposia for each of the last five meetings of the Pacific-rim chemical societies at the Pacificchem conferences held every five years in Hawaii.

The last in this series was held at the 2010 Pacificchem Meeting in December. Following that meeting, Howard Zimmerman retired from the University of Wisconsin-Madison and became a professor emeritus of chemistry.

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Celebration of the Career of Professor Howard E. Zimmerman (center) at the University of Wisconsin, held in Madison, WI, on Sept. 17, 2011.

A symposium honoring the career of Professor Howard Zimmerman was held in Madison the following fall on Sept. 17, 2011. Over 100 friends, colleagues, and students attended the meeting and dinner held in his honor in a tribute to his long and distinguished career as a mentor and scientist. A photograph of the group is shown above.

On February 12, 2012, Howard Zimmerman passed away after a fall while dining out. A year later, an issue of the *Journal of Organic Chemistry* was dedicated to his work. This issue contained numerous articles submitted by his former colleagues and students. The cover depicts highlights of Howard Zimmerman's career and his contributions to science and education.

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PRINCIPAL AWARDS AND HONORS

- 1948 Phi Beta Kappa
- 1950 Chittenden Award (top Bachelor of Science graduate in the class of 1950), Yale University
- 1960 Alfred P. Sloan Fellow
- 1971 Northeast ACS Award for Photochemistry
- 1976 James Flack Norris Award in Physical Organic Chemistry
- 1980 Elected a Member of the National Academy of Sciences
- 1980 Halpern Award of the New York Academy of Sciences
- 1986 American Institute of Chemists, Chemical Pioneer Award
- 1988 Senior Alexander von Humboldt Fellowship
- 1990 Hildale Award and Chair in the Physical Sciences from the University of Wisconsin
- 1991 Arthur C. Cope Scholar Award from the American Chemical Society
- 2006 Porter Medal from the International Union of Pure and Applied Chemistry

ENDNOTES

- 1 Zimmerman, H. E. (1961) *17th National Organic Symposium of the American Chemical Society, Abstracts*, pp. 31–41, Bloomington, IN.
- 2 See H. E. Zimmerman publication (1963) : A New Approach to Mechanistic Organic Photochemistry, In *Advances in Photochemistry*. Editors: W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr. pp. 188-190. New York: Interscience.
- 3 See the two communications on Hückel-Möbius Correlation Diagrams in the *Journal of the American Chemical Society* in 1966.
- 4 See publication by Zimmerman and Somasekhara (1963), *J. Am. Chem. Soc.* 85:922.

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