BOOK REVIEW

The Foundations of Physical Organic Chemistry: Fifty Years of the James Flack Norris Award, E. Thomas Strom and Vera V. Mainz, Eds., ACS Symposium Series 1209, Oxford University Press, 2016, 336 pp, ISBN 9780841230712, $170.

The field of physical organic chemistry arose during the 1930s largely because of the kinetic research of Christopher K. Ingold at University College London and of Louis P. Hammett at Columbia University. Ingold's work stressed organic reaction mechanisms, whereas Hammett's emphasized the thermodynamics of free energy relationships of acid-base reactions. The field blossomed with work along these lines in the 1940s and 1950s, but the scope immediately expanded. The principles were applied in organic chemistry to solvent effects, NMR spectroscopy, conformational analysis, reactive intermediates, aromaticity, isotope effects, noncovalent interactions, catalysis, photochemistry, molecular mechanics, and semiempirical and ab initio calculations. Applications moved beyond organic chemistry to embrace inorganic and organometallic chemistry, biochemistry, materials chemistry, medicine, industrial chemistry, and even geology. The defining theme was the relationship between molecular structure and molecular properties, both micro and macro and of interest to both the pure chemist and the applied chemist. The properties included kinetic, thermodynamic, spectroscopic, medicinal, practical, and on and on.

The publication of Louis P. Hammett's classic book *Physical Organic Chemistry* in 1940 is considered to be the founding act of this field. Twenty-five years later, the American Chemical Society (ACS) initiated the James Flack Norris Award in Physical Organic Chemistry, the first two winners of which were Ingold and Hammett, followed by Saul Winstein, who may have been the greatest physical organic chemist because of the originality of his approaches (although many may arguably put Paul D. Bartlett in his place). In 1988 the Award for Early Excellence in Physical Organic Chemistry was initiated by the publisher Wiley to recognize individuals in the early stages of their careers. Many monographs have become physical organic classics, including Edwin S. Gould's *Mechanism and Structure in Organic Chemistry* (1959), Ernest L. Eliel's *Stereochemistry of Carbon Compounds* (first edition 1962), Kenneth B. Wiberg's *Physical Organic Chemistry* (1964), Jerry March's *Advanced Organic Chemistry* (first edition 1968), and today's standard, *Modern Physical Organic Chemistry* by Eric V. Anslyn and Dennis A. Dougherty (2006). In 1959 the first edition of a textbook for undergraduate organic chemistry by R. T. Morrison and R. N. Boyd was released, with a novel approach that employed physical organic concepts, particularly reaction mechanisms and aromaticity. The first journal devoted to the field probably was *Journal of the Chemical Society*, which split in two in 1966, Part B of which was subtitled "Physical Organic Chemistry." The journal, however, evolved into *Journal of the Chemical Society Perkin Transactions II* in 1972. The *Journal of Physical Organic Chemistry*, devoted entirely to the field in all its manifestations, began in 1988.

On the occasion of the approaching 50th anniversary of the Norris Award (and, I might add, the 75th anniversary of the publication of Hammett's *Physical Organic Chemistry*), E. Thomas Strom and Jeffrey I. Seeman organized a symposium at the 247th National Meeting of the ACS in Dallas, TX, in 2014 under the auspices of the Division of the History of Chemistry, to recognize the field and its contributors. This book, edited by Strom and by Vera V. Mainz and published in the ACS Symposium Series (number 1209), brings together papers written by the participants, expanded with an introductory chapter and two chapters by students of key Norris Awardees who are deceased. Unfortunately, two chapter authors passed away soon after the book was published.

The leadoff article by Arthur Greenberg summarizes the life and scientific work of Norris, whose birth in 1871 made him senior to Ingold and Hammett by more than 20 years. Norris in turn was slightly younger than those chemists mentioned by Greenberg who developed many of the concepts on which physical organic chemistry was based—Paul Walden and Victor Meyer for stereochemistry and Julius Stieglitz and Moses Gomberg for reactive intermediates. To these names should be added that of Arthur Lapworth for developing concepts of reaction mechanisms. These chemists, including Norris, set the scene for the research of Ingold and Hammett. Greenberg describes Norris's specific contributions to physical organic chemistry, primarily at MIT, and the endowment provided by his widow, Anne Chamberlin Norris, which resulted first in the Norris Award for Outstanding Achievement in the Teaching of Chemistry (1951) and ultimately in the Norris Award in Physical Organic Chemistry.

Three of the contributing award winners describe work that interweaves theory and experiment. Wiberg briefly discusses his experimental, theoretical, and spectroscopic work, but focuses his discussion on his work with optical activity, almost all of which was published after his retirement from Yale in 1997. Andrew Streitwieser's focus is on isotope effects with almost no mention of theory, although he returns to that topic in a later, collaborative chapter. Interestingly, both Wiberg and Streitwieser began their work as graduate students in the laboratory of William von Eggers Doering. In fact, this volume includes four authors who were Doering students.

Paul von Ragué Schleyer is represented by two chapters in this volume. One chapter constitutes the subject of his lecture at the symposium, the norbornyl cation. It is fitting that this topic be covered in this volume, because of the central role of this cation in the field during the 1960s and 1970s. The so-called norbornyl controversy pitted two giants of the field, Saul Winstein and Herbert C. Brown, who initially debated the topic in classic lectures at UCLA and Caltech in 1963. The debate became so intense and, many thought, extended, that the field of physical organic chemistry itself suffered. Schleyer died just before he could finish his article for this volume, so the editors (Mainz and Strom) carried it to completion to ensure its inclusion. Every conceivable kinetic, structural, theoretical, and spectroscopic tool was applied to the problem, but ultimately it was X-ray crystallography that resolved the issue in favor of the delocalized structure, the so-called nonclassical version. This inapt term fed the controversy but never disappeared. Brown died in 2004, but I am not sure he ever agreed that the norbornyl cation was anything but localized.

Schleyer is represented by a second, autobiographical paper. Jeffrey Seeman had developed an autobiographical series of monographs for the ACS during the 1990s and asked Schleyer to contribute a volume on his work. During an extended hospitalization, he finally had time to write the bulk of the volume, which he entitled "From the Ivy League to the Honey Pot," to emphasize the transition from his position at Princeton, where he was primarily an experimentalist, to Erlangen, Germany, where he was primarily a computational chemist. The title was intended to highlight the fundamental differences in funding mechanisms between the American and European systems, in particular for obtaining computer (and, I add, spectroscopy) time. Basically, the German system enabled Schleyer to carry out the calculations he previously could not afford. The sociological differences between American and German universities also were important in his decision to move from Princeton and ultimately to remain at Erlangen until the compulsory retirement age by German law, the primary flaw in the honey pot. Schleyer never finished his manuscript, although Seeman had a draft. Interestingly, the volume is listed on amazon.com with a publication date in hardcover of June 1, 1998, apparently anticipated as Seeman assured me it was never published. Thus it fell to Streitwiester to complete the task, so that this volume at last presents Schleyer's autobiography to the public.

Edward M. Arnett presents his unique contributions to structure and mechanisms through the use of calorimetry, in addition to providing a brief exposition on the period of physical organic chemistry that immediately followed the publication of Hammett's book, the 1940s and early 1950s. In the true tradition of physical chemistry, Arnett and his students built their own calorimeters.

The results that rolled off of this unique instrumentation included the importance of solvation in solution acidity and basicity, such as the apparently inverted order of basicity of amines from ammonia to tertiary structures. Calorimetry was ideally suited for the quantitative assessment of physical organic concepts. In the true physical organic tradition, Arnett synthesized the unknown *ortho*-di-*tert*-butylbenzene and then determined the strain energy between the closely nestled *tert*-butyl groups to be 22 kcal mol^{-1}.

Ronald Breslow describes his contributions to one of the evergreen subjects of physical organic chemistry. The series of 4*n*+2 (Hückel) cyclic hydrocarbons provided an ineluctable attraction to physical organic chemists, with neutral six-membered benzene at the early center of attention and the charged five-membered cyclopentadienyl anion demonstrating the potential of the series. Then in 1954 Doering and Knox proved the existence of the seven-membered tropylium ion to complete the aromatic triad. The question remained as to whether the extra stability of aromaticity would countermand the expected ring strain in the three-membered cyclopropenium ion. Breslow and his students made the first substituted such cation in 1957 followed by the more satisfying unsubstituted cation in 1967. He also considered the issue of antiaromaticity, which embraced the four-membered constituents of the series, cyclobutadiene and its charged forms. Breslow, along with Myron Bender, was one of the pioneers of applying physical organic chemistry to biochemistry, and the remainder of his chapter is concerned with those contributions.

Three chapters focus on reactive intermediates, as well as the chapter already mentioned in which Schleyer summarized the norbornyl cation field. The editor Strom together with Kathleen Trahanovsky, both graduate students of Glen Russell, celebrated his life and research with a well-illustrated and enjoyable chapter. Free radicals also were the topic of the chapter by Keith Ingold, who was a member of the only father/son pair to receive the Norris Award. Ingold includes not only an insightful summary of his own work, but a pair of remarkable look-alike photographs of himself and his father when both were 12 and when both were in their 70s. Diradicals are the subject of the only chapter by what might be called a younger generation, by Weston Thatcher Borden. His chapter of course is strong on theory, but the focus is on the rich variety of diradicals that he has studied over his very productive career.

Last to be mentioned is the chapter by Ronald Magid and Maitland Jones on "Life in the Research Laboratory of William von Eggers Doering." Based on two "unpublishable" manuscripts by these authors, this expurgated version only makes one want to go to the website cited in the chapter for the full versions. What comes over strongly in the chapter are two highlights of Doering's research—originality and fun. Indeed the title begins with "Lost in the Funhouse." I can attest to the fun that Doering always injected into his research and his lectures. The year after I moved from my position as an undergraduate in Doering's group at Yale to a graduate student in Southern California, the National ACS Meeting came to Los Angeles in 1963, and with it, Bill Doering. I could not miss his lecture, which oddly was held in a movie theater. When he began his lecture on the stage, he discovered he lacked a pointer, and the slides were well above the length of his arm. Despite an acerbic request for a pointer, nothing was forthcoming, so Doering disappeared off stage and came back with … a broom. He preceded to grab its bristly head and point to relevant parts of the slide with the tip of the shaft. At last someone arrived breathlessly with a pointer, and Doering found himself with both a broom and a pointer. He then began sweeping the stage as he took the broom behind the curtain to dispose of it.

This book provides an eclectic group of essays on physical organic chemistry and physical organic chemists, which provides enjoyable as well as edifying reading.

Joseph B. Lambert, Department of Chemistry, Trinity University, One Trinity Place, San Antonio, TX 78209; jlambert@northwestern.edu.