

Some personal views on the past and future of physical organic chemistry

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Biography: Andrew Streitwieser was born in Buffalo, NY, on June 23, 1927, and was educated in the public schools of New York City. He served in the Army Medical Department during 1946–1947. He attended Columbia College (A. B. 1949) and Columbia University (M. A. 1950, Ph. D. 1952 with Professor William von E. Doering), was an A.E.C. Postdoctoral Fellow at MIT, 1951–1952 (with Professor John D. Roberts), and since 1952 has been on the faculty of the University of California. He became Emeritus Professor in 1993 and in 1995 was recalled as Professor of the Graduate School and Vice-Chair of Instruction in the Department of Chemistry.

He has a number of awards including the American Chemical Society James Flack Norris Award in Physical Organic Chemistry (1982) and he was elected to the National Academy of Sciences in 1969. He was a coeditor of 11 volumes of *Progress in Physical Organic Chemistry* and is currently an associate editor of the *Journal of Organic Chemistry*. He has served on the Commission of Physical Organic Chemistry of IUPAC. He has many publications in theoretical and physical organic chemistry and his chemical autobiography, *A Lifetime of Synergy with Theory and Experiment*, will appear in late 1996 from the American Chemical Society.

An attempt to estimate where physical organic chemistry will be going in the future requires first an appreciation of where it has been and where it is now, or at least, my view thereof. Physical organic chemistry has long been concerned with structure and reactivity, with experimental quantitative results from kinetics and equilibria interpreted with theory and electronic structure concepts at various levels. The interpretation of reaction rates required a knowledge of reaction mechanisms. Much of the thrust of physical organic chemistry in the middle decades of this century was directed towards the reaction mechanisms of homogeneous reactions in solution and the development of tools for such study, such as kinetic order, stereochemistry, substituent effects, primary and secondary isotope effects, and radioactive tracers. The development of new tools and machines has had a vital effect in extending the range of physical organic studies to clusters and macromolecules, crystals and solids, the gas phase, and to excited states; examples are NMR, glove boxes, molecular beam equipment, and lasers. An especially important tool has been the computer, for both automatic control of experiments and for theoretical computations.

These developments lead us to where we are now with an exceptionally broad range of activity, both experimental and theoretical. Much of the language derived from physical organic studies is now used throughout chemistry; examples are S_N1 and S_N2 reactions, initiation and propagation, carbocations and carbanions, contact and solvent-separated ion pairs, internal return, and nucleophilicity. The result is a discipline that has become rather diffuse. The physical tools used by physical organic chemists include those of modern physicists and physical and biophysical chemists as well as molecular biologists and theoreticians. The intellectual tools of physical organic chemistry have been taken up by organometallic, bio-organic and synthetic chemists, and many scientists who are doing what I consider to be at least in part physical organic chemistry call themselves something else. Of course, this is simply the result of successful science. Physical organic chemistry has shown itself to be an exceptionally useful science. Many of the tools of traditional physical organic chemistry are now used commonly by synthetic chemists to facilitate stereochemically oriented syntheses.

There follows from this present day state of affairs a straightforward extrapolation to the future. Many “traditional” physical organic chemists will continue in the mold of the past examining various organic reactions with increasing detail and understanding. Others will continue to apply both traditional and newer tools to important synthetic reactions, especially those involving inorganic and organometallic reagents and

macromolecules and excited states. The more significant the reaction is in modern synthesis, the more useful this new understanding will be to the synthesis practitioner. The computation of structures, electronic structures, and reaction transition states will continue to be exceptionally important and will be supplemented increasingly by modelling of reactions in solution and in the surface and solid state. The development of Monte Carlo methods and of intermolecular potential functions will nurture this development. Increasingly it will be possible to compute an experimental property to any desired degree of precision, leading to what I think is and will continue to be one of the important roles of physical organic chemistry: the development of fundamental concepts.

Merely reproducing experiment with precise computations doesn't teach us much unless the results are analyzed to provide understanding of the important contributions to the quantitative numerical value in terms of reference systems and simpler models and concepts. Such concepts as steric hindrance, hyperconjugation, orbital hybridization, charge delocalization, and inductive effects have pervaded much of chemistry. Chemistry is a complex science because we generally cannot take a simple "effect" and study it in isolation. We must deal with real compounds in which any change in structure introduces a number of "effects". As a result, the applications of our simplified concepts and their mutual interactions are a continuing concern. Because of their knowledge of organic and physical and theoretical chemistry, physical organic chemists are ideally positioned to elaborate many of these principles. Because simplifying concepts are used by all practicing chemists their continuing development is especially important. In particular, the widespread use of these concepts by synthetic chemists in their increasingly sophisticated molecular engineering will undoubtedly be an important factor in funding. This aspect of physical organic chemistry and of computational studies has already started to question some traditional ideas, for example, of structure and acidity and of the relative roles of covalence and ionic bonding. Further such studies will refine our use of symbols such as resonance structures, the curved arrow, and the line as bond, that will add understanding and precision in thinking to all of chemistry. As one example, our present symbols can represent charge transfer and delocalization effects but they serve inadequately to represent polarization effects. Just as the introduction of the present symbols and concepts changed completely the teaching and thinking of organic chemistry in the middle of the twentieth century, I think the modifications in the uses and meanings of these symbols as well as new symbols and concepts in the coming decades will change completely the teaching and thinking of organic chemistry in the twenty-first century.