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A Review of: "Modern Physical Organic Chemistry, by Eric V. Anslyn and Dennis A."

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Book Review

Modern Physical Organic Chemistry, by Eric V. Anslyn and Dennis A. Dougherty, University Science Books, 2006; xxviii + 1095 pages; $132.50.

Eric Anslyn and Dennis Dougherty are congratulated for writing a book that will rapidly become the standard for advanced courses in topics such as physical organic chemistry, reaction mechanisms, and theoretical organic chemistry. Their book was written for a two-semester sequence. (Full disclosure: I have adopted this book for a one-semester course titled Organic Reaction Mechanisms) The book comes with brief endorsements from B. Carpenter, T. M. Swager, and N. J. Turro.

The authors seek to produce a text with the traditional material of physical organic chemistry and also to introduce topics in emerging fields in topics as diverse as biological systems and conjugated and conducting polymers that have benefited from the approaches of physical organic chemistry. They have clearly been very successful in this endeavor.

Over the past forty years or so, physical organic chemistry has benefited from increased computing power. This had led to considerable progress in quantum chemistry, molecular mechanics, and rapid solution of crystal structures. The subject has also benefited from modern instrumentation for X-ray crystallography, NMR, and high-powered lasers with temporal resolution down to the femtosecond regime. The text does a good job of elucidating out most of these topics.

The book consists of three parts and a total of seventeen chapters. Part I is Molecular Structure and Thermodynamics. The chapters are titled Introduction to Structure and Models of Bonding; Strain and Stability; Solutions and Non-Covalent Binding Forces; Molecular Recognition and Supramolecular Chemistry; Acid–Base Chemistry; and Stereochemistry. Part II is Reactivity, Kinetics, and Mechanisms. The chapters are titled Energy Surfaces and Kinetic Analyses; Experiments Related to Thermodynamics and Kinetics; Catalysis; Organic Reaction Mechanisms, Part 1: Reactions Involving Additions and/or Eliminations; Organic Reaction Mechanisms, Part 2: Substitutions at Aliphatic Centers and Thermal Isomerizations/Rearangements; Organotransition Metal Reaction Mechanisms and Catalysis; and

Organic Polymer and Materials Chemistry. Part III is Electronic Structure: Theory and Applications. The chapters are titled Advanced Concepts in Electronic Structure Theory; Thermal Pericyclic Reactions; Photochemistry; and Electronic Organic Materials. An appendix with six topics follows these. These are Conversion Factors and Other Useful Data; Electrostatic Potential Energy Surfaces for Representative Organic Molecules; Group Orbitals of Common Functional Groups: Representative Examples Using Simple Molecules; The Organic Structures of Biology; Pushing Electrons; and Reaction Mechanism Nomenclature. An index of 17 pages ends the book. At the end of each chapter, there are lists of challenging problems and references for further reading. A problem solutions manual by M. Sponsler is available. Throughout the text, blocked-out sections labeled Connections and Going Deeper enrich the discussion.

Are there topics omitted or presented in lesser detail than desirable? The authors discuss the barrier in ethane, but not the origin of the barrier. For more than twenty years, the Cambridge Structural Database has been a valuable repository of crystallographic data allowing easy searching for both covalent and noncovalent interactions. Although there is a Connections section that uses this approach on p. 170 and a discussion of the Bürgi–Dunitz angle, a broader exposure would be desirable. The subject of the different meanings of the term "bond length" when determined by different methods is not treated. There are discussions of "exciton coupling," and "exciton migration," but the term "exciton" is not defined. The topic of charge-transfer complexes is dealt with at several places throughout the text. Although it is stated that such an interaction often leads to a new band in the electronic spectrum, the role of the energy difference between the ionization energy of the donor and electron affinity of the acceptor in controlling the energy of the charge-transfer transition is not discussed. The mixed-stack crystallographic array of weak charge-transfer complexes is not discussed. I would have added several additional references to the list for π Donor–Acceptor Interactions on p. 205. On p. 1033, TTF-TCNQ is described as a cocrystal, but that quasi-one-dimensional metal tetrathiafulvalenium 7,7,8,8,-tetracyanoquinodinethanide term is not defined. The segregated-stack structure and partial electron transfer of TTF-TCNQ are presented, but the reasons for electron transfer are not discussed.

The discussion of hydroboration kinetics on p. 555 is at variance with at least one study. The reaction of tetraisoamyldiborane with olefins is second order, first order in the diborane and first order in olefin. The possible dissociation of the dimer is not kinetically significant. (See *J. Am. Chem. Soc.*, **83**, 3417 (1961).) The Connections section

on p. 757 deals with gel permeation chromatographic estimate of molecular weight of poly(methylmeth-acrylate) exposed to gamma radiation. The reaction with the structure drawn has "hν" over the arrow. The "hν" is appropriate for ultraviolet irradiation, but another symbol is appropriate for the use of ionizing radiation.

The book is generally free of typos and related mistakes. On p. 185, "diacetylene" is not spelled correctly. On p. 980, the products in Eq. (16.66) seem to have lost a methyl group.

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