

Additions and Corrections

L-Methionine Methyl Is Specifically Incorporated into the C-2 and C-7 Positions of the Porphyrin of Cytochrome c_3 in a Strictly Anaerobic Bacterium, *Desulfovibrio vulgaris* [J. Am. Chem. Soc. 1993, 115, 12185–12186]. HIDEO AKUTSU,* JANG-SU PARK, AND SEIYO SANO

Page 12186: The source of the IUPAC-IUB atom-numbering scheme for heme c (Figure 2A) is a paper by Mei-Hing Chau, Meng Li Cai, and Russell Timkovich [*Biochemistry* 1990, 29, 5076–5087]. We regret the omission of this reference. Also, the bond between C5 and C6 of the heme c in Figure 2A should be a double bond.

Computer Software Reviews

AMPAC, Version 4.5. Semichem, Inc.: 7128 Summit, Shawnee, Kansas 66216. Voice: (913)268-3271. FAX: (913)268-3445. E-mail: aholder@vax1.umkc.edu. List price: \$9995.00; educational discounted price \$800.00.

AMPAC 4.5 is the second commercial release of Prof. Michael J. S. Dewar's general purpose semiempirical molecular orbital program. Prof. Michael Dewar has handed over the development responsibilities and commercial rights to Dr. Andrew Holder, President of Semichem (also, a professor at the University of Missouri–Kansas City). Dr. Holder not only is responsible for supporting the AMPAC software but also will continually be adding new capabilities. The distinguishing factor between previous versions of AMPAC and the commercial one is that the commercial version has a graphical user interface (GUI). The GUI enables the user to prepare input structures for computation and to analyze the computational results. Since the GUI was programmed to Motif/X Window System specifications, it will run on any computer which supports X. The real advantage of an X-based GUI is that the program can reside on a main computer (e.g., a Cray supercomputer) and the GUI may be used remotely over ethernet on several different workstations. The GUI is not integrated with the computational module of AMPAC which means that the user cannot directly submit jobs for computation from the GUI and must do so from the command-line interface. Computers which are supported in running the computational module and the GUI include Silicon Graphics, DEC, IBM RS6000, Hewlett-Packard, Convex, and Sun. People who want to know more detailed information about these supported computer systems should contact Semichem.

AMPAC is distributed in two ways: magnetic media (e.g., tape) or electronically (ftp to a host computer at Semichem). The actual installation of the software is straightforward. A software key-license file must be installed in the appropriate directory for running the GUI and the computational module. This key-license file will notify the user of the expiration of the license. Scripts are provided for running the computational module and may need some minor editing, depending on the particular computer environment. For example, on a Silicon Graphics Indigo computer, no script modifications were necessary; however, the scripts needed some minor modifications to take into account the batch environment of a Cray supercomputer with the Unicos operating system. Another consideration in installing the program is choosing the particular computational module executable which depends on the amount of memory (RAM) and the particular computer. For example, the executable, amp100.exe, will run fine in 32 Mbytes of memory on most computer systems (the Cray is an exception) and is limited to a molecule with no more than 100 heavy atoms and 100 hydrogens.

Some of the capabilities of AMPAC 4.5 computational module are: SAM1, AM1, PM3, MNDO, MNDOC, and MINDO/3 Hamiltonians; RHF, UHF, and CI (useful for predicting UV–visible spectra) methods; geometry optimization to local minima or transition states; reaction coordinate path calculation; intrinsic reaction coordinate calculation; simulated annealing for multiple minima searches; force constants and vibrational frequency analysis; solvation properties of molecules in aqueous solution; electrostatic potential surface and derived atom charges; and polarizability (nonlinear optical) properties.

The SAM1 method is the new, improved successor to the AM1 procedure and is available for H, C, N, O, F, Si, P, S, Cl, Br, and I. This new theoretical model computes the two-center two-electron repulsion integrals in a manner different from the previous methods which should allow the study of molecules containing elements with d orbitals. In fact,

it is planned that future releases of AMPAC will include metals from the first transition series. For geometry optimizations of minima or transition-state structures, the eigenvalue following (EF) algorithm is available. Methods are available for studying reactions paths: (1) drive a particular reaction (internal) coordinate of interest, (2) determine a transition-state structure between two minima, and (3) given the transition-state structure, calculate the properties at points along the reaction pathway from reactants to products. Simulated annealing is one of the newer capabilities and is used to collect a variety of possible conformational structures for a particular molecular system. This technique uses a Monte Carlo approach with explicit boundaries defined by the user for the changing coordinates. In my work, this method has been especially useful in finding most, if not all, of the minima structures of a 14-membered ring and its acyclic counterpart. One note of caution is that this capability requires significant computer time (e.g., the 14-membered ring required almost 10 h of Cray YMP time).

The remainder of this review will focus on the GUI since this is the part of the software package with which users will interact the most. As noted above, the GUI provides the means of setting up the input file for submission to the computational module. Molecules may be constructed an atom at a time, each selected with a particular coordination geometry, or from fragments which have been pre-minimized at the AM1 level. Bond distances, angles, and dihedral angles may be readily modified. For better viewing, the molecular structure may be rotated about or translated along the x , y , or z axes, using the three-button mouse. The molecule may be displayed and manipulated in wireframe or ball-and-stick mode. After the molecule has been built, its internal coordinates may be modified by bringing up the z -matrix editor window. Selecting a row in the z -matrix for modification highlights the corresponding atom on the screen. Atom ordering, optimization flags, and connectivity may all be changed within this editor. Although I found this feature to be a useful visual aid in fine-tuning the internal coordinate representation of a molecule, it could be greatly improved by clearly displaying the atom numbers next to the atoms at all times and by highlighting all the atoms involved in the internal coordinate representation of an atom when it is selected/changed in the editor. Finally, some of the computation keywords and associated values may be selected/set through a combination of dialog windows. Not all of the computational capabilities and input parameters are accessible through the GUI, and it will be necessary to edit the saved input file for certain types of computation. However, for geometry optimizations and vibrational frequency analyses, the GUI is quite satisfactory.

The GUI may also be used to analyze computational results. For a reaction coordinate path calculation in which an internal coordinate is varied incrementally, the energy as a function of the reaction coordinate may be displayed in a two-dimensional plot. The actual reaction coordinate may be animated as well in which the molecular structure changes as the program cycles through the reaction coordinates. The vibrational frequencies may be displayed in line format with a rough idea of what the relative intensities might be. A particular vibrational mode may be animated based on the corresponding Cartesian displacements in order to identify the normal mode. A graphical representation of the simulated annealing results may be displayed in which the conformer energies are sorted (lowest to highest) and plotted relative to the lowest energy structure. The user may view any of the minima structures by cycling through the points on the graph or by directly selecting a point on the graph.

The manual does a very good job of explaining the setup of an input file for the computational module. All the keywords are briefly defined,

and examples are presented in a tutorial fashion, providing guidance in properly constructing input files and in correctly interpreting the output files. General background material is presented on the underlying theoretical concepts for the computational methods. A reference list is provided at the end of the manual for those individuals wanting to pursue greater details of the computational methods. The manual also contains a chapter on how to use and customize the GUI. On-line help is also available within the GUI. Customer support from Semichem is readily accessible over the phone or by electronic mail. Dr. Holder, in fact, was usually the one who promptly responded to my questions about the GUI or the computational methods.

Overall, AMPAC 4.5 provides a solid semiempirical molecular orbital package which will be of great interest to both academic and industrial

users. The graphical user interface is a practical and helpful feature, but the real power of this software package is its computational capabilities. Simulated annealing is the most exciting computational feature, allowing the user to quickly and reliably explore the conformational space of a monomer unit which may be of importance in polymeric materials. Semichem is a young company that is constantly improving its product. The additions and enhancements to the computational module as well as the graphical user interface between versions 4.0 and 4.5 have impressed me, and I expect a similar performance from this company in the future.

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Book Reviews

Fundamentals of Photoinduced Electron Transfer. By George J. Kavarnos. VCH Publishers: New York, 1993. viii + 360 pp. \$75.00. ISBN 0-89573-751-5.

Photoinduced electron transfer has become one of the key unifying reactions of the various subdisciplines of chemistry. As such, it has attracted voluminous contributions both to the original and review literature. (A brief listing of a number of these reviews can be found in the editor's introduction to the special issue on electron transfer in *Chemical Reviews* published in May of 1992.) It is entirely appropriate, therefore, that Kavarnos has prepared a text with a strong pedagogical bent. The author describes in the preface his goal in writing the text: as a primary or secondary text in introductory and advanced chemistry courses at the undergraduate and graduate level. In this niche, the book fulfills its mission very well.

Chapter 1 is an introductory discussion of elementary concepts of organic and inorganic photochemistry. It is followed by a chapter on the use of spectroscopic methods for characterization of oxidized and reduced intermediates and radical ion pairs. Chapter 3 provides many examples of organic transformations initiated by photoinduced electron transfer. Chapter 4 deals with physical aspects of photoinduced electron transfer, covering such topics as through-bond and through-space coupling and electron transfer occurring through rigid and flexible bridges. Chapter 5 focuses on the use of organized assemblies and interfaces for controlling electron transfer. Chapter 6 provides a clear presentation of both the classical and quantum mechanical theories used routinely to describe both thermal and photoinduced electron transfers.

As is consistent with its pedagogical orientation, the text includes at the end of each chapter suggestions for further reading which are selected articles and reviews dealing with the topics considered in each chapter. The section is followed by problems whose solutions can be found by reference to the original literature. Although a subject index is included, an author index is not, making it unnecessarily difficult to locate particular investigations.

The interested reader should approach this book as a text rather than as a monograph in order to avoid disappointment. The literature cited is far from comprehensive, and it was often unclear to this reader why particular examples were chosen rather than others. Attribution for work was often weak, and although a reference is cited for each topic, the choice of topics is sometimes rather arbitrary. In an advanced text, one would expect to have identified the key players in a research area by name in a monograph text. In other cases, key contributors to the topics being considered are either neglected completely or at least undercited with respect to their key experiments: among the many significant omissions in the text is a lack of emphasis on a work by Farid and Gould on electron transfer in ion pairs and of Mataga on intra- and intermolecular electron transfer. The work of Fujishima and Honda, which stimulated much of the work on water splitting on semiconductor surfaces, is neglected, and the many contributions of Grätzel and Fendler, among others in this area, are undercited. Many of the figures included within the text cite a review by Kavarnos in *Topics in Current Chemistry* rather than the original literature. This reviewer often also found the absence of chemical or quantum yields distracting in discussions of the applicability of photoinduced electron transfer as a synthetically viable method.

For optimal teaching value, the chapter on theory should have appeared earlier and more practical applications should have been emphasized. For example the pioneering work of Closs and Miller on long distance electron transfer seems to be missing from the place one would have expected it in dealing with long distance electron transfer (Chapter 4). Instead, one finds it in Chapter 6. Similarly, the reader would have to

guess that one of the principal applications to have emerged from semiconductor-mediated photoinduced electron transfer is in photocatalytic oxidative degradation, for this topic is not covered at all in Chapter 5. The section on photosynthesis similarly neglects the elegant work of Norris, Fleming, and others in characterizing the operative pathways in photosynthetic reaction centers.

All of these omissions, however, can be overlooked if one considers the book as a beginning text which does provide, indeed, an interesting overview of the fundamental scientific concerns of this important area. It is quite appropriate for use in a special topics course for students who have completed a year of undergraduate organic and physical chemistry.

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Catalysis by Metal Complexes. Volume 14. Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds. Edited by K. Kalyanasundaram and M. Grätzel (Swiss Federal Institute of Technology of Lausanne). Kluwer Academic Publishers: Dordrecht, Boston, and London, 1993. xvi + 465 pp. \$192.00. ISBN 0-7923-2261-4.

This monograph comes at an opportune time to complement the recent monographs *Photosensitive Metal–Organic Systems—mechanistic principles and applications in the Advances in Chemistry series* (C. Kutal and N. Serpone, Vol. 238, American Chemical Society, 1993), *Charge Transfer Photochemistry of Coordination Compounds* (O. Horvath and K. L. Stevenson, VCH Publishers, 1993), and *Fundamentals of Photoinduced Electron Transfer* (G. J. Kavarnos, VCH Publishers, 1993). Other related monographs are *Supramolecular Chemistry* (V. Balzani and L. De Cola, NATO ASI Series C371, Kluwer Academic Publishers, 1992) and the earlier series of volumes *Photoinduced Electron Transfer* (M. A. Fox and M. Chanon, Elsevier, 1988). The present monograph will be an excellent addition to a researcher's personal library.

This monograph is basically organized into four parts. In the first part (Chapter 1), A. W. Adamson recounts some historical perspectives of the birth of inorganic photochemistry from the work in his laboratory (Adamson's Rules, the hexi state, redox quenching, etc.) and those of others since the 1950s; it is mixed with some nostalgia about the *good old days* when the inorganic photochemical community was a relatively small family which met at informal gatherings, now full-fledged international symposia. As Prof. Adamson aptly put it: inorganic photochemistry has come a long way from our first, unintentional photochemistry in 1950. The next three chapters (Part 2) consider the basic principles and concepts that govern electron and energy transfer (V. Balzani and M. Maestri) which have been covered extensively by the authors in several other fora, photocatalysis by Hennig and co-workers, and the chemistry of charge transfer excited states by Vogler and Kunkely. The five chapters of Part 3 cover the photochemistry of classical Werner-type transition metal complexes and their applications (e.g., photoreduction of CO₂ and CO, and photosensitization of large bandgap semiconductors). Polypyridine complexes such as rubipy, Ru(bpy)₃²⁺, and its analogs have received the greatest attention, building up to polynuclear/supramolecular devices based on the rubipy systems and subsequently represented by the metalloporphyrin units. The following and last five chapters (Part 4) focus on several inorganic and organometallic systems (polyoxometallates, metal carbonyls, organometallics, ground-state complexes of inorganic salts, and electron donor/acceptor complexes of organometallics such as metal alkyls and metallocenes) where photocatalytic transformations of