Additions and Corrections

Accurate Calculations of Reactivities and Diastereoselectivities in Complex Molecules: An AM1 Study of 1,3-Dioxolan-4-ones and Related Oxygen Heterocycles [*J. Am. Chem. Soc.* **1995**, *117*, 607−614]. ATHELSTAN L. J. BECKWITH* AND ANDREAS A. ZAVITSAS*

Page 609, left column, lines 24−27 should read as follows: Abstraction from α-methyl-γ-butyrolactone occurs preferentially to give **6**, not **5**;[17] the AM1 CI = 2 calculation shows **6** to be more stable than **5** by 1.80 kcal/mol.

JA975409B

S0002-7863(97)05409-7

Computer Software Reviews

pro Fit 5.01 for the Mac. Cherwell Scientific Publishing, Inc., 744 San Antonio Road #27 A, Palo Alto, CA 94303. Tel: 415/852-0720. Fax: 415/852-0723. List price $399.00; educational discounted price $299.00. 1997.

pro Fit is a curve fitting and graphing package designed specifically for scientists. The program was designed to very closely follow the Macintosh user interface guidelines and fully supports most system 7 features (including drag and drop, publish and subscribe, and AppleScript). Extensive on-line help is provided via Apple Guide and balloon help. The new user will very quickly master its fundamentals, with minimal need to refer to the large, spiral bound manual. Versions are provided which support 68K (with and without FPU) and PowerPC processors, running system 7. Minimal and suggested RAM requirements are 1.5 and 2.5 Mbyte, respectively, for 68K Macs, while the PowerPC version requires a minimum of 2 Mbyte of RAM (3 Mbyte suggested). A full install of the software (including numerous example files) requires 5−6 Mbyte of disk space, although the program itself is a lean 1.2 Mbyte (the help files add an additional 1.1 Mbyte). A demo version of the software is available for download from http://www.cherwell.com.

The real strength of this program is in its curve fitting. There is a small set of predefined functions for fitting; however, complex user-defined models can be fit as well. User-defined functions are straightforward to define and are written in a subset of the Pascal language, allowing the use of conditional branching, looping, and storage of intermediate calculations. For the novice, the help system will generate a fully configured function shell, and in most cases, the fitted equation can then be entered in a single line of code. For more advanced users, the function can call subroutines (including external routines compiled in languages such as Fortran, Pascal, or C), look up values in the associated data file, or access any number of system functions. The user functions are fully compiled prior to use, and fitting of even fairly complex functions is extremely fast. Although not required, the user-defined function can specify partial derivatives for some or all parameters, to further speed fitting and to help avoid local minima. Finally, the software provides directly for the placement of upper and lower limits on fitted parameters (constraining a rate constant to be positive, for example). This can be of great help in keeping a fit away from unreasonable local minima.

A unique and very useful feature of the pro Fit software is something called the "Preview Window". The current data set and associated function can be automatically plotted into the preview window. Changes in parameters are then immediately reflected in the plot of the function. However, the user may also choose to "float" one of the parameters. In this case, the user may then click on a portion of the plotted function and drag it closer to the data. Subject to constraints imposed by the function and its other parameters, pro Fit adjusts the floating parameter and the plotted function in real time. This is useful not only for obtaining better initial guesses for a fit, but also for providing insight into how each parameter influences the shape of the function. The preview window can also be used as a progress window to monitor iterations of an ongoing fit.

In addition to the traditional Levenberg−Marquardt algorithm, Robust and Monte Carlo approaches can also be applied for fitting. In any case, measured errors, or specific error distributions, in both independent (x) and dependent (y) values can be used in weighting the fit. As for most such programs, the standard deviations of the fit parameters are reported by default. However, for nonlinear fitting functions or in cases where the errors in the data are not normally distributed, standard deviations are not necessarily appropriate. Instead, pro Fit can generate more meaningful (nonlinear) confidence intervals for the fit parameters. The manual has a readable introduction to analysis of fit quality and fit parameter uncertainties, a topic from which many scientists could benefit. Similarly, the Apple Guide help facility shows how to quickly generate residual plots (although this is not indexed in the printed manual). Finally, the manual and help files provide valuable guidance on performing fits with multiple dependent and/or independent variables (for example, a system of simultaneous differential equations).

Although basic data transformation (ranging from simple column arithmetic to Fourier transforms) can be achieved without resorting to programming, the latter is a notable strength of pro Fit. Programmability goes beyond defining fitting functions; programs (as distinct from functions) can be written to control almost every aspect of the pro Fit software, from executing curve fits to drawing specific elements into a plotting window. This allows for extremely powerful automation of repeat analyses. Using AppleScript, one can generate a "drag and drop" solution which analyzes data and provides a specific report, automatically (one could similarly imagine data acquisition software sending data directly to pro Fit for immediate workup). The on-line help menu, with a large variety of preconfigured shells, greatly facilitates program development.

Plotting is geared toward the presentation of scientific data. Bar and pie charts are supported only as add-ons, as is graphing of 3D data and functions. Options for the presentation of conventional 2D data and curve fits, however, allow precise control over the final plot. Data plotting allows specification of various types of error bars, including asymmetric ones. The drawing (plotting) window offers a reasonable selection of drawing tools. Multiple plots can be placed amid any user-created text or graphic elements. Unfortunately, editing of legends and scales (to change font or size, for example) requires going through a dialog box. Indeed, even static text placed on the drawing must be entered and edited via a dialog box and is limited to single lines of 128 characters each. This is a serious limitation for those wishing to include extensive explanatory text in a drawing, without exporting to a separate drawing program. For plotting, named style sets may be defined and saved; however, there is no direct provision for overall page templates (this can, however, be achieved via programming). One notable strength of the function plotting is that, by default, pro Fit records only as many points as necessary to faithfully represent the function. This can result in a significant reduction in size for exported graphics. Drawings can be exported at various resolutions and in a variety of formats.

In summary, the package stands out on several fronts. The printed

documentation is very readable, and the on-line help is excellent. The program and supporting documentation encourage more than a simplistic analysis of the quality of fit, and the analysis of errors in fit parameters includes the ability to generate nonlinear confidence intervals. The preview window provides a unique perspective into the effects specific parameters have on the fit function. Finally, almost every aspect of pro Fit is programmable, providing the potential for creating very powerful analysis packages.

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JA965929R

S0002-7863(96)05929-X

Book Reviews *

Dynamics of Solutions and Fluid Mixtures by NMR. Edited by Jean-Jacques Delpuech (Université Henri Poincare). Wiley: New York. 1995. xi + 587 pp. $79.95. ISBN 0-471-95411-X.

The time dependence of NMR spectra has been used to study the dynamics of small molecules since the early days of NMR spectrometers. As instrumental resolution and sensitivity have improved, the methods have been extended to larger molecules which are intrinsically mobile. Complex internal motions of synthetic polymers and biological macromolecules can now be studied. This 10-chapter book provides a timely review of the theory and experimental techniques with an extensive collection of examples taken from chemistry, biochemistry, and biology. It will provide a useful reference for workers in the field, but its use as a text for newcomers will probably need a supplementary introduction to relaxation phenomena.

In the preface, the editor indicates that he planned to produce an authentic textbook by collecting all the existing basic information necessary for newcomers, especially in the fields of chemistry and biochemistry. Material is presented in a logical sequence, but the text is multi-authored, and the flow between chapters is not always seamless. This is perhaps most important in the first three chapters which cover the fundamentals of the subject. Chapters 1 and 3 are both written by the editor, and they are appropriate for his intention. The first chapter introduces the very basic principles of NMR spectroscopy with emphasis on time-dependent aspects. Liberal use of vector diagrams and other illustrations helps to make the explanations clear for new workers. Unfortunately, the authors of Chapter 2 do not obviously proceed from that point. Writing on the use of relaxation phenomena to study molecular reorientation, they do not explain fundamental techniques such as the spin echo experiment and the Carr−Purcell−Meiboom−Gill method at the same simple level. Newcomers without a strong physics background will find this chapter heavy going, but it does contain a lot of information including a brief survey of techniques other than NMR. Also, the basic message that nuclear spin relaxation can provide accurate information about rotational motions is clearly emphasized.

The third chapter is centered on nuclear site exchange and provides an overview of molecular rate processes which have been studied by dynamic NMR over a 50-year period. Topics include experimental methods, determination of rate constants, and intermolecular and intramolecular processes. There are 100 pages and 223 references to illustrate the types of intermolecular and intramolecular exchanges which can be studied by dynamic NMR. Examples come from biochemistry as well as organic, inorganic, and organometallic chemistry and provide interesting reading for any chemist.

Since the early days of NMR, it has been well known that small concentrations of hydrated paramagnetic ions cause a considerable increase in proton relaxation rates. Chapter 4 addresses relaxation in systems which contain paramagnetic species. A number of applications of paramagnetic enhanced nuclear spin relaxation in homogeneous and microheterogeneous systems containing hydrated transition metal ions are considered. Some recent theoretical results relating to paramagnetic complexes in microheterogeneous systems are also included. Following is a largely theoretical chapter to consider quadrupolar nuclei and their use as chemical probes in solution.

Chapter 6 shows how a variable pressure NMR approach can be used to investigate solvent exchange on metal ions. In this unusual method, the pressure dependence of the rate constant at a fixed temperature is described by transition state theory. The activation volume (the difference between the partial molar volumes of the transition state and the reactants) can be determined from this pressure dependence and used to deduce information about the mechanism.

One major objective in classical NMR relaxation experiments is to obtain the best possible homogeneity for both magnetic fields. A field gradient will alter the results of spin echo experiments because of translational diffusion of molecules in the sample. Chapter 7 shows how deliberate application of a static field gradient can be used to determine the self-diffusion coefficient. Therefore, the traditional relaxation experiments described in chapters 2 and 3 can be used to study rotational motion; experiments using field gradients can be used to study translational motion.

With the demonstrated ability to study both rotational and translational motions, the dynamics of large complex molecules is introduced in the last three chapters. Microheterogeneous solutions, micelles, and emulsions are covered in Chapter 8. Synthetic polymers in solutions and melts and the dynamics of biopolymers are covered in the two parts of Chapter 9. Chapter 10 contains three illustrative examples selected from the general theme of liquid-like molecules which are contained as inclusions or adsorbates in solid materials, or which constitute soft matter. First is Swollen Polymers and Gels which deals with polymeric systems above or near the glass transition temperature. Zeolites and heterogeneous catalysts are considered next in the section titled Fluids in and on Inorganic Materials. The third part is titled Magnetic Resonance in Food Science.

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JA955294G

S0002-7863(95)05294-2

Annual Review of Biophysics and Biomolecular Structure, Volume 25. Edited by Robert M. Stroud (University of California−San Francisco). Annual Reviews, Inc.: Palo Alto. 1996. xii + 492 pp. $67.00. ISBN 0-8243-1825-0.

This is a volume of the continuing series published by Annual Reviews Inc., a nonprofit scientific publisher established to promote the advancement of sciences. The volumes are organized by Editors and Editorial Committees who invite qualified authors to contribute critical articles. After a preface by the editorial board, there are 16 chapters organized under the following headings: Structural Principles (including chapters on Bridging the Protein Sequence-Structure Gap by Structure Predictions; and The Sugar Kinase/Heat-Shock Protein 70/Actin Superfamily), Structure and Function (including chapters on Using Self-Assembled Monolayers to Understand the Interactions of Man-Made Surfaces With Proteins and Cells; Engineering the Gramicidin Channel; and Protein Function in the Crystal); Dynamics (including a chapter on Use of ^{19}F NMR to Probe Protein Structure and Conformational Changes); and Emerging Techniques (including chapters on Circular Oligonucleotides: New Concepts in Oligonucleotide Design; and Modeling DNA in Aqueous Solutions: Theoretical and Computer Simulation Studies on the Ion Atmosphere of DNA). There is a subject index, a cumulative index of contributing authors, and a cumulative index of chapter titles.

JA965690E

S0002-7863(96)05690-9

*Unsigned book reviews are by the Book Review Editor.