Additions and Corrections

NMR Motional Averaging in the Isotopically Perturbed Cope Rearrangement [*J. Am. Chem. Soc.* **1998**, *120*, 1489−1493]. Eric R. Johnston,* Jodi S. Barber, Marc Jacomet, and James C. Barborak

Page 1492: Equation 6 of the text is incorrect as written. The correct expression is

$$\lambda_- = R + \frac{(\omega_B - \omega_C)^2}{4(k_{BC} + k_{CB})} + i(\omega_B p_B + \omega_C p_C)$$

Page 1493: An omission of text appears in the discussion of chemical exchange of multiple quantum coherence. The correct full sentence should read as follows: During the evolution period t_1 of the HMQC experiment the zero quantum coherence (ZQC) and double quantum coherence (DQC) of C2/H2 in conformer *B* couple *via* exchange with the respective ZQC and DQC of C7/H7 in conformer *C*.

JA9855038

S0002-7863(98)05503-6

Computer Software Reviews

SymApps Version 1.0 (Windows 95 or NT). By Karl R. Nedwed. Bio-Rad Laboratories, Sadtler Research Division (formerly published by SoftShell International, Ltd.), 1600 Ute Ave., Grand Junction, CO 81501; (970) 242-6469. List Price $599 for the complete ChemWindows Suite (which includes SymApps), $399 as an upgrade from any other chemistry drawing software. Academic and student discounts are available.

SymApps is a component in the ChemWindows suite of programs. It serves as a means for the rendering of molecules and fragments of extended structures in three-dimensional depictions in four styles: wireframe, stick, ball-and-stick, and space filling. It can assign a Schoenflies point group symmetry, display individual symmetry elements, and produce graphical output. The program can accept as input molfiles, Gaussian, Mopac, Brookhaven protein data, and Cartesian *xyz* coordinates. Additionally, 2-D renderings generated by ChemWindow or ISIS Draw can be converted to 3-D by using the included molecular mechanics (MM2 force field) program. SymApps can be run from within Microsoft Word and other OLE compliant applications, but the program does not support OLE drag-and-drop functions. Various animation features are included which can be used to combine figures and create “movies”.

The publisher gives as minimum system requirements a “fast” 486 running Windows 95 (with 8 MB RAM) or Windows NT (with 16 MB RAM). Our evaluations were run on various Pentium and Cyrix 6×86 platforms running at 120 MHz or faster with 32 MB RAM and high-quality video processors with 2 MB. Under these conditions, all applications executed with acceptable speed. Performance would undoubtedly degrade rapidly with slower processors and less RAM.

Installation was effortless and the program itself is a model of clean, intuitive design. Only minimal reference to the manual was required to get started; a few mouse clicks and a few pokes at the on-screen “tools” and the user quickly feels right at home. We found the program free of bugs and generally capable of doing what it claimed it could do.

We used several high-symmetry molecules to test the program’s ability to determine point-group symmetry (with adjustable tolerances) and to display the symmetry elements. We could find no instance in which it failed, even when confronted with D_{2d} symmetry derived from a minor distortion from tetrahedral, D_{3d} symmetry on a 75-atom molecule, and various distortions of O_h symmetry. It was also able to display correctly the symmetry elements. Unfortunately, this is also where the program lacks polish. It displays mirror planes as confusing wire-frame planes which obscure large sections of the molecule. A simple medium-grey “transparent” plane with darker shades where overlapped would have been preferable. High-symmetry molecules with several mirror planes disappear into the clutter. It would have been nice to have had the ability to prune the display to show elements individually, rather than collectively.

By comparison to some competitive packages, the display functions lacked sophistication. The lighting was difficult to set up and the rendering rather ordinary. Even on a machine displaying 1024 × 768 pixels at a color depth of 65 thousand colors, annoying banding was obvious in the spheres of space filling and ball-and-stick models. The deficiencies become all the more apparent when compared to RasMol, a free program for viewing PDB files, or a more reasonably priced commercial package, such as HyperChem Lite (Hypercube, Inc. $149 academic) and PC Spartan (Wavefuction, Inc. $299 academic).

While the author’s demonstration routines of dyes and other organic molecules worked flawlessly, several problems were encountered in the conversion of 2-D images created in ChemWindows 3.1 to 3-D images. Inorganic and organometallic examples were not correctly interpreted, and in general, the routines constructed incorrect geometries, omitted parameters, and failed to recognize the phenomenon of coordination. A molecule as simple as ferrocene produced error messages about the “excessive” number of bonds to iron; nor was it happy generating an iron-centroid bond. Since it is not possible to edit structures once they have been read in and add or subtract bonds as needed, this is a serious deficiency.

We also viewed as a deficiency the inability of the program to accept as input fractional coordinate data from sources such as the Cambridge Crystallographic Database and to render complete molecules from fragments based on space-group symmetry. Fractional-coordinate crystallographic data are, by far, the most common source of structural information.

The bottom line: while the symmetry functions are useful and well done, the rest of the program lacks polish when compared to other offerings on the market, especially if there is much interest in inorganic systems. If you are a current ChemWindows user and frequently work with structures where it is difficult to determine point-group symmetry, SymApps may be a valuable addition. It may also find value as a symmetry instructional/tutorial program in undergraduate courses. However, it is, in and of itself, not a compelling program, nor a reason to acquire the suite.

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JA965935N

S0002-7863(96)05935-5

The Merck Index, 12th Edition, CD-ROM (Macintosh): An Encyclopedia of Chemicals, Drugs & Biologicals. Edited by S. Budavari, M. O'Neill, A. Smith, P. Heckelman, and J. Kinneary (Merck & Co., Inc.). Chapman & Hall: New York. 1997. $250.00. ISBN 0-412-75940-3.

The Merck Index has served many organic chemists as a convenient, comprehensive, and highly accurate source of detailed information on 10,000 drugs and common chemical intermediates. This resource is now available in a searchable electronic version. The Apple Macintosh version was evaluated for this review. A Macintosh PowerPC or 68040 processor, a color monitor (minimum 640 × 480 and 256 colors), a quad speed CD-ROM drive, 8 Mbyte of RAM, 12 Mbyte of hard disk space, and Mac OS 7.5 or higher are required.

The search engine for *The Merck Index* is quite powerful, with three search routines with increasing complexity and power. The "Quick Search" is a simple search of all fields that uses Boolean logic operators as well as truncation and wild card operators. The "Menu Search" is more detailed, permitting combined searches in any of the available fields which include all names; all text; all entries; additional name; boiling point; CA name; CAS registry number; density; derivative type; drug code; manufacturer name; melting point; molecular formula; molecular weight; monograph number; note; properties; refractive index; rotation; therapeutic category; title name; toxicity; trade name; use; and UV maxima.

The "Command Search" is less structured but more powerful than either of the simpler routines, and searches can be save and then combined to find, for example, entries that meet the restrictions of multiple searches. In addition, there is a substructure searching routine that can be used alone or in combination with text searches. Dedicated Macintosh users will find the interface a bit awkward at first, but facility with the program is gained quickly and easily. The search engine is used with other electronic databases available from Chapman & Hall, and operations not appropriate to *The Merck Index* are dimmed. This is a nice feature for users who will frequently use the engine with several of these databases which include The Dictionaries of Natural Products, Organic Compounds, and Inorganic and Organometallic Compounds.

Chemical structures found with any of the search methods can be copied to the clipboard and used in other applications. The clipboard information is compatible with both Chemintosh (Softshell) and ChemDraw (CambridgeSoft Corp.), and structures pasted into either of these applications can be fully manipulated.

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JA975911W

S0002-7863(97)05911-8

Book Reviews

Applied Homogeneous Catalysis with Organometallic Compounds. A Comprehensive Handbook in Two Volumes. Edited by B. Cornils (Hoechst AG Germany) and W. A. Herrmann (Tech. University München, Germany). VCH: Weinheim. 1996. xxxvi + 1246 pp. DM 598. ISBN 3-527-29286-1.

This impressive two-volume set covers homogeneous catalysis via organotransition metal (and related) compounds in a very thorough manner, with extensive use of recent references through 1995 and in some cases 1996. The editors have selected 97 contributors for the various chapters and subsections, with 86% from Europe (most from Germany) and the remainder from Canada, Japan, and the U.S. Approximately 50% of the contributors are from industry, so these books are especially noteworthy and, indeed, unique because they represent a nice balance of academic and industrial perspectives on this area. The predominant focus is on applied homogeneous catalysis, which the editors define as application oriented.

The editors define homogeneous catalysts as molecularly dispersed (gas phase conversions are excluded), unequivocally characterized chemically and spectroscopically, synthesized reproducibly, modifiable in a rational fashion, and amenable to the determination of kinetics related to the metal atom(s) involved. The editors also include some less well-defined systems (e.g., Ziegler−Natta polymerization catalysts other than classical polyethylene/polypropylene syntheses, supported catalysts, and clusters) if the catalyst system "passes a detectable catalyst cycle or parts thereof". Compounds without metal−carbon bonds such as metal nitrosyl and metal phosphine complexes are included.

Volume 1 begins with a nice introduction (18 pages) by the editors which covers the history of organometallic homogeneous catalysis since Roelen's work on the oxo synthesis (hydroformylation). An interesting part of this history is the inclusion of six pages of photographs of a number of intellectual leaders (from W. C. Zeise to R. F. Heck), along with brief summaries of their scientific contributions. The Introduction discusses the symbiotic relationship between organometallic chemistry and homogeneous catalysis, compares and contrasts homogeneous and heterogeneous catalyses, describes the key contributions from process technology (e.g., separation methods) and ligand design and synthesis, and notes the increasing importance of enantioselective synthesis. The advantages of homogeneous catalysts, in terms of variability and adaptability, are illustrated by examples from the development of hydroformylation and acetic acid synthesis via carbonylation of methanol.

The remainder of volume 1 is entitled Applied Homogeneous Catalysis. It includes subchapters on CO and synthesis gas chemistry; hydrogenation; reactions of unsaturated compounds; oxidation; hydrocyanation; hydrosilylation and related reactions of silicon compounds; hydroamination; reactions of hydrocarbon and saturated compounds; and asymmetric synthesis.

Space constraints prevent this reviewer from summarizing every chapter, so instead several chapters will be highlighted to illustrate the scope. The first section of Chapter 2 on CO/syn gas chemistry is a 75 page review of hydroformylation which covers the history, development of new ligand-modified Co and then Rh catalysts and biphasic systems with water-soluble catalysts, kinetics, mechanistic aspects, process conditions and flowsheets, effect of market forces, and economics of various processes. The review takes an industrial perspective, including process engineering, yet includes recent results from academic research. The section on homogeneously catalyzed alkene polymerization is a concise treatment which focuses more on stereospecificity of C_2-symmetric catalysts and less on general mechanistic and kinetic details of alkene polymerization. The alkene metathesis chapter is rather sparse (14 pages), does not discuss ROMP in sufficient detail, and represents only a general survey of this important area.

Volume 2 includes two chapters, entitled Recent Developments and Epilogue: Homogeneous Catalysis − *Quo vadis*?. The first is subdivided into three sections: (1) Development of Methods (includes heterogenization of homogeneous catalysts, immobilization, organometallic catalysts on surfaces, clusters and colloids, molecular modeling, parahydrogen labeling, chemical reaction engineering, multicomponent and multifunctional catalysts, Heck rections, cyclopropanation, Fischer−Tropsch molecular models, and arene coupling), (2) Special Catalysts and Processes (biocatalysis, template and host−guest relations, membrane reactors, rare earth metals, metallocenes for synthesis of fine chemicals, homologation, electrocatalysis, photocatalysis, olefins from aldehydes, water−gas shift, McMurry coupling, hydrogenation and hydrogenolysis of thiophenic compounds, and double bond isomerization), and (3) Special Products (enantioselective synthesis, diols via dihydroxylation, hydrovinylation, CO_2 as C_1 source, reductive carbonylation of nitro compounds, C−H activation, Pauson−Khand reaction, alkyne cyclooligomerization, alkyne carbonylation, reactions in homogeneous aqueous systems, cyclic hydrocarbons from diazoalkanes, and propene conversion to acrolein and acrylonitrile). The sections on heterogenization and immobilization of homogeneous catalysts, including biphasic approaches, are noteworthy as excellent and up-to-date reviews. The Epilogue (25 pages) is one of the best summaries this author has seen on future trends and pioneering areas in homogeneous catalysis, and borrows from the conclusions and outlook summaries of other chapters.

Most chapter sections are really excellent reviews, and many include discussion of recent developments and future prospects. Some chapters are terse to the point that other literature sources are more useful, especially for students. Each section has more of an industrial or academic perspective, and most sections have extensive and thorough patent and literature references. Occasional English typos were noted in some sections but do not detract from the excellence of the volumes.

As the Foreword notes, homogeneous catalysis is a “significantly still growing and industrially vital domain of catalysis”, so this two-volume set will be indispensable to industrial chemists, organic chemists with interests in the production of commodity and fine chemicals by organotransition metal-mediated homogeneous catalysis, and of course organometallic chemists for whom homogeneous catalysis has represented one of the most important and significant applications. The price will put it out of the reach of advanced students in courses on homogeneous catalysis (for which less comprehensive but more readable texts exist), but the books will be indispensable to faculty teaching these courses. The stress on the applied aspects is very useful for those academic researchers who wish to learn more about industrial approaches, perspectives, and research opportunities outside of what can be gleaned from the patent literature, and this constitutes perhaps the greatest contribution of this two-volume set.

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JA9755020

S0002-7863(97)05502-9

Progress in Inorganic Chemistry. Volume 46. Edited by Kenneth Karlin (Johns Hopkins University). Wiley: New York. 1997. v + 488 pp. $125.00. ISBN 0-471-17992-2.

This volume of the long-running series contains four articles that should find interest among a broad range of chemists.

The first paper, Anion Binding and Recognition by Inorganic Based Receptors by Beer and Smith, deals with the issue of molecular recognition and should find the widest audience. Starting with a brief introduction to anionic recognition in biological and organic systems, the authors provide a thorough survey of inorganic hosts including neutral metal-containing Lewis acids and a variety of charged metal ion-containing complexes of macrocycles, calixarenes, and smaller ligand systems. Distinction is made between hosts that bind through orbital overlap interactions and those that bind primarily through electrostatic interactions. The 86-page paper is nicely illustrated and contains 262 references through 1996. There is a balanced presentation of the authors’ own work and that of others.

The second, and briefest (44 pp), paper, Copper(I), Lithium, and Magnesium Thiolate Complexes: An Overview with Due Mention of Selenolate and Tellurolate Analogues and Related Silver(I) and Gold(I) Species by Janssen, Grove, and van Koten, deals with the syntheses and structures of the title compounds. The first part of the article covers copper(I) thiolates while the second part presents lithium and magnesium thiolates. An extensive list of reported thiolates of Cu(I), Ag(I), and Au(I) is provided; however, only the structures of the copper compounds are discussed. This presentation is thorough and well-illustrated and comprises both monomeric and polynuclear complexes, including mixed-metal species. The list of structurally characterized Li and Mg compounds includes a few Se and Te analogues; however, once again only the thiolate structures are discussed. The paper is extensively referenced with 165 listings through 1996. One wonders whether the actual coverage justifies the rather long and cumbersome title.

The third paper, The Role of the Pyrazolate Ligand in Building Polynuclear Transition Metal Systems by La Monica and Ardizzoia, focuses on systems which have potential catalytic activity; however, the general theme of making extended frameworks of metal ions bridged by small ligands is of interest in a number of applications. Following an introduction to the pyrazolate ligand and its coordination modes, the authors survey the various types of complexes starting with homoleptic copper, silver, and gold pyrazolates which tend to have polymeric structures. Complexes containing a dimetal pyrazolate-bridged core and other ligands are organized by metal triad. Separate sections deal with “heterobridged” complexes in which the metal centers are linked by pyrazolate and non-pyrazolate bridges, complexes containing monodentate pyrazolates and dinucleating functionalized pyrazolates, and the catalytic activity of the bridged complexes. The authors have standardized the molecular graphics which facilitates viewing and interpreting the crystal structures. The discussion, with 217 references through 1997, integrates synthetic methods, spectral characterization, structures, and some reaction chemistry.

The final and longest (190 pp) article, Recent Trends in Metal Alkoxide Chemistry by Mehrotra and Singh, occupies half of this volume. A brief but useful historical introduction is followed by six main sections on synthetic procedures, properties and structures, compounds derived from unusual alcohols, oxoalkoxides, alkoxides as synthons for organometallic derivatives, and alkoxides as precursors to ceramic materials. The authors’ stated goal is to offer an account of the field since 1985. The coverage is comprehensive with 590 references through 1996, though a few recently reviewed areas such as oxovanadium and -molybdenum alkoxide clusters are omitted. This paper will likely be the standard review for much of this chemistry for years to come.

A minor criticism is that in the large tables of crystal data provided, certain space group symbols are consistently misprinted, such as “$P2_{1/n}$” instead of “$P2_1/n$.” Also, the large number of crystal structure diagrams reproduced directly from the original literature vary widely in quality. Rather than a reflection on the authors, this serves as a testament to the lack of a consistent standard in the graphical presentation of X-ray structural results. Overall, this volume is an interesting and useful addition to the series.

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JA975639Q

S0002-7863(97)05639-4