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Book reviews

Dias, J. R.: Handbook of polycyclic hydrocarbons. Part A: Benzenoid hydrocarbons; Part B: Polycyclic isomers and heteroatom analogs of benzenoid hydrocarbons. Elsevier, Amsterdam, 1987 (Part A), 1988 (Part B)

These two volumes are parts of the very useful series "Physical sciences data" that is published by Elsevier and represent titles No. 30A and No. 30B in the series. The author Professor Jerry Ray Dias from Department of Chemistry, The University of Missouri, Kansas City, MO 64110, USA is a well-known researcher in the area of applications of graph theory and topology to the chemistry of benzenoid hydrocarbons and their analogs. He is best known for developing the graph-theoretical framework which allowed him to set a formula periodic table for benzenoid hydrocarbons. Many interesting results are derivable from this table as the author has shown in his work.

Part A of the *Handbook of polycyclic hydrocarbons* is a reference book which updates the field of benzenoid hydrocarbons with novel (chemical, physical, biological) data on these compounds. It is linked to the very successful book *Polycyclic hydrocarbons* by Professor Eric Clar published in 1964 (Academic Press, London). The author has collected many known properties of benzenoid hydrocarbons together under one cover and has extensively used the concepts of chemical graph theory.

Part A of the *Handbook* is organized in the following way: (1) Nomenclature for fused benzenoid hydrocarbons; (2) a formula periodic table for polycyclic aromatic hydrocarbons; (3) benzenoid isomer enumeration; (4) spectroscopy of benzenoid hydrocarbons; and (5) compilation of polycyclic hydrocarbons and their chemical propertes. The total number of references is 453.

Part B of the *Handbook of polycyclic hydrocarbons* is the first reference book in the chemical literature on non-benzenoid hydrocarbons and aza-analogs of benzenoid hydrocarbons. In this volume the author has again extensively used graph-theoretical definitions and methods. It also contains data compilation of benzenoid hydrocarbons not included in Part A, and additions and corrections to Part A.

Part B of the *Handbook* is organized as follows: (0) Overview; (1) nomenclature; (2) chemical graph theory; (3) isomer enumeration; (4) spectroscopy; (5) compilation of polycyclic conjugated hydrocarbons and their chemical properties; (6) compilation of aza and related heteroatom analogs of benzenoid hydrocarbons and Supplement to Part A. The total number of references is 587.

Data given for each molecule in both, Part A and Part B, consist of the following: molecular formula, name of the molecule (after IUPAC or otherwise), melting and boiling points, solubility, Hückel MO parameters [E_π, HOMO, LUMO (only in Part B)], the number of Kekulé structures, synthesis and/or data on isolation and detection, spectral data (UV, NMR, PES). Biological data are either carcinogenicity (Part A, Supplement to Part A) or toxicity (Part B). Carcinogenic data are given in terms of "Yes" or "No" boxes. If the "Yes" box is checked, then the evidence of carcinogenicity is compelling. The compilation for each molecule ends with uses of the compound and the references (the references cited are those which judged by the author are being most pertinent, significant and recent). Graph-theoretical work reported in the *Handbook* is mostly the author's own. He elaborated upon the graph-theoretical concepts related to polycyclic hydrocarbons and their heteroatom analogs so that the reader does not need to consult other sources. In addition, the author in the list of references pointed to several recent books on chemical graph theory in which the interested reader may find additional information on graph-theoretical concepts used in chemistry.

This is a well-written and carefully prepared *Handbook.* Nevertheless, there are some misprints, i.e, the title of Chap. 5 given in the Table of contents does not exactly match the one given in the text (p. 102). This reviewer does not agree with the author's assignment of kekulene as a non-benzenoid in Part B. A proper place for it would be either Part A or Supplement to Part A. For the most of aza-derivatives E_π are missing, but for many of them the HOMO's and LUMO's are given. Like Clar's book, this *Handbook* lacks a subject index. To trace desired data the reader will have to understand the organization principle which is based on the author's formula periodic table. The absence of a subject index is, in part, related to the difficulty of nomenclature of large benzenoids and related molecular systems. However, this *Handbook* possesses extensive contents and listings of all figures and tables at the front of each volume. One would, also, have wished for more references and additional experimental summaries. But these are minor deficiencies when compared to the monumental effort by the author to compile these two volumes containing lots of useful data for anybody who is interested in the fascinating ever-green chemistry of polycyclic conjugated hydrocarbons, in general and benzenoid hydrocarbons, in particular. Theoretical chemists, mathematical chemists, analytical chemists, synthetic chemists, environmental chemists and many other chemists will find this reference an indispensable source of information.

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Stereochemical applications of gas phase electron diffraction. (Eds.: Hargittai, I., Hargittai, M.) VCH Verlagsgesellschaft, Weinheim Basel Cambridge New York. Set price DM 375.00; individual volumes: DM 210.00

It seems almost preposterous to publish about 1 000 pages pertaining to gas phase electron diffraction, bearing in mind that only 20 groups (counting everyone in the whole world) actively participate in such electron diffraction experiments, but, as this reviewer hopes to elucidate, the recently published two volumes on "Stereochemical applications of gas phase electron diffraction" contain information of interest to a much greater audience.

It is, to be sure, a publication mainly written by active gas phase electron diffractionists, but gas phase electron diffraction has come a long way since the time when the structures of very simple molecules could be estimated from a look at the crude diffraction patterns on photographic plates.

The 1 000 pages are divided into two volumes. Volume A is generally of theoretical and technical interest, whereas volume B is a review of structural information obtained for various classes of chemical compounds.

For the non-diffractionist, Chap. 1 (and 6) brings a compressed survey of the historical development of electron diffraction as well as a technical description of the apparatus and the theoretical interpretation of the data necessary to obtain structural information on molecules that rotate and vibrate, but can be considered isolated in space, this being the biggest difference to traditional X-ray diffraction studies.

Going deeper into the electron scattering theory, L. S. Bartell (Chap. 2) maintains that the accuracy of today's measurements would, in favourable cases, allow for a determination of internuclear distances accurate to the order of 10^{-4} Å, were it not for the fact that the conventional theoretical expressions do not allow for such precision because they are based on approximations. The problem lies with the potential encountered in the Schrödinger Equation describing the scattering of an electron with mass m, energy E and spacial coordinates $\underline{r}$:

$$\hat{H}\psi(\underline{r}) \equiv \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\underline{r})\right)\psi(\underline{r}) = E\psi(\underline{r})$$

The scattering potential, $V(\underline{r})$ expresses the influence of a molecule (consisting of nuclei and electrons) on the electron. For a general potential, it is numerically impossible to solve the Schrödinger Equation, so the potential must be reduced to a good approximation, which conventionally involves assumptions of 1) the independent atom model (spherically averaged atomic densities); 2) harmonic (or nearly harmonic) nuclear motions; 3) the Born approximation (the scattering potential being so weak that the electron wave encountering each volume element remains the incident plane wave, unattentuated by the surroundings).

A general correction of these deficiencies would require quantum mechanical calculations of molecular charge distributions and potential energy surfaces that would increase the difficulty and expense of structure determinations considerably.

Having arrived at the point where theoretical chemical calculations are important in order to estimate the reliability of the diffraction experiment, Chaps. 3 and 4 continue along this path, looking into small angle electron scattering by gas molecules, a technique that at the moment can only be applied in four different laboratories. Whereas incident high energy electrons that come close to the nuclei are deflected to large angles because of the strong fields connected with the nearly naked nuclei, those electrons that pass apart from the nuclei are deflected to a small angle because of the weak fields associated with the bound electrons. This experimental information (in principle the differential cross section of this encounter) can be compared with theoretical values, based on the calculations of charge densities and molecular wavefunctions. In other words, the small angle scattering can be used as a very sensitive test of the calculated electron densities. This information is in principle also obtainable using X-ray diffraction, but in the case of electron diffraction, the unperturbed electron density of a molecule that is free from environmental effects is provided. The main interest of electron diffractionists, however, is the determination of molecular structures. In this search, the influence of vibrations is still a major obstacle. How information on the vibrational potential can be either incorporated into the describing structural model—or can be extracted from the electron diffraction data themselves, is the topic of Chaps. 5, 7, and 8. In Chap. 5 it is shown that the high precision diffraction data now allow (for simple two- or three atomic molecules) for a determination of the temperature dependence of the structural parameters and thus a check on the assumed force field.

In Chap. 7 the formalism for the combination of high resolution spectroscopic data with the electron diffraction results is shown. Particular emphasis is placed on the effects of the anharmonic parts of the force fields, a problem that increases with the "floppiness" of the molecule.

A table is included containing references to the more than 100 molecules whose structures have been determined from the combined use of electron diffraction and high resolution spectroscopic data. The traditional way of doing the joint structure determination is to handle the electron diffraction and the spectroscopic data separately until the final fit, making sure that the weighting of the different kinds of data is feasible. A different approach is outlined by V. Spiridonov (Chap. 8), who tries a global fit of the electron diffraction data by means of the cumulant-moment-method. This analysis (in a few favourable cases) leads to a determination of the equilibrium structure and force field without incorporating spectroscopic data. In other cases, it has been found useful to include spectroscopic information in the global fit.

Chapters 11 and 12 deal, broadly speaking, with conformational studies, but it is realized that often (especially if the barrier separating different conformations is low) electron diffraction cannot solve the posed questions without help from other sources. The way of seeking help is the topic of Chaps. 9, 10, 14, and 15, as well as Chap. 10 of volume B.

Chapters 9 and 10 in part A and 10 in part B deal with the interaction between theoretical chemical calculations (mostly *ab initio* at a high level) and the analysis of the scattering data, an interaction that has provided much food for thought and insight, as well to the experimentalist as to the theoretician, especially in the (albeit rare) cases, where only one method seems to confirm "plain common sense".

Chapters 14 and 15 describe two experimental methods that are not so generally applicable as chemical calculations, but in some cases (for specific classes of molecules) yield data that can complement the diffraction data. These methods are Liquid Crystal NMR and low resolution microwave spectroscopy.

Finally two chapters on X-ray analysis of gases (13 and 16) round up volume A.

It is widely believed that such studies ceased to be of practical use a long time ago, but the advent of the synchrotron, which provides a high and stable flux of X-rays, has opened up the path for new activities. In Chaps. 13 and 16, extended X-ray absorption fine structure analysis (EXAFS) and gas phase X-ray diffraction, respectively, are described and compared with gas phase electron diffraction and the possibilities of complementarity or combined studies discussed.

Volume B:

The headings of the individual chapters in volume B reviewing various structure determinations read as follows:

1) Boron and silicon compounds
2) Nitrogen and phosphorus compounds
3) Oxygen and sulfur compounds
4) Fluorine derivatives
5) Saturated organic molecules
6) Unsaturated organic molecules
7) Substituted benzene derivatives
8) Organometallic compounds of main group elements
9) Metal halides

Obviously, this is no chemistry textbook covering all chemical substances of interest, but because the individual chapters are written by researchers specializing in the areas they describe, and since a lot of the work is by nature comparative, these selected topics will be of interest to most structurally oriented chemists. Finally, it must be mentioned that the list of references is (to say the least) quite extensive.

With this publication even the non-diffractionist is provided with a comprehensive review of the methods and results related to gas phase electron diffraction.

Dines Christen, Tübingen