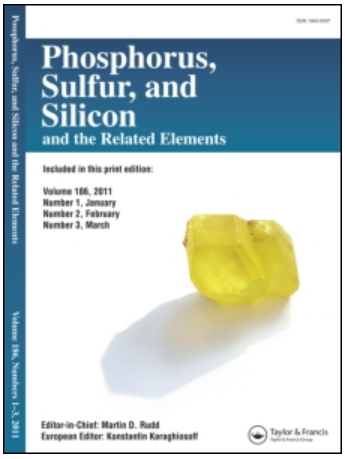

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Book Review

PENTACOORDINATED PHOSPHORUS, Volume 1: Structure and Spectroscopy; Volume 2: Reaction Mechanisms, by Robert R. Holmes. ACS Monographs 175 and 176, ACS, Washington D.C. 1980. Volume 1: 479 pp. $92, Volume 2: 237 pp. $52.

Volume 1 is a review and a thorough discussion of the structural and spectroscopic aspects of pentacoordinated phosphorus and is the basis for the next volume where the structural principles elucidated here are applied to selected reaction mechanisms.

Chapter 1 is a short introduction to the basic structures of pentacovalent phosphorus as well as their nonrigidity and role as intermediates in reaction mechanisms. It is actually a synopsis for the two volumes (7 pages). The next chapter contains an impressive list of structures with figures and tables of bond lengths and angles. Distortions from regular trigonal bipyramidal and square pyramidal symmetries are convincingly shown to follow the local C_{2v} constraint along the Berry coordinate. It is also shown that the structures agree with the electron pair repulsion model (VSEPR). In addition to the structures found by microwave and diffraction methods (76), there is a section dealing with vibrational spectroscopy of pentacoordinated phosphorus compounds. Fundamental frequencies are given for some simple trigonal bipyramidal and square pyramidal molecules, and there is a description of the relevant modes. Chapter 2 also contains a short supplementary text on symmetry and spectroscopy for the non-expert.

In Chapter 3, the NMR spectroscopy of pentacoordinate phosphorus is treated. High-resolution NMR spectroscopy is the most widely used method used to obtain structural information on pentacoordinated phosphorus compounds. The NMR time scale is such that intramolecular exchange processes in the pentacoordinated state can often be followed by temperature-dependent studies. The chapter focuses on structural principles that can be used to formulate mechanisms involving pentacoordinate intermediates. Many spectra are discussed and classified, both of simple trigonal bipyramidal systems with monodentate ligands and of various cyclic systems—most including oxyphosphoranes. Models for intramolecular exchange mechanisms are discussed, both theoretically and in terms of actual spectra. Also, the effect of internal rotation in ligands is treated.

Chapter 4 treats the potential functions governing intramolecular ligand exchange. Included in the chapter is a brief introduction to normal-coordinate analysis and a description of the normal-mode amplitudes for the various vibrations in simple pentacoordinated molecules. The results of the vibrational analyses and energy calculations presented in this chapter clearly favor the Berry exchange mechanism over other alternatives.

The last pages of Chapter 4 are an introduction to the molecular mechanics approach to pentacoordinate phosphorus stereochemistry. Based on the well-known MMI program of Allinger and coworkers, the author and his coworkers have developed a program that is tailored to the stereochemistry of phosphorus. It is adapted to the trigonal bipyramid-square pyramid conversion and it contains an energy term that corrects for electron-pair repulsion effects. The success of this program in simulating phosphorane structures is illustrated in Figure 4.21.

Finally, Volume I contains two appendices. Appendix I is a compilation of vibra-

tional spectra for simple pentacoordinate molecules with assigned IR and Raman frequencies as well as a listing of fundamental modes. Appendix II contains expressions for G and F matrix elements in the secular equation for vibrations. Thus, they represent supplements mainly for Chapters 2 and 4, respectively.

Volume 2 contains a thorough discussion of reaction mechanisms pertaining to pentacoordinated phosphorus compounds. In the first Chapter the author discusses the various theoretical models for bonding in pentacoordinated phosphorus compounds used to explain the electronic structures and polytopal rearrangements. The topic is presented in a way that does not demand mathematical training from the reader, which makes it valuable for organic chemists and biochemists with a more scanty knowledge of quantum mechanical calculations. However, for workers who wish to do their own calculations on polytopal rearrangements, there also is included a computer program at the end of the chapter.

Of special interest in Chapter 1 is the comparison of various energy barriers in different polytopal rearrangements. The author has presented data that show overwhelming evidence that the Berry exchange mechanism is favored energetically in comparison with the turnstile mechanism.

Further, in the same chapter are discussed the effect of π-bonding and ring size in cyclic phosphoranes on the exchange rate of various substituents. The ring-size problem is illustrated with many examples where the energy of the postulated square pyramidal and trigonal bipyramidal configurations have been calculated on the basis of relative values of ring strain, and compared with corresponding observed free energies of rearrangement.

In Chapter 2 the author has focused on those reactions in organophosphorus compounds that most clearly give evidence for the presence of pentacovalent intermediates or transition states. From the huge amount of material which now exists in this field, the examples presented have been especially chosen from works on hydrolysis of phosphate esters and alkaline decomposition of phosphonium salts. These reaction types give the most clear evidence in support of the Berry exchange process which has been the main subject of the author's discussion in connection with the polytopal rearrangements presented in Chapter 1. From this point of view, the author argues that several of the rate data and stereochemical observations can be explained not only from the trigonal bipyramidal preference rules, but also according to a set of rules based on square pyramidal structures.

Chapter 2 also presents interesting data from nucleophilic substitutions at tricoordinated phosphorus as well as studies of reactions in connection with phosphate enzyme systems.

The two volumes give an integrated approach to the stereochemical, spectroscopic and mechanistic aspects of pentacoordinate phosphorus. It also is of great value for research involving the pentacoordinated state in general, and it has great value as a review.

Every chapter has an up to date list of literature citations to which those of the author and his coworkers make an impressive contribution.

Tables and figures are clear and comprehensible and make the book easier to read.

In sum, "Pentacoordinated Phosphorus" is the most comprehensive and important contribution to the dynamic aspects of the chemistry of pentacoordinated phosphorus to date.

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THE CHEMISTRY OF THE SULPHONIUM GROUP, C. J. M. Stirling (Ed.), Parts 1 and 2, ISBN 0 471 27655 3, J. Wiley & Sons, 1981; 847 p., $211.00.

This is another volume in Patai's legendary series "The Chemistry of Functional Groups" and covers the following subjects: general and theoretical aspects, structural chemistry, analysis and determination, thermochemistry, photochemistry, electronic spectra, electrochemistry, isotopically labelled sulfonium salts, electronic effects of the sulfonium group, stereochemistry and chiroptical properties, synthesis of sulfonium salts, reactivity of sulfonium salts, cyclic sulfonium salts, organosulfur cation radicals, heterosulfonium salts, synthetic applications, and the biochemistry of sulfonium salts. There is also an author and a reasonably detailed subject index. The deadline of the literature search is not stated, but it appears that the literature is fully covered up to and including 1978, a few 1979, 1980, and even 1981 references notwithstanding.

The physical appearance of the book is excellent. A few defective formulas (which appear to be concentrated in chapter 13, for instance Eq. (197) on p. 445 and Eqs. (201) and (203) on p. 446) cannot detract from the overall superb legibility and esthetic appeal of the artwork. A few oddities appear to be deliberate: $\overline{BF_4}$ (with bars of varying length) instead of BF_4^-, O and ^{18}O instead of ^{18}O, and the consequent spelling sulph ... in a text that otherwise employs U.S. spelling throughout.

The presentation is remarkably consistent and uniform for a multi-author volume and clearly reflects the editor's competence and dedication. There is, however, one instance of serious overlap: the synthesis of thiopyrylium salts is treated both in chapter 11 ("Synthesis of sulphonium salts") and in chapter 13 ("Cyclic sulphonium salts"). Since the literature coverage of the two presentations is far from congruent one is left in a state of confusion and with some doubt as to how much might be missing altogether.

Chapter 2 (E. F. Perozzi and I. C. Paul, "The structural chemistry of sulphonium salts") appears somewhat unusual by addressing itself to a crystallographic rather than general, audience. However, the extra reading effort imposed upon non-crystallographic readers is rewarded with a wealth of useful information. For some strange reasons the authors have not seen fit to quote Laur's monumental 1972 review (which is mentioned elsewhere in this book). For the synthetic chemist Lowe's chapter 11 ("Synthesis of sulphonium salts", 272 references), Dittmer's and Patwardhan's chapter 13 ("Cyclic sulphonium salts", 861 references), and Oae's, Numata's, and Yoshimura's chapter 15 ("Heterosulphonium salts", 576 references) are especially useful while Shine's chapter 14 ("Organosulphur cation radicals") and Block's chapter 16 ("Synthetic applications of sulphonium salts and sulphonium ylides") are a source of inspiration regardless of one's primary interest. Mechanism buffs will find ample consolation in chapters 5 (J. D. Coyle, "Photochemistry of sulphonium compounds"), 8 (L. F. Blackwell, "Isotopically labelled sulphonium salts"), 9 (J. Shorter, "Electronic effects of the sulphonium group"), 10 (K. K. Andersen, "Stereochemistry and chiroptical properties of the sulphonium group"), and 12 (A. C. Knipe, "Reactivity of sulphonium salts"). Unfortunately, Barrett's excellent chapter 6 ("Electronic spectra") is not accompanied by parallel IR, NMR, and MS reviews. Maw's chapter 17 ("The biochemistry of sulphonium salts") adds another dimension to the saga of the sulfonium compounds by documenting their biochemical relevance and pharmacological importance. Though richly illustrated with structural formulas this chapter contains a considerable number of pages without a single formula and might have become more accessible for the casual

reader by a more liberal use of structural formulas including repetition of the formulas of key compounds. The remaining chapters 1 (M. Simonetta and A. Gavezotti, "General and theoretical aspects"), 3 (M. R. F. Ashworth, "Analysis and determination"), 4 (R. Shaw, "Thermochemistry of the sulphonium group"), and 7 (J. Grimshaw, "Electrochemistry of the sulphonium group") round off the picture with additional material as indicated in the respective titles.

Altogether, "The Chemistry of the Sulphonium Group" is an indispensable source of information for research chemists and a must for any self-respecting chemical library.

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