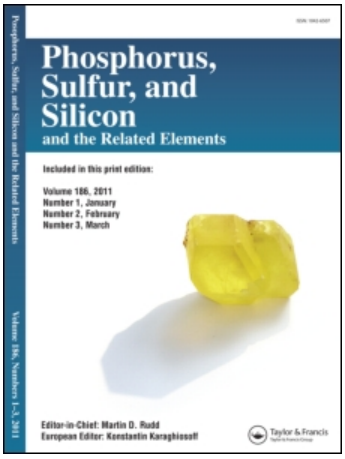

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Hägele, Gerhard(1999) 'Application of Efficient Program Systems for Spectral Analysis of Phosphorus Containing Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 659 — 661
To link to this Article: DOI: 10.1080/10426509908546331
URL: http://dx.doi.org/10.1080/10426509908546331

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 659-661
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Application of Efficient Program Systems for Spectral Analysis of Phosphorus Containing Compounds

GERHARD HÄGELE

Institut für Anorganische Chemie und Strukturchemie Heinrich-Heine-Universität Düsseldorf, D-40225-Düsseldorf, Germany

Some principles of modern PC program systems designed for manual and automated spectral analysis and simulation of HR 1D NMR spectra are described. Applications for phosphorus containing compounds are demonstrated. Stationary and dynamic molecules are considered using nuclei ^{1}H, ^{13}C, ^{19}F, ^{31}P.

Keywords: NMR; spectral analysis; simulation; PC programs

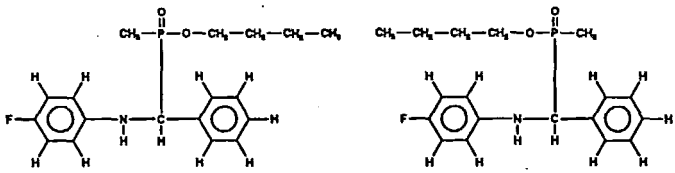
INTRODUCTION

Polyphosphorus compounds give rise to interesting and often complex ^{31}P and proton decoupled $^{31}P\{^{1}H\}$-NMR spectra having static or dynamic properties. Organophosphorus compounds intrique by ^{1}H-, $^{1}H\{^{31}P\}$-, ^{13}C- and $^{13}C\{^{1}H\}$-NMR-spectra of corresponding organic substituents, where in general, in the absence of higher symmetries, the complexity of spectra increases with the number of spins involved in the total system. Similar considerations hold for fluorinated organophosphorus compounds involving additionally indicative ^{19}F spins. An introduction into the computerized analysis of NMR spectra of some relevant classes of organophosphorus compounds will be given. Particular attention will be paid toward the ^{1}H- and $^{1}H\{^{31}P\}$-NMR of alkyl- and aryl-substituted phosphorus compounds. Practical examples will be analyzed using novel pro-gram versions developed in Düsseldorf, of **WINDAISY** [1] running under **WINNMR** [2]. The program **VISITOR** [3], a novel convenient tool, will produce film-like sequences of NMR spectra to find starting parameters for iterations in cases of difficult iterability. Examples will be shown including free acids, salts and esters derived from phosphorus-, phoshonic-, phosphinic acids. Recent results from biorelevant phosphonocarboxylic, aminophosphonic acid and -phosphinic acid derivatives will be discussed. **WINDYNA** [4] is used to elucidate dynamic NMR spectra. Double resonance spectra are simulated using **WINDOR** [4]. The above mentioned tools are based on

WINDOWS®, while additional programs [5] listed below were designed for simulations on PCs working with DOS®: **DSYMPC, DCYMPC, MINILA, LAOPC, SPINAAT, NMRFILM, DNMR-SIM, NMRDR.** Aromatic Ring Current Effects may be calculated with **JAHMA.** Two examples are demonstrated on the following pages. More material and some programs are available on request from the author.

Example 1

N-(p-fluorophenylamino-1-phenyl-methane phosphinic acid n-butylyl, ester **1** existing in two pairs of diastereomers, formally described by



attracted interests as a member of a series of biorelevant derivatives. Each diastereomer is characterized by a complex 26 spin system involving 23 proton, 1 nitrogen, 1 fluorine and 1 phosphorus atoms, which give rise to a specific set of HR NMR spectra. The frag-mentation principle of **WINDAISY** is used, to effectively brake down this complexity into simpler, independent sub-systems. The mixture of diastereomers and one of the diastereomers were characterized by ^{1}H-, $^{1}H\{^{31}P\}$-, ^{19}F- and $^{31}P\{^{1}H\}$-NMR spectra. An assignment of diastereomers via Aromatic Ring Current arguments using **JAHMA** was supported by molecular modeling and X-ray diffraction studies [6].

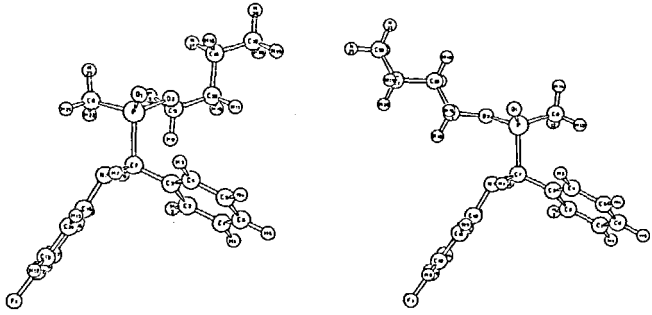
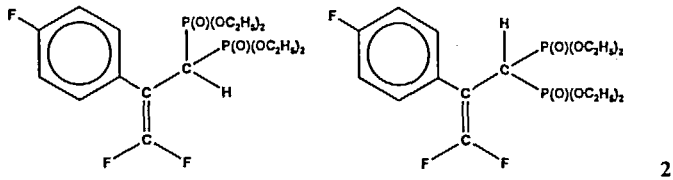


FIGURE 1 The simulated structures for a pair of diastereomers of **1**

Example 2

In connection with our studies concerning biorelevant bisphosphonates we observed that fluoroaryl substituted difluorallyl bisphosphonates [7], e. g. **2**



2

undergo dynamic exchange involving the rotation of the CHP_2 unit around the C-C axis. connecting sp^2-sp^3 carbon centers. This gives rise to an interchange of the two specific $ABMX_2$ systems formed by the pair of olefinic fluorines, the tertiary proton and both phosphorus atoms from the geminal phosphonate substituents.

Acknowledgments

This study was supported by the Fonds der Chemischen Industrie, Academic Research Collaboration (ARC, DAAD), Bruker Analytische Meßtechnik, Rheinstetten, Germany.

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